COLL 1

Surface induced bond strengthening via back donation: A first-principles discovery

Scott Simpson[1]*, scottsim@buffalo.edu, James Hooper*[2]*, Donna Kunkel*[3]*, Axel Enders*[3]*, Eva Zurek*[1]*.Â (1) Chemistry, State University of New York, University at Buffalo, Buffalo, NY 14260, United StatesÂ (2) Department of Theoretical Chemistry, Jagiellonian University, KrakÃ³w, PolandÂ (3) Department of Physics and Astronomy, University of Nebraska-Lincoln, Lincoln, NE 68588, United States*

The interaction between benzene and the Cu(111) surface can be explained by the Dewar, Chatt, Duncanson model in which electron density is donated from the adsorbate HOMO to the metal surface, with concomitant back donation from the surface to the molecular LUMO. During surface adsorption the C-C bonds elongate since an MO which is pi-bonding between adjacent carbon atoms is depopulated, and an MO which is C-C pi-antibonding becomes partially filled. We, on the other hand, report a first-principles study which illustrates that back donation from a coinage metal surface into the LUMO of an organic adsorbate can actually strengthen the intramolecular bond within the organic. This finding is in stark contrast to the countless examples which illustrate that back donation results in a weakening and lengthening of the bond into which electron density is donated. We further illustrate that the level alignment between the Fermi level of the surface and the frontier molecular orbitals of the organic, the topology of the LUMO and its overlap with the metal bands are important in discovering molecule/surface combinations which may result in bond strengthening as a result of backdonation. Finally, the effect of the coverage on the change in the bond lengths is examined.

COLL 2

Super-resolution mapping of photogenerated electron and hole separation in single metal-semiconductor nanocatalysts

Ning Fang[1,2]*, nfang@iastate.edu, Ji Won Ha*[1,2]*, Rui Han*[1,2]*.Â (1) Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa 50011, United StatesÂ (2) Ames Laboratory, U.S. Department of Energy, Ames, IA 50011, United States*

Metal-semiconductor heterostructures are promising visible light photocatalysts for many chemical reactions. Here, we use high-resolution super-localization imaging to reveal the nature and photocatalytic properties of the surface active sites on single Au-CdS hybrid nanocatalysts. We experimentally reveal two distinct, incident energy-dependent charge separation mechanisms that result in completely opposite photo-generated active sites (e^- and h^+) and divergent energy flows on the hybrid nanocatalysts. The specifically designed Au-tipped CdS heterostructures with a unique geometry (two Au nanoparticles at both ends of each CdS nanorod) provide more

convincing high-resolution single-turnover mapping results and clearly prove the two charge separation mechanisms. Engineering the direction of energy flow at the nanoscale can provide an efficient way to overcome important challenges in photocatalysis, such as controlling catalytic activity and selectivity. These results bear enormous potential impact on the development of better visible light photocatalysts for solar-to-chemical energy conversion.

COLL 3

Oxidation of PbSe and PbS quantum dots: Theoretical insights

Svetlana Kilina*, skilina@gmail.com, Michael Mayo.Chemistry and Biochemistry, North Dakota State University, Fargo, ND 58108, United States*

Quantum Dots (QDs) show promise for many technological applications, including photocatalysis and photovoltaics. However, their photophysical properties are sensitive to surface oxidation, resulting in uncontrollable luminescence quenching. Using density functional theory (DFT) and time dependent DDFT (TDDFT), we simulate the oxidation process on the surface of $Pb_{16}Se_{16}$ and $Pb_{68}S_{68}$ QDs and its effect on their electronic and optical properties. When oxygen is substituted for Se/S ions, the electronic properties of the QD are insignificantly perturbed. In contrast, if oxygen is adsorbed on the QD surface and coordinated with two Pb ions, it introduces additional unoccupied states inside the QD's bandgap, so called mid-gap states. Such states are hybridized between the oxygen and the QD's surface atoms and contribute to the lowest-energy optically dark or semi-dark transitions resulting in quenching of luminescence of QDs. In contrast, if the oxygen is coordinated with Se/S and Pb ions on the surface, the mid-gap states are not present and the optical transitions are similar to those of the non-oxidized QDs.

COLL 4

Mechanism of selective recognition of cubic platinum nanocrystals by peptides in aqueous solution

Hadi Ramezani-Dakhel[1]*, hr15@zips.uakron.edu, Lingyan Ruan*[2]*, Yu Huang*[2,3]*, Hendrik Heinz*[1]*.Â (1) Department of Polymer Engineering, University of Akron, Akron, Ohio 44325, United StatesÂ (2) Department of Materials Science and Engineering, University of California, Los Angeles, California 90095, United StatesÂ (3) California NanoSystems Institute, University of California, Los Angeles, California 90095, United States*

Shape, size, and surface modification regulate functionality of metal nanocrystals in catalysts, sensors, and electrode materials. In-situ synthesis of metal nanocrystals of different shapes facilitates the exploration of new functionalities although the underlying shape-controlling mechanisms still remain poorly understood. Oligomers of naturally occurring amino acids have been employed as efficient regulating agents to engineer the structure of nanocrystals. A naturally selected, non-charged peptide named T7 (Acyl-TLTTLTN-Amide) was reported to bind to platinum nanocubes enclosed by six {100} facets and directs the formation of single crystalline platinum cubes in reductive synthesis. We explain the mechanism of specific cube recognition and of cube formation from cuboctahedral seed crystals using molecular dynamics simulation with the CHARMM-METAL force field. We found a higher mobility of water molecules near the edges of nanocubes compared to the center of the facets and a unique match of polarizable atoms in T7 (N, O, C) to the square pattern of epitaxial sites on the cube surface. Water competes strongly with the peptide anywhere on the {100} facets, yet higher mobility of water near the edges of the cube favors peptide adsorption (–5.8±0.8 kcal/mol). These data are also in agreement with peptide desorption on extended {100} facets experimentally and a positive energy of peptide attachment in the simulation (+13±2 kcal/mol). In the synthesis of Pt nanocrystals in the presence of T7 peptides, cuboctahedral seed crystals are initially formed. The simulation of cuboctahedral seeds in contact with several peptides then shows that T7 peptide locates on {100} facets with a slight preference over {111} facets which suggests faster growth of the {111} facets and is consistent with the experimentally observed formation of cubic nanocrystals. The results therefore explain the likely mechanism of nanocrystal growth and show that force fields such as CHARMM-METAL and INTERFACE-METAL can predict selective adsorption and preferred nanocrystal shapes.

COLL 5

Using 3D particle tracking to study long-range nanoparticle-interface interactions

Luyang Zhao, Fang Chen, Yaqing Zhao, Bhanu Neupane, ***Gufeng Wang****,*
gufeng_wang@ncsu.edu.Chemistry, North Carolina State University, Raleigh, NC 27695, United States

Molecular transport near a liquid-solid interface is of vital importance in both fundamental sciences and advanced applications. In this study, we track three-dimensional (3D) trajectories of negatively charged nanoparticles being retained by samely charged glass surface using astigmatism-based 3D super-localization fluorescence microscopy. We show that retention of nanoparticles by the surface can happen at long distances, i.e., a distance beyond the working range of van der Waals interaction, without significant contribution from adsorption. The particle distribution suggests that surface attractive sites serve as both attractive and repulsion centers in retaining these nanoparticles at different time scales. The retained particles diffuse actively in the potential energy well with a lateral size on the order of magnitude of 1 square micrometer. This view may shed new light on how biomolecules/nanoparticles interact with a solid or semi-fluidic membrane surface.

COLL 6

Acac as an anchoring group: Does surface morphology influence charge transfer dynamics?

Edwin Mghanga[1]*, edwin.mghanga@wmich.edu, Jameel Hasan*[1]*, Semere Bairu*[1]*, Gary Wiederrecht*[2]*, Ramakrishna Guda*[1]*.Â (1) Chemistry, Western Michigan University, Kalamazoo, MI - Michigan 49008, United StatesÂ (2) Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439, United States*

The influence of anchoring group on the interfacial charge-transfer dynamics in dye sensitized TiO_2 nanoparticles has garnered enormous interest in recent years mainly for their applications in dye solar cells and nanoscale devices. Among several groups, acetylacetonate (acac) as an anchoring group has been recently used for its robustness when it is bound to TiO_2. However, the influence of different binding modes of acac on the dynamics of electron injection and charge recombination dynamics is not clear. Also, the influence of semiconductor morophology on the different binding forms of acac is quite unknown. This study was carried out to understand the interfacial charge transfer dynamics across molecules possessing acac as an anchoring group and TiO_2 nanoparticles in both solution phase and thin films to address these problems. Femtosecond fluorescence upconversion and transient absorption measurements were carried out to probe the dynamics of charge injection and charge recombination processes. Unlike the chromophores with other anchoring groups, investigated molecules with acac as an anchoring group, have shown contrasting charge transfer dynamics in solution and thin film phases. For the molecule/TiO_2 composites in solution phase, the transients took significant time to grow and the final transients lived long. However, for the same molecule/TiO_2 composites in thin films, the transients formed within instrument response and the transients decayed with different time constants. The differences in two phases were attributed to different binding geometries. Steady-state optical absorption and infrared measurements were able to show the evidence for different binding geometries.

COLL 7

DFT calculations of ΔG° and $\Delta G^\ddagger$ during contact electrification of liquid electrets

Diana M Gooding[1]*, dmgooding14@transy.edu, George K Kaufman*[2]*.Â (1) Department of Physics, Transylvania University, Lexington, KY 40508, United StatesÂ (2) Department of Chemistry, Transylvania University, Lexington, KY 40508, United States*

Contact electrification is a process in which materials contact one another and then separate, each with a resulting charge distribution. This process is familiar and applied extensively in processes like electrophotography and energy harvesting, but it is not completely understood. The triboelectric series is a qualitative or semi-quantitative ordering of materials according to their tendency to develop a positive or negative net charge when tribocharged against other materials. It is remarkable that, despite differences in surface preparation, modes of contact among materials, and laboratory conditions, triboelectric series generated by different groups remain mostly consistent with each other. This talk examines a triboelectric series of liquids, bearing various functional groups, flowed against polyethylene (PE) or polytetrafluoroethylene (PTFE). We use density functional theory (DFT) calculations of ΔG^o and $\Delta G^\ddagger$ to explore

homolytic and heterolytic bond dissociation, followed by material transfer, as mechanisms that may lead to contact electrification. Combinations of these mechanisms may occur simultaneously but at different rates, which may help to explain the charges evolved on these liquids and their positions on the triboelectric series.

COLL 8

Covalent functionalization of (110) surfaces of III-V semiconductors

*Aaron J Bradley[1], Miguel Moreno Ugeda[1,2], **Wenjun Liu**[2,3], wjliu@lbl.gov, Min Yu[2,4], Donald T Tilley[3], Rubén Pérez[5], Jeffrey B Neaton[4], Michael F Crommie[1,4].Â (1) Physics, University of California at Berkeley, Berkeley, CA 94720, United StatesÂ (2) Joint Center for Artificial Photosynthesis, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United StatesÂ (3) Chemistry, University of California at Berkeley, Berkeley, CA 94720, United StatesÂ (4) Material Science Division, Lawrence Berkeley National Laboratory, Berkeley, Ca 94720, United StatesÂ (5) FÃsica TeÃ³rica de la Materia Condensada, Unversidad AutÃ³noma de Madrid, Madrid, Madrid 28049, Spain*

Chemical functionalization provides a potentially useful route for tuning the electronic properties of semiconductor surfaces for a variety of energy-related applications[1]. Controlled covalent attachment of molecular elements on III-V semiconducting surfaces has been widely pursued in the past few decades. For these zinc-blende semiconductors, the chemistry of the (100) and (111) surfaces is relatively well understood and a wealth of covalent attachment strategies are known; however, functionalization of the (110) surfaces has been much less successful[2]. Indeed, the partial polar character of these (110) surfaces and its potential influence on their chemical reactivity remains largely unexplored.

Here we report[3] on a thermally-driven covalent attachment of perfluorophenyl azide (pfpa) on GaP(110). We have studied the adsorption of pfpa molecules at room temperature and after gentle heating by means of high-resolution scanning tunneling microscopy and spectroscopy measurements in combination with first principles calculations. We show a progression from a physisorbed state at room temperature to a chemisorbed state after exposure to slightly higher temperatures (~50^{o}C). The developed approach is expected to be valid for various other functional groups attached to the azide, as well as other III-V semiconductors.

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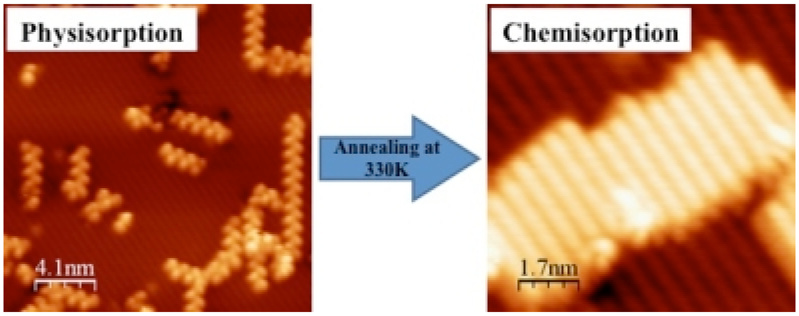
(2) M. M. Ugeda *et al*, submitted to J. Phys. Chem. C.

(3) A. J. Bradley *et al*., in preparation.



COLL 9

Single-molecule, single-particle approaches for exploring the structure and kinetics of nanocatalysts

Tetsuro Majima, *majima@sanken.osaka-u.ac.jp.The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047, Japan*

We report the in situ observation of photochemical reactions on individual nano objects of solid catalysts using single-molecule, -particle fluorescence spectroscopy. The use of high-resolution imaging techniques with suitable fluorogenic probes enables us to determine the location of the catalytically active sites that are related to the structural heterogeneities on the surface of the solid catalyst and the temporal fluctuation of photochemical reactivity. Recent developments of single molecule spectroscopy will extend the range of applications by adding new tools. Advanced “nanoscopy” techniques such as two or three-dimensional stimulated emission depletion microscopy and photoactivated localization microscopy/stochastic optical reconstruction microscopy have achieved optical imaging at high spatial resolution beyond the optical diffraction limit (around half the wavelength of the light in the lateral direction). This feature should be highly advantageous and useful in exploring the active sites heterogeneously distributed over the materials. However, it should be noted that the localization accuracy might be less than that expected from a certain S/N ratio due to “distorted” field distributions of the emitter in the vicinity of metal nanostructures. Another important aspect is that molecular adsorption/ desorption kinetics are strongly associated with the surface structures of the catalysts. The molecular recognition and transformation on specific surfaces should play a crucial role in controlling reaction efficiency and selectivity. The combination of fluorescence microscopy with several microscopic techniques such as TEM, SEM, AFM, Raman microscopy, and optical absorption microscopy will become extremely powerful approaches to gain structural and dynamic information on broad spatial and temporal ranges. We believe that single-molecule, -particle approaches will serve as the basis for designing and identifying new materials for applications in a variety of areas including biomedicine, catalysis, and optoelectronics.

COLL 10

Plasmon enhanced light harvesting

***Peter Nordlander**, nordland@rice.edu.Department of Physics and Astronomy, Rice University, United States*

The “plasmon hybridization”concept, shows that the plasmon resonances in complex metallic nanostructures interact and hybridize in an analogous manner as atomic wavefunctions in molecules. The insight gained from this concept provides an important conceptual foundation for the development of new plasmonic structures for enhanced light harvesting and important applications. Examples that will be discussed include plasmonic substrates for surface enhanced spectroscopies, chemical and biosensors, nonlinear optical devices, photodetectors, photocatalysists, and solar light driven steam generators and autoclaves.

COLL 11

Evidence of direct membrane penetration by gold nanoparticles in life cells and membrane models

***Mathias Brust**, M.Brust@liv.ac.uk.Department of Chemistry, University of Liverpool, Liverpool, Merseyside L69 7ZD, United Kingdom*

Owing to the growing potential of nanoparticles for applications as biomedical agents, and the current concens regarding the toxicity of nanoscale objects, there is a topical interest in understanding and possibly controlling the mechanisms by which such materials transfer across biological membranes. The currrent paradigm implies that only very small and neutral molecules are capable of direct transfer due to their ability to partition between the hydrophobic membrane and its aqueous environment. Nevertheless, there is a growing number of observations that suggest that also larger units such as functionalised gold nanoparticles can cross membrane boundaries without depending on complex biological processes such as endocytosis. In this contribution, such observations from both cell cultures and model membrane systems are discussed, and attemps are made to rationalise the possibility of direct membrane penetration by nanoscale objects. In particular, the effects of size, charge and surface functionality will be investigated, and cases of both apparent direct cellular uptake of nanoparticles, and of direct nanoparticle transfer across intracellular membrane boundaries will be discussed.

COLL 12

On synthesis of CdSe quantum dots in live cells: Synthesis, mechanism, and beyond

*Ran Cui[1], Yong Li[1], Hui-Hui Liu[2], Bei-Bei Chen[1], Peng Zhang[2], Zhi-Xiong Xie[2], Zhi-Ling Zhang[1], Bin Hu[1], Zhi-Quan Tian[1], **Dai-Wen Pang**[1], dwpang@whu.edu.cn.Â (1) Key Laboratory of Analytical Chemistry for Biology and Medicine (Ministry of Education),* *College of Chemistry and Molecular Sciences, and State Key Laboratory of Virology, Wuhan University, Wuhan, ChinaÂ (2) College of Life Sciences, Wuhan University, Wuhan, China*

The intercross between chemistry and biology can offer opportunities for controllable synthesis of nanomaterials. Herein, we give an example of a new strategy of “Live Cell Synthesis by Space-Time Coupling” of intracellular irrelated biochemical reactions of live cells to controllably synthesize nanomaterials for biolabeling. By such a new strategy we have successfully and controllably realized the desired synthesis of fluorescent CdSe nanocrystals with diverse monocolours of fluorescence that can never occur in live cells in nature. We also have successfully extended such a strategy/principle from the intracellular to mimetic systems, *i.e.* to construct quasi-biosystems for synthesis, and established multiple methods to synthesize nanomaterials for biolabeling under mild conditions, such as water-dispersible ultrasmall near-infrared Ag_2Se, near-infrared PbSe nanocube and nanocage QDs, Au nanoparticles, Au-Ag alloy nanoparticles, Au clusters, and so on. In this presentation we will give a brief introduction to the synthesis, mechanism and beyond.

COLL 13

Manipulating nanoparticle configurations in colloidal heterotrimer isomers

*James Hodges, **Raymond Schaak**, schaak@chem.psu.edu.Department of Chemistry, Pennsylvania State University, University Park, PA 16802, United States*

Colloidal hybrid nanoparticles integrate multiple materials into a single particle platform, resulting in multi-functionality and the emergence of synergistic properties. For hybrid nanoparticles that contain more than two domains, multiple configurations with distinct connectivities and functionalities are possible, and these can be considered as nanoparticle analogues of molecular isomers. However, accessing one isomer relative to others in the same hybrid nanoparticle system can be challenging, particularly when the formation of a target isomer is disfavored relative to more stable or synthetically accessible configurations. This talk will introduce a solid-state protecting group strategy for directing the nucleation of a third domain to an otherwise disfavored site of a heterodimer seed particle, resulting in the ability to predictably target two distinct heterotrimer isomers.

COLL 14

Layer-by-layer assembled particles in the biological domain

***Frank Caruso**, fcaruso@unimelb.edu.au.Chemical and Biomolecular Engineering, The University of Melbourne, Melbourne, Victoria 3010, Australia*

Layer-by-layer (LbL) template-assembled particles have recently emerged as a promising class of materials for biological applications, with studies progressing from in

vitro to in vivo. In this presentation, recent studies on the development of LbL-assembled polymer capsules for efficient cargo encapsulation, triggered release and antibody-mediated targeting will be highlighted. It will also be shown that LbL particles with well-controlled physicochemical properties can be used to uncover several key principles that govern particle-cell interactions. For example, redox-responsive capsules associate with cells in a time-dependent manner, which is mediated by the exofacial thiols on cell membranes, and during endocytosis, the LbL particles distort in shape and accumulate in lysosomal compartments. Furthermore, the role of shape of LbL particles on cellular interactions, through the use of LbL particles with different aspect ratios, will be discussed. It is expected that LbL systems represent a class of novel materials for therapeutic delivery as well as an interesting paradigm to attain detailed knowledge of complex nano-bio interactions. This knowledge may aid in the rational design of nanoengineered materials (beyond LbL systems) for biological applications.

COLL 15

Regulating cell signaling in live cells at the single molecule level

*Daeha Seo[1,2,3], Jiwook Kim[4], Justin Farlow[5,6], Hyunjung Lee[1], Paul Alivisatos[2,3], Jinwoo Cheon[4], Zev J Gartner[5,6], **Young-wook Jun**[1], yjun@ohns.ucsf.edu.Â (1) Department of Otolaryngology, University of California, San Francisco, San Francisco, California 94115, United StatesÂ (2) Chemistry, University of California, Berkeley, Berkeley, CA 94720, United StatesÂ (3) Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United StatesÂ (4) Department of Chemistry, Yonsei University, Seoul, Republic of KoreaÂ (5) Department of Pharmaceutical Chemistry, University of California, San Francisco, San Francisco, California 94158, United StatesÂ (6) Tetrad Graduate Program, University of California, San Francisco, San Francisco, California 94158, United States*

Notch signaling defines the cell-to-cell communication mechanism, which plays a central role during development and in normal tissue maintenance and cancer. Signals exchanged between neighboring cells via Notch can reinforce molecular differences which eventually direct the fate decision of individual cells. Despite increasing knowledge of these signaling events, little is known about how spatiotemporal dynamics of the receptor signaling across a cell influence the signal exchange. In this talk, we present an advanced nano-probe system that mimics binary cell communication via Notch, while providing systematic control of the spatiotemporal distribution of Notch signaling. This new nanosystem enabled simultaneous observation of Notch dynamics and signal activation with single molecule resolution in live cells for the first time. We envision this nano-probing system as a next generation force microscopy technology platform to quantify and control force-mediated biological processes at the subcellular level.

COLL 16

Glycan-stabilized plasmonic nanoparticles: An attractive nanomaterial for bio-applications

Marek Grzelczak[1,2]*, mgrzelczak@cicbiomagune.es, Isabel García*[3]*, Ana Sánchez-Iglesias*[1]*, Marco Marradi*[3]*, Soledad Penadés*[3]*, Luis M Liz-Marzán*[1,2]*.Â (1) BioNanoPlasmonics Laboratory, CIC biomaGUNE, Donostia-San SebastiÃ¡n, SpainÂ (2) Ikerbasque, Basque Foundation for Science, Bilbao, SpainÂ (3) Laboratory of Glyconanotechnology, Biofunctional Nanomaterials Unit, CIC biomaGUNE/CIBER-BBN, Donostia-San SebastiÃ¡n, Spain*

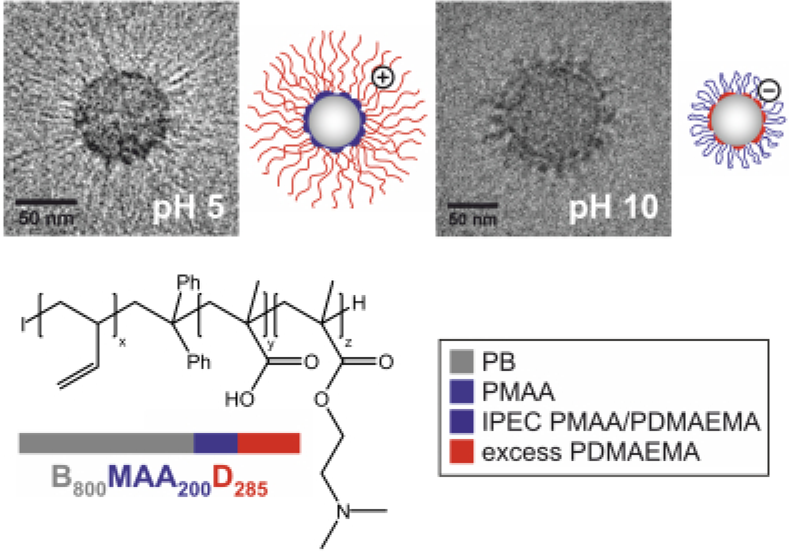
Gold nanoparticles exhibit unique optical properties and low toxicity that make them attractive nanomaterial for the use in biological environment. The application of plasmonic nanoparticles in drug delivery or biosensing requires the use of proper stabilizing agents that prevent the aggregation of the colloids and exclude uncontrolled interaction with local environment. Poly(ethylene glycol)-coated gold nanoparticles have garnered considerable attention in the use for bio-related application that is due to low protein affinity and relatively high cellular uptake. However, the bulky ligands of the polymer often alter the mobility of the nanoparticles and physicochemical interaction with biomolecules. Here we showed that glycans with low molecular weight effectively stabilize gold nanoparticle with variety of shapes, including spheres, nanorods or nanostars. We experimentally correlated colloidal stability of glucose-stabilized gold nanoparticles in different biological environments and evaluated the transport of the nanoparticles in the complex medium by means of electrophoretic mobility, showing low protein affinity to glycan-based corona. Finally, chemical modification of glycan corona makes possible specific binding of the nanoparticle with desired proteins. We showed that lectin proteins are highly specific for glucosamine-conjugated gold nanoparticles, which was not observed in the case of gold nanoparticles stabilized with glucose.

COLL 17

Stimuli-responsive multicompartment micelles as highly efficient non-viral gene transfection agents

Felix H Schacher[1]*, felix.schacher@uni-jena.de, Anja Schallon*[1]*, Alexandra Rinkenauer*[1]*, Michael Wagner*[1]*, Ulrike Günther*[1]*, Ulrich S Schubert*[1]*, Eva Betthausen*[2]*.Â (1) Organic and Macromolecular Chemistry, Friedrich-Schiller-University Jena, Jena, - - Bitte wÃ¤hlen - - 07743, GermanyÂ (2) Macromolecular Chemistry II, University of Bayreuth, Bayreuth, Germany*

The controlled non-viral delivery of genetic material using cationic polymers into cells has been of interest during the last three decades, yet the ideal delivery agent featuring utmost transfection efficiency and low cytotoxicity still has to be developed. Here, we demonstrate that multicompartment micelles from stimuli-responsive triblock terpolymers, poly(butadiene-*block*-poly(methacrylic acid)-*block*-poly(2-(dimethylamino)ethyl methacrylate) (BMAAD), are promising candidates. The structures exhibit a patchy shell, consisting of amphiphilic (interpolyelectrolyte complexes, MAA and D) and cationic patches (excess D), generating a surface reminiscent to those of certain viruses and capable of undergoing pH-dependent changes in charge stoichiometry. After polyplex formation with plasmid DNA, superior transfection efficiencies can be reached for both adherent cells and human T-lymphocytes. Compared to the gold standard PEI, remarkable improvements and a number of advantages were identified for this system, including increased cellular uptake and an improved release of the genetic material, accompanied by fast and efficient endosomal escape. Furthermore, high sedimentation rates might be beneficial regarding *in vitro* applications.



COLL 18

Impact of DNA assembly on nanomaterial-cell interactions

Leo Y.T. Chou[1,2], *leo.chou@mail.utoronto.ca, Kyryl Zagorovsky*[1,2]*, Warren C.W. Chan*[1,2,3,4]*.Â (1) Institute of Biomaterials and Biomedical Engineering, University of Toronto, Toronto, Ontario M5S 3G9, CanadaÂ (2) Donnelly Centre for Cellular and Biomolecular Research, University of Toronto, Toronto, Ontario M5S 3E1, CanadaÂ (3) Department of Chemical Engineering, University of Toronto, Toronto, Ontario, CanadaÂ (4) Department of Materials Science Engineering, University of Toronto, Toronto, Ontario, Canada*

Developing nanomaterials with dynamic physicochemical properties open new opportunities to control their interactions with biological systems. Here, we used permutations of DNA-coated nanoparticles to construct a library of biodegradable colloidal superstructures displaying distinct physicochemical properties. In vitro screening against a model cell line demonstrates that cellular uptake of superstructures was dependent on both individual nanoparticle design and assembly configuration. Additionally, endosomal internalization of superstructures triggered their rapid degradation into dispersed components, facilitating subsequent extracellular escape in a design-dependent manner. This use of molecular assembly to design nanomaterial-cell interactions provides new possibilities to engineer the biological delivery and clearance of nanocarriers that is not possible using solid nanoparticles.

COLL 19

Nanoparticle interactions with lipid membranes studied by nonlinear optics

***Franz Geiger**, geigerf@chem.northwestern.edu.department of Chemistry, northwestern U, evanston, il 60208, United States*

Membrane-colloid interactions are notoriously difficult to probe using experimental in situ methods without relying on spectrochemical labels. Here, we present the first nonlinear optical studies of how 4 nm-sized gold metal nanoparticles containing positively and negatively charged ligands interact with supported lipid bilayers that are positively and negatively charged. Second harmonic generation probes the nanoparticles at the membrane surface under aqueous conditions ranging from 1 to 100 mM NaCl in tris buffer. Vibrational sum frequency generation probes the degree of disruption exhibited by the underlying lipid bilayer. Results using lipopolysaccharides are presented and discussed in the context of nanoparticle uptake and viability assays using single-(shewanella) and multicellular (daphnia magna) organisms.

COLL 20

Chiral solvent auxiliaries as a tool to amplify chirality within self-assembled monolayers at the liquid/solid interface

***Iris Destoop**[1], iris.destoop@chem.kuleuven.be, Elke Ghijsens[1], Kunal Mali[1], Kazukuni Tahara[2], Yoshito Tobe[2], Steven De Feyter[1].Â (1) Department of Chemistry, KU Leuven - University of Leuven, Leuven, BelgiumÂ (2) Division of Frontier Materials Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka, Japan*

The unique handedness of chiral molecules affects chemical, physical and biological phenomena. Due to geometrical restrictions upon two-dimensional confinement, transmission of chiral information is particular selective at liquid/solid interfaces. Overall chiral nanostructured surfaces can be obtained by the self-assembly of enantiopure molecules as they only form one handedness on the surface (mirror-image patterns are absent). Achiral molecules, on the other hand, leave the surface globally achiral as they will give rise to the formation of mirror-image patterns on the surface. So far, homochirality has been created in achiral enantiomorphous monolayers by merging chiral modifiers in the monolayer or by exposing the monolayers to magnetic fields. Alternatively, the potential role of chiral solvents in chirality amplification and emergence of homochirality remains largely unexplored. Here we show that chiral solvents can induce macroscopic chirality within self-assembled monolayers of achiral building blocks on an achiral surface. We report a set of scanning tunneling microscopy experiments of self-assembled achiral dehydrobenzo[12]annulene derivatives at the interface between

graphite and chiral 2-alcohols revealing both chain length dependence and odd/even dependence chirality amplification.

COLL 21

Organizational chirality expression as a function of the chirality measure for simple amino alcohols on Cu(100)

***Giorgio Contini**[1,4], giorgio.contini@ism.cnr.it, Riccardo GAtti[1,2], Guido Caponi[1], Stefano Colonna[1], Gianluca Galeotti[1,2], Daniele Catone[1], Stefano Turchini[1], Tommaso Prosperi[1], Nicola Zema[1], Amedeo Palma[3], Paola Gori[1,4].Â (1) Istituto di Struttura della Materia, Consiglio Nazionale delle Ricerche (CNR), Roma, ItalyÂ (2) Institut National de la Recherche Scientifique, Ã‰nergie, MatÃ©riaux et TÃ©lÃ©communications, UniversitÃ© du QuÃ©bec, Varennes, Quebec, CanadaÂ (3) Istituto per lo Studio dei Materiali Nanostrutturati, CNR, Monterotondo S. (RM), ItalyÂ (4) Centro Interdipartimentale Nanoscienze & Nanotecnologie & Strumentazione (NAST), University of Rome “Tor Vergata”, Rome, Italy*

Chiral self-assembled molecular networks are important both for technological and fundamental reasons. In spite of the large number of works in this field, the subtle mechanism of chirality transfer from single molecules to large scale two-dimensional (2D) networks is not well understood yet. This work reports on the self-assembly of simple amino alcohols on Cu(100) with different chirality measure; ethanolamine, alaninol (2-amino-1-propanol) and butanolamine (2-amino-1-butanol) have been investigated with scanning tunneling microscopy (STM), low-energy electron diffraction (LEED) and photoelectron spectroscopy (PES), corroborated with density functional theory (DFT) calculations. This systematic study addresses the role of the single-molecule handedness in the global chirality expression, indicating that the chirality measure of the precursors is an important variable for the formation of globally chiral superstructures.

COLL 22

Chirality, shape, and orientation influencing the self-assembly of organic molecules at interfaces

***David Amabilino**[1], amabilino@icmab.es, Hong Xu[2], Wojciech J. Saletra[1], Rasmita Raval[3], Steven De Feyter[2], Sam Haq[3].Â (1) Institut de Ciencia de Materials de Barcelona (ICMAB-CSIC), Cerdanyola del Valles, Barcelona 08193, SpainÂ (2) Department of Chemistry, KULeuven, Heverlee, BelgiumÂ (3) Department of Chemistry, University of Liverpool, Liverpool, United Kingdom*

The packing of organic molecules in three dimensional space is practically impossible to predict, while the situation at interfaces is considerably more straightforward given certain design criteria. However, in this presentation we shall show that simply modifying the shape of a molecule as well as the chirality of the component parts can have a dramatic effect on the outcome of adsorption. In particular, a homologous series of aromatic molecules substituted with lactic acid on one side and alkyl chains on the other display a plethora of intriguing phases at the graphite-liquid interface. On the other hand, the consitution of aromatic molecules has a direct consequence on their chemistry at a metal surface. The presentation will put the results obtained into the context of the supramolecular chemistry of molecules in two and three diemnsional systems.

COLL 23

Chiral supramolecular self-assembly in 2D

Wolf-Dieter Schneider, *wolf-dieter.schneider@epfl.ch.Institute of Condensed Matter Physics, Ã‰cole Polytechnique FÃ©dÃ©rale de Lausanne (EPFL), Lausanne, SwitzerlandDepartment of Chemical Physics, Fritz-Haber-Institute of the Max-Planck-Society, Berlin, Germany*

Combining STM observations and manipulations with first-principle electronic structure calculations, 1-nitronaphthalene molecules are found to become pseudo-chiral upon adsorption on Au(111). Hydrogen bonds are at the origin of their self-assembly into two-dimensional supramolecular clusters and chains [1-3]. Conservation of chirality is observed in a hierarchical supramolecular self-assembly of pentagonal symmetry of the organic molecule rubrene on Au(111) [4]. We show the spontaneous chiral resolution of the racemate into disjoint homochiral complex architectures and demonstrate the ability to monitor directly the evolution of chiral recognition processes on the molecular and supramolecular level [4-9]. A competition between long-range repulsive interactions, caused by substrate-induced molecular charging, and short-range attractive forces leads to the observed characteristic chiral supramolecular patterns [10].

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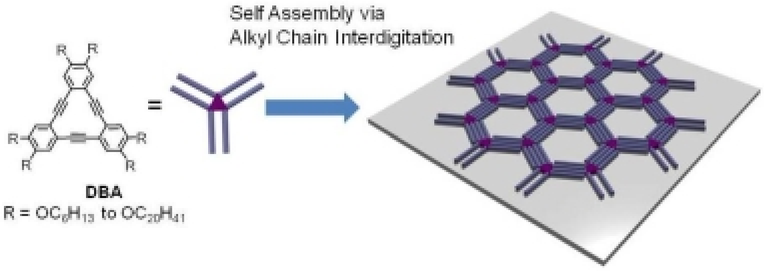
COLL 24

Adaptable molecular building block in on-surface self-assembly

Yoshito Tobe*, tobe@chem.es.osaka-u.ac.jp.Graduate School of Engineering Science, Division of Frontier Materials Science, Osaka University, Toyonaka, Osaka 560-8531, Japan*

Our research on porous molecular networks formed by self-assemblyof alkoxy-substituted dehydro[12]annulenes (DBAs) at the liquid/solid interface has been evolving thanks to the high level of adaptability of this building block. DBAs are adaptable not only to (i) modification of the pore size, (ii) pore functionalization for selective binding of guest molecules, and (iii) installation of reaction sites for covalent bonds between themselves leading to 2D polymers and with the substrate as well, but also for (iv) generation of chirality on surfaces at single molecular as well as supramolecular levels and (v) formation of superlattice structures on surfaces. In this presentation will be focused adaptable featues of the molecular building block.



COLL 25

Bio-inspired nanostructures: Patterning and mechanisms

Magali Lingenfelder, *magali.lingenfelder@epfl.ch.Max Planck-EPFL Center for Molecular Nanoscience and Technology, Lausanne, Vaud 1015, SwitzerlandThe Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States*

Starting from the single molecule level all the way to 2D and 3D systems the study of self-assembly by scanning probe techniques offers an atom-by-atom trip to the core of hybrid materials. Bio-inspired nanostructures open up new possibilities for energy applications.

Two systems are at the focus of our research: On one hand, the mimicking of catalytic centers by model 2D Metal-Organic Coordination Networks (MOCNs). On the other hand, CO_2 sequestration on natural self-assembled protein layers is tracked *in-situ* by Atomic Force Microscopy and X-Ray Absorption Spectroscopy at the liquid–solid interface.

By this approach we obtain molecular insight into both: bio-sequestration of CO_2 by natural systems and mechanistic pathways in engineered artificial photosynthesis.

COLL 26

Controlling the nucleation, growth, and ripening of surface-confined supramolecular networks: Implications to induction of homochirality on surfaces

Kunal S. Mali[1]*, kunal.mali@chem.kuleuven.be, Elke Ghijsens*[1]*, Oleksandr Ivasenko*[1]*, Yuan Fang*[1]*, Kazukuni Tahara*[2]*, Yoshito Tobe*[2]*, Steven De Feyter*[1]*.Â (1) Division of Molecular Imaging and Photonics, Department of Chemistry, KU Leuven-University of Leuven, Leuven, Flemish brabant 3001, BelgiumÂ (2) Division of Frontier Materials Science, Graduate School of Engineering Science, Osaka University, Toyonaka-Osaka, Osaka 560-8531, Japan*

Controlling the crystallization of materials-be it in solution or on surfaces, is of immense scientific and technological importance. This is because of the fact that various functional properties of materials are ultimately determined by the way in which molecules pack in crystals. One of the fascinating implications of this process is the propensity of certain materials to crystallize into non-superimposable opposite handed crystals that are related to each other by mirror image symmetry. In this contribution, we demonstrate a strategy to control the 2D crystallization of an organic molecule by controlling the nucleation and ripening processes transpiring at the liquid-solid interface. By careful choice of chiral dopant molecules and using a temperature assisted ripening process we illustrate how one can selectively stabilize or destabilize enantiomorphous molecular domains such that the handedness of the surface-confined network can be precisely controlled in a preprogrammed fashion. These results will have far-reaching implications in the strategies to control surface crystallization of materials.

COLL 27

2D self-assembled hydrogen-bonded molecular substitutional solid solution

Jennifer MacLeod[1], *macleod@emt.inrs.ca, Josh Lipton-Duffin*[1], *Dmitrii Perepichka*[2], *Federico Rosei*[1]*.Â (1) Ã‰nergie, MatÃ©riaux et TÃ©lÃ©communications, Institut National de la Recherche Scientifique, Varennes, Quebec J3X 1S2, CanadaÂ (2) Department of Chemistry, McGill University, Montreal, Quebec H3A 2K6, Canada*

Two-dimensional (2D) molecular self-assembly allows for the formation of well-defined supramolecular layers with tailored geometrical, compositional and chemical properties. However, to date, random intermixing and entropic effects in these systems have been associated with glassy phases and imperfect crystals. Here, we describe a 2D crystalline molecular self-assembled system that incorporates random substitutional defects. Density functional theory calculations elucidate certain aspects of the formation of this mixed lattice. This work provides insight into the manifestation of entropy in a crystallographically well-defined system, as well as into the applicability of Vegard's Law at the nanoscale.

COLL 28

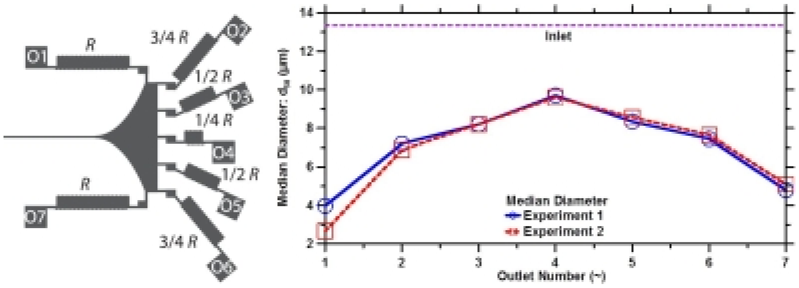
Application of inertial microfluidics for continuous separation of inorganic mineral particles

Aditya Kumar[1], *adityaku@ucla.edu, Peter Lewis*[1], *Jeffrey Bullard*[3], *Dino Di Carlo*[2], *Gaurav Sant*[1]*.Â (1) Department of Civil and Environmental Engineering, University of California Los Angeles, Los Angeles, CA 90095, United StatesÂ (2) Department of Materials Science and Engineering, University of California Los Angeles, Los Angeles, CA 90095, United StatesÂ (3) Materials and Construction Research Division, National Institute of Standards and Technology, Gaithersburg, Maryland 90024, United States*

The chemical reactivity of cement is relevant in describing the progress of early age reactions and microstructure development. The microstructure in turn, dictates the performance of and service life of a concrete material. However, the chemical reactivity, and to some extent, the composition of the cement particles is size-dependent. Since reactivity is a key variable which drives the progress of reactions, it would be valuable to fractionate cementing minerals (particulates) into well-defined size ranges, wherein, by eliminating aspects of size distribution, the mixed influences of surface area (i.e., particle size) and chemistry (i.e., particle composition) on reactivity can be unraveled.

This study applies a newly developed microfluidics based inertial separations method, first developed for cellular biotechnological applications, to the fractionation of cement particles, based on size. Inertial microfluidic separation uses a unique balance of inertial lift forces that lead to size dependent dynamic equilibrium positions within the cross-section of a high aspect-ratio channel. This research describes device designs and protocols to achieve separations of cementing particles to unique equilibrium

positions within the lateral space of the devices, from which they can be more easily retrieved in a size-dependent manner using symmetric outlets with tuned fluidic resistances.



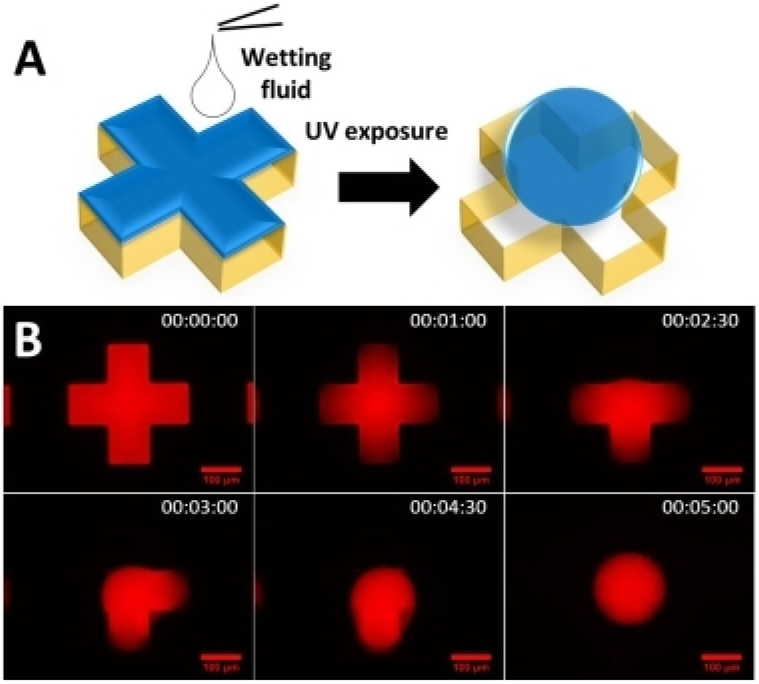
Special focus is placed on establishing the applicability of this method to: (1) the separation of cementing powders to assess the applicability of the procedure and (2) establishing the yield, efficiency and separation fidelity of the method as functions of parameters such as the fluid flow rate and solid loading in liquid suspensions.

COLL 29

Preparation of monodisperse microspheres from surface tension-mediated droplet formation in micromolds

Chang-Hyung Choi[1]*, changhyung.choi@gmail.com, Sung-Min Kang*[1]*, Jinkee Lee*[2]*, Chang-Soo Lee*[1]*.Â (1) Department of Chemical Engineering, Chungnam National University, Daejeon, Daejeon 305-764, Republic of KoreaÂ (2) School of Mechanical Engineering, Sungkyunkwan University, Republic of Korea*

Monodisperse microspheres are widely used in many applications such as micro-electromechanical systems (MEMS), chemical release systems, optical materials and various biological applications. Although droplet-based microfluidics allow for making monodisperse microspheres, it still definitely requires pressure driven flow as well as use of surfactant to achieve their uniformity. Here, we present a micromolding method that generates monodisperse microspheres through surface-tension-induced flow. Two immiscible fluids that consist of photocurable hydrophilic monomer and hydrophobic oil are sequentially loaded onto the polydimethylsiloxane(PDMS) mold. The mold geometry results in Laplace pressure induced droplet formation, and these droplets formed are individually localized into each micromold. We also quantitatively calculate the minimum pressure difference required to provide spherical droplets. Photopolymerization of the droplets allow for the formation of polymeric microspheres with narrow size distribution (CV=1.9%). We obtained the microspheres with diameter ranging from 60 to 200 μm by modulating mold dimensions. Moreover, we demonstrate the capability to produce microspheres through various solidification schemes: UV-polymerization, sol-gel reactions and solvent evaporation- induced colloidal assemblies.



COLL 30

Dynamics of surfactant-covered and surfactant-free drops in a microfluidic parking network

Siva A Vanapalli, *siva.vanapalli@ttu.edu, Swastika S Bithi.Chemical Engineering, Texas Tech University, Lubbock, Texas 79409, United States*

Immobilized arrays of monodisperse droplets represent a powerful platform for directly visualizing the kinetics of nucleation. To develop this microfluidic platform, we study the transport of a train of surfactant-covered (non-coalescing) and surfactant-free (coalescing) drops in a microfluidic parking network, which consists of a series of loops capable of parking drops. With non-coalescing drops, we find that collective interactions between drops in the network cause crowding and collisions between droplets. These collisions often cause droplets to break, producing significantly polydisperse droplet arrays. In striking contrast, with surfactant-free drops we identify collective mechanisms that lead to droplet arrays with exceptional monodispersity, without the need to tune drop size and spacing of the train. In particular, we find that moving drops rectify the volume of underfilled or overfilled parked drops through coalescence at junctions, followed by confinement-guided break-up. We identify a state diagram that quantifies this regime of self-rectification and find that it is sufficiently broad enough to allow robust storage of arrays of not only equal-sized drops but also of different volumes. We will discuss how we plan to use the flexibility provided by this platform to investigate the kinetics of nucleation in simple liquids.

COLL 31

New high-throughput microfluidic device for the production of monodisperse double emulsions and polymersomes

Kevin Y-S. Huang[1,2], *khuang05@gmail.com, Jennifer L. Bento*[1], *Michael Stredney*[1], *Douglas H. Adamson*[1,2]*.Â (1) Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269, United StatesÂ (2) Department of Chemistry, University of Connecticut, Storrs, Connecticut 06269, United States*

We introduce here a new microfluidic device for the rapid formation of monodisperse double emulsions. The device consists of three coaxial capillaries set in a single block of ultra-high molecular weight polyethylene (UHMWPE). We characterize the water-in-oil drop formation by measuring the diameter of the drops produced as a function of varying inner and outer Reynolds, Weber, and Capillary numbers. These parameters were subsequently used to characterize the dripping to jetting transition across a wide range of capillary channel diameters. We also observe that when produced using solutions of amphiphilic block copolymers, the double emulsions produced can be processed to form large numbers of monodisperse polymersomes in a highly efficient and controlled manner.

COLL 32

Fabrication of multiple-droplet array for miniaturizing microwell plate

Si Hyung Jin, *jsh8652@gmail.com, Heon-Ho Jeong, Young Moo Noh, Chang-Soo Lee.Department of chemical engineering, Chungnam National University,, Daejeon, Chungcheongnam-do 305-764, Republic of Korea*

Microwell plate is well-established platform to carry out high-throughput screening of various biochemical reactions. However, microwell plate based assays have limited in consumption of reagent and reaction time, quite labor-intensive protocol, and scale-up. There are several approaches to solve limitations of microwell plate. Vanapali and Hansen group, one of the pioneering groups, successfully presented microdroplet array format as an transformation of microwell plate into small scale. They can facilitate efficient and sensitive reaction with high throughput manner.

Here, we present another fully integrated format of droplet array for miniaturizing microwell plate. This system includes droplet generation, array, storage, fusion, and elimination on a single device. The device consists of two functional regions that are droplet generator and hydrodynamic traps. To achieve multiple-droplet array, we perform repeated two step operations such as arraying and storage process. In the arraying process, droplets are sequentially trapped into hydrodynamic traps by using hydraulic pressure balance in microstructures. The unit operation of trapping can be controlled by varying the volume of droplets. In the storage process, droplets are moved from trapping sites to corresponding reaction chambers by microvalving action. In this

experiment, each of reaction chambers is filled with chemically distinct twelve droplets. To demonstrate programmability and controllability, we generate complex fluorescent gradient array under the fully automated system

Finally, we believe that the droplet array with high throughput manner overcome disadvantages of conventional microwell plate assay.

COLL 33

Self-propelled motion of microscale capsules

***Annie Xi Lu**[1], xilu0306@yahoo.com, Don DeVoe[2], Srinivasa Raghavan[1].Â (1) Department of Chemical Engineering, University of Maryland, College Park, Maryland 20742, United StatesÂ (2) Department of Mechanical Engineering, University of Maryland, College Park, Maryland 20742, United States*

This talk will describe a class of microscale capsules that move in the presence of a chemical fuel. These structures are created *in situ*within a microfluidic platform using the biopolymer chitosan as precursor. Two chitosan droplets of different sizes are brought into contact by a channel expansion, whereupon they are crosslinked into a permanent dimer. The overall dimer resembles a Janus particle, and the shape and functionality of each lobe in the dimer can be varied. To create microswimmers, we load one lobe of the dimer with catalytic nanoparticles. When a chemical fuel is introduced into the solution, the fuel reacts with the catalyst, generating gas bubbles, which ultimately drive the motion of the dimer structure. The motion can be tuned by varying the size and concentration of the nanoparticles, the concentration of chemical fuel, and the extent of crosslinking of the dimer. Our approach is simple and versatile and can be easily adapted to produce a variety of capsules with motile capabilities.

COLL 34

Rapid generation of solubility curves using drop-based microfluidics

***Jihye Kim**, zhay0809.kim@ttu.edu, Siva Vanapalli.Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States*

Knowledge of solubility of a solute is important in industries such as pharmaceutics, foods, and cosmetics. Current methods used to measure solubility are time-consuming and labor-intensive and require a large amount of sample. Drop-based microfluidics is a powerful tool to determine solubility curves where each droplet acts as a microreactor. Benefits of this approach include less consumption of sample and flexible manipulation of drop volumes and composition.

We develop a microfluidic device that allows rapid generation of arrays of immobilized droplets and assess the capability of the device to measure solubility curves of inorganic salts. Droplets of volume 200 nL and a given potassium nitrate concentration are stored in the drops, followed by a thermal quenching and heating cycle. As temperature is lowered to the solubility limit, the salt inside droplets starts crystallizing. The temperature when all droplets contain crystals is recorded as the lower bound of solubility (super saturation curve). On the completion of crystallization, temperature is slowly increased to dissolve the crystals, and the temperature at which no crystal is detected is recorded as dissolution point (super solubility curve). By repeating these measurements at various salt concentrations in the same device, we recover the solubility curve of potassium nitrate, which is in good agreement with literature data. We also design a droplet-based device that allows simultaneous screening of multiple concentrations of salt enabling rapid determination of high-resolution solubility curves.

COLL 35

Microfluidic flow-focusing: Alginate gel drop formation in Newtonian and non-Newtonian fluids

Thomas Ward[1]*, thomasw@iastate.edu, Yi-Lin Wang*[2]*, Rex Jeffries*[3]*, Christine S. Grant*[3]*.Â (1) Department of Aerospace Engineering, Iowa State University, Ames, Iowa 50011-2271, United StatesÂ (2) Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei City, Taiwan Republic of ChinaÂ (3) Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, United States*

In this talk we present data for the formation of alginate gel drops in both Newtonian and non-Newtonian fluids. The Newtonian fluid continuous phase experiments have been recently studied by others. But the non-Newtonian continuous phase fluid case presents a novel study on viscoelastic multi-phase fluid flow in microchannels. A microfluidic flow focusing geometry is used to study alginate gel drop formation using pressure driven devices. This allows for the determination of the pressure ratio versus drop size curves for comparison with Newtonian fluid studies. Stable jet formation also appears during drop formation for Newtonian liquids while unstable jet formation appears in the non-Newtonian continuous phase fluid experiments. It appears that the non-Newtonian fluid introduces an additional time scale into the flow dynamics which yields unstable results for drop formation that we characterize for a wide range of inlet pressures.

COLL 36

Atomic layer deposition overcoating of supported transition metal nanoparticle catalysts

Junling Lu[3]*, Bin Liu*[4]*, Jeffrey P Greeley*[5]*, Jeffrey W Elam*[2]*,* ***Peter C Stair***[1,6]*, pstair@northwestern.edu.Â (1) Department of Chemistry, Northwestern University, Evanston, IL 60208, United StatesÂ (2) Energy Systems Division, Argonne National Laboratory, Argonne, IL 60439, United StatesÂ (3) Department of Chemical Physics, University of Science and Technology of China, Hefei, ChinaÂ (4) Department of Chemical Engineering, Kansas State University, Manhatten, KS 66506, United StatesÂ*

(5) School of Chemical Engineering, Purdue University, West Lafayette, IN 47907, United StatesÂ (6) Chemical Sciences & Engineering Division, Argonne National Laboratory, Argonne, IL 60439, United States

The ability of atomic layer deposition (ALD) to produce conformal oxide coatings on porous, high-surface area materials can provide completely new types of catalyst structures. When applied to supported transition metal nanoparticles, aluminum oxide overcoating layers provide a porous encapsulating shell that stabilizes the nanoparticles against sintering. For overcoating thicknesses less than ca. 2 nm, the porosity appears to be a consequence of the reactivity between ALD precursors and different surface atom geometries combined with a self-poisoning effect caused by precursor ligand adsorption on the surface. The preference for reaction of the alumina ALD precursor, trimethylaluminum, at under-coordinated atoms on Pd nanoparticles imparts a control over the geometry of the surface sites that are available for catalyzed reactions with pronounced effects on reaction selectivity.

COLL 37

Chemistry of alkoxide-containing precursors during atomic layer deposition of supported VO_x and TiO_2

Alexis M Johnson[1]*, alexis.johnson@northwestern.edu, Brian R Quezada*[2]*, Laurence D Marks*[3]*, Peter C Stair*[1,4]*.Â (1) Chemistry, Northwestern University, Evanston, Illinois 60208, United StatesÂ (2) McCormick School of Engineering, Northwestern University, Evanston, Illinois 60208, United StatesÂ (3) Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, United StatesÂ (4) Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439, United States*

Atomic layer deposition (ALD) is a thin film deposition technique that is comprised of a series of self-limiting reactions to grow materials one layer at a time. Recently ALD has become a promising method in catalyst development because of its controlled growth of uniform thin films and noble metal nanoparticles. While applications of ALD have significantly increased, fundamental understanding of the chemistry that takes place is still lacking. Through XPS and mass spectrometry, reaction mechanisms and properties of ALD formed systems were explored. Specifically, we studied two precursors containing alkoxide ligands - vanadyl triisopropoxide (VOTP) and titanium tetraisopropoxide (TTIP).

VOTP was used to create supported vanadium oxide monomers, which are active catalysts for oxidative transformations of organic molecules; however, their reactivity depends on their molecular structure. We found that reactive adsorption of VOTP onto amorphous Al_2O_3 resulted in tridentate VO_x species with three bonds to the surface. However, on a $SrTiO_3$ (001) surface VO_xforms a bidentate species with only two bonds to the surface. The number of V-O-M bonds to the surface correlates with the reaction site density of the substrate, indicating that the substrate structure strongly influences what monomeric structures can form on a given surface.

TTIP is a precursor that is commonly used for TiO_2 growth in atomic layer and chemical vapor depositions. We found that the chemistry of TTIP deposition onto MoO_x is pressure dependant, where at low pressures TiO_2 catalyzed dehydration of the precursor occurs leading to chemical vapor deposition rather than atomic layer deposition for the growth mode of TiO_2. These results likely extend to any surface, highlighting the common problem of “pressure gap” chemistry in catalysis and emphasize the need to study these reactions under relevant conditions.

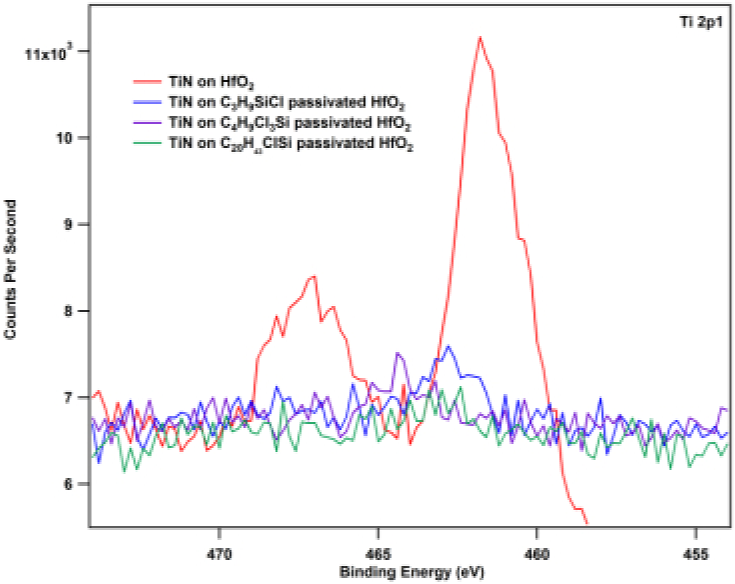
COLL 38

Selective deposition of TiN on HfO_2

***Sonali N Chopra**, snchopra@utexas.edu, Joseph M McCrate, John G Ekerdt.McKetta Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712, United States*

Conductive films are used in a variety of devices ranging from optics to microelectronics, sensors, and advanced memory. In devices such as spin-transfer torque random access memory (STT-RAM), TiN is increasingly used for the word line because of its high conductivity and diffusion barrier properties. HfO_2 commonly forms the gate oxide of the device because of its high dielectric constant. Bottom-up approaches utilizing area selective atomic layer deposition (AS-ALD) to deposit materials such as HfO_2 and TiN in STT-RAM have recently piqued interest because of their potential to reduce cost and save material in the fabrication process. Further, approaches to passivate regions of the HfO2 chemically offer to eliminate lithography and etching steps. ALD is advantageous over other chemical and physical vapor deposition processes because of its ability to perform low temperature conformal depositions with precise thickness control.

Using x-ray photoelectron spectroscopy, water contact angle measurements, and x-ray reflectivity, our presentation will reveal how silane-functionalized molecules can be used to effectively passivate HfO_2 thin films toward subsequent TiN deposition. All experiments were performed in a custom built vacuum chamber to allow for vapor phase deposition of the silane-functionalized passivants. We show how attachment of silane molecules to the HfO_2 surface act as a blocking layer to the TiN precursors in the ALD process. Furthermore, we analyze the limits of this passivation and also explore its potential uses for patterning devices.



COLL 39

Molecule engineering for ALD applications

*Jie Huang, Antonio Lucero, Lanxia Cheng, **Jiyoung Kim**,
jiyoung.kim@utdallas.edu.Department of Materials Sci. & Eng., University of Texas at
Dallas, Richardson, TX 75080 75080, United States*

In this presentation, two different enigineering approaches to employ molecules for ALD applications will be discussed. One is modification of substrates using molecules (e.g. self-assembled monolayers) to prevent (or enhance) nucleation of ALD (Atomic layer deposition). Self-assembled monolayers (SAMs), as an important sub-group of organic molecules, such as octadecyltrichlorosilane (OTS) etc., are frequently considered as ultrathin materials suitable for surface engineering with nano-scale dimensions. We have demonstrated selective-area deposition using electron-beam patterned SAMs as a nucleation inhibition layer followed by atomic layer deposition (ALD). Nano-line patterns with sub-30 nm resolution and 100 nm in pitch were achieved.

The other approach is direct implements of a small molecule as a molecule precursor to deposit self-limiting organic layers which eventually allows layer-by-layer deposition like ALD. A certain linker, such as OTS, Hydroquinone (HQ), was applied to construct multilayers of the organic molecules. Conventional inorganic ALD films can be embedded between the organic layers to form organic-inorganic hybrid nano-laminates. It was found that the thin film characteristics can be varied from insulating and semi-conducting layers as altering the organic component from alkane to aromatic based molecules. This methodology would provide a new route to build 2D nanosheets with unique properties.

COLL 40

Real-time studies of the atomic layer deposition of metal oxides using ambient pressure X-ray photoelectron spectroscopy

Ashley R Head[1]*, ahead100@gmail.com, Shilpi Chaudhary*[1]*, Sofie Yngman*[1]*, Niclas Johansson*[1]*, Olesia Snezhkova*[1]*, Jan Knudsen*[1,2]*, Hendrik Bluhm*[3]*, Anders Mikkelsen*[1]*, Timm Rainer*[1]*, Joachim Schnadt*[1]*.Â (1) Division of Synchrotron Radiation Research, Department of Physics, Lund University, Lund, SwedenÂ (2) Max IV Laboratory, Lund University, Lund, SwedenÂ (3) Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States*

Performing atomic layer deposition (ALD) of metal oxides at pressures around 0.01 mbar slows the half reactions of the process to allow in situ and real-time probing of changes in the surface electronic structure using ambient pressure X-ray photoelectron spectroscopy (APXPS). By monitoring the ALD process as it occurs, new details on the mechanisms of interface formation and thin film growth can be obtained. The deposition of HfO_2 on InAs and the deposition of TiO_2 on rutile titania from transition metal coordination complexes and water were studied with APXPS. Predictable, cyclic chemical shifts of ligand and substrate ionizations are seen in the growth of both films. However, the kinetics of the film growth differs for the two systems. Upon exposure to the titania surface, the titanium precursor reacts straightaway and gradually proceeds to completion. In contrast, the halfnium precursor does not interact with the surface immediately. Once an activation barrier is surpassed, the reaction occurs instantaneously. During the interface formation between the HfO_2 and InAs, the self-cleaning of the native arsenic oxide is observed through the disappearance of a component in the As 3d ionization. By understanding the reactivity of different precursors, the ALD process can be more easily optimized in applications that require thin films of metal oxides such as metal-oxide-semiconductor devices and catalytic surfaces.

COLL 41

Selective copper atomic layer deposition of $Cu(thd)_2/H_2$ on palladium and its application to DNA sequencing

Xiaoqiang Jiang*, xij09001@engr.uconn.edu, Han Wang, Willis G. Brian.Department of Chemical & Biomolecular Engineering, University of Connecticut, Storrs Mansfield, Connecticut 06269, United States*

<h3>Selective copper atomic layer deposition using copper bis (2,2,6,6-tetramethyl-3,5-heptanedionate) ($Cu(thd)_2$)/H_2 on palladium is useful for the nanofabrication of tunneling-based electronic devices. Real-time in-situ spectroscopic ellipsometery (RTSE), ex-situ x-ray photoelectron spectroscopy (XPS), and x-ray diffraction (XRD) were applied to study the mechanism and selectivity of the copper ALD process. Good selectivity of copper film growth was achieved on palladium over silicon dioxide and

silicon nitrides surfaces. High-resolution RTSE with submonolayer sensitivity was achieved to track adsorption and desorption of precursor molecules during each half-cycle. Different from literature reports, we present a mechanism that proceeds through chemisorbed hydrogen intermediates that react with $Cu(thd)_2$ during precursor dosing. It is found that diffusion of palladium into copper is facile during growth and is exacerbated by high temperatures and long purge times. Moreover, Pd diffusion leads to substrate effects that persist during growth. Under optimal conditions, high purity Cu films can be grown. Tunneling structures for fast and inexpensive single molecule DNA sequencing have been nanofabricated using a procedure involving a combination of lift-off and e-beam photolithography. This presentation will discuss the application of ALD Cu to these devices, including emphasis on good selectivity, controlled growth rate, and copper film quality. </h3>

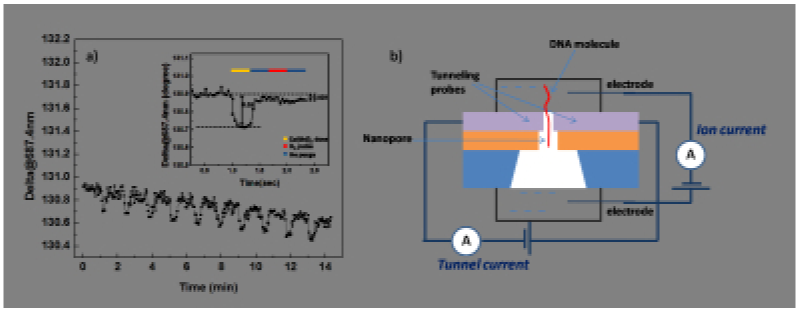


Figure-1 . a) SE results of 10 cycle copper ALD and one cycle of copper ALD (inset); b) tunneling electrodes-Nanopore device for DNA nucleotides sequencing

COLL 42

Strategies for selective deposition of organic and inorganic materials on patterned substrates

*Fatemeh S. M. Hashemi[2], Chaiya Prasittichai[1], **Stacey F Bent**[1], sbent@stanford.edu.Â (1) Department of Chemical Engineering, Stanford University, Stanford, CA 94305, United StatesÂ (2) Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305, United States*

Many applications require use of materials that are patterned or consist of 3-D shapes. For example, in electronic devices, 3-D structures such as those found in FinFETs are becoming more prevalent. To achieve such complex structures with nanometer-scale feature sizes, selective deposition processes may help facilitate the fabrication process. Here we describe area selective deposition using a combination of self assembled monolayers (SAMs) and atomic or molecular layer deposition (ALD/MLD). ALD and MLD are good choices for selective deposition because they are based on self-limiting reactions between gas phase precursors and specific functional groups at the growth surface. This chemical specificity provides a means to achieve selectivity in ALD/MLD on a spatially patterned substrate. Selectivity is obtained by passivation of the surface using SAMs in the regions where deposition is not desired. We will describe two systems. In the first, we explore strategies for achieving area selective deposition of dielectric materials by selectively depositing an organic SAM as the blocking layer on metal parts of a metal/dielectric substrate pattern. We show that both alkanethiol and alkylphosphonic acid SAMs can prevent subsequent deposition of metal oxide dielectric films via ALD on copper. We also introduce results showing that regeneration of the alkanethiol SAM protecting layer between ALD cycles is effective in improving the blocking properties of the SAM on Cu. This strategy provides the ability to carry out selective deposition for film thicknesses greater than 30nm, opening up the possibility for new applications in next generation electronic devices. In the second system, we explore whether similar approaches can be used to block MLD of organic films. Interestingly it is found that it is more difficult to completely block polyurea MLD than it is to block ZnO ALD. An explanation based on the nucleation mechanisms of both processes is proposed.

COLL 43

Toward organic electronics: Methods for the selective deposition of semiconductors

Zhiwei Shi, Jing Yang, ***Amy V Walker****, amy.walker@utdallas.edu.Department of Materials Science and Engineering, University of Texas at Dallas, Richardson, Texas 75080, United States*

Robust methods for the chemically selective deposition of semiconductors are developed and applied in the construction of complex two- and three-dimensional structures. These methods are easily parallelized, afford precise nanoscale placement and are compatible with photolithography. This work has important applications including in photovoltaics, molecular and organic electronics, and other technologies. Several recent developments in our laboratories are discussed including the chemical bath deposition (CBD) and atomic layer deposition (ALD) of ZnO and the formation of Cu and Cu_xS “wires” on micron-scale patterned surfaces. We demonstrate that the deposition selectivity and film morphology can be controlled by the deposition technique, the experimental conditions and the underlying substrate chemistry. Optimization and further development of these techniques requires a detailed understanding of the reaction pathways involved in the interaction of organic thin films with organometallic compounds, ions, and other compounds.

COLL 44

Membrane mechanics

Subra Muralidharan*, subra.murali@wsu.edu.School of Molecular BioSciences, Washington State University, Pullman, WA 99164, United States*

Mechanical properties of cell and synthetic membranes play a significant role in their response

to extracellular stress and molecular transport. Cell membrane mechanics is dynamic unlike

synthetic membranes, which tend to be static. Understanding cell membrane mechanics is

integral to understanding the role extracellular mechanical stress in many diseases like cancer.

Recent developments in this area will be discussed.

COLL 45

Membrane synthesis

Subra Muralidharan, *subra.murali@wsu.edu.School of Molecular BioSciences, Washington State University, Pullman, WA 99163, United States*

Modeling and understanding biomembrane structure, dynamics, and transport have resulted

in novel synthetic strategies. These in addition to providing insights have also yielded novel

compounds. Highlights of recent membrane synthesis will be discussed.

COLL 46

Membrane structure

Subra Muralidharan, *subra.murali@wsu.edu.School of Molecular BioSciences, Washington State University, Pullman, WA 99164, United States*

Cell membrane structure due the complex milieu of molecules that are self-assembled

continues to provide opportunities for newer studies aided by many developing methods.

Significant aspects of recent developments will be discussed.

COLL 47

Membrane dynamics

***Subra Muralidharan**, subra.murali@wsu.edu.School of Molecular BioSciences, Washington State University, Pullman, WA 99164, United States*

The dynamics of self-assembled molecules in biomembranes imparts membrane dynamics

features that influence structure, molecular transport, response to extracellular mechanical

stress, and signaling pathways. Important advances in understanding membrane dynamics will

be discussed.

COLL 48

Techniques

***Subra Muralidharan**, subra.murali@wsu.edu.School of Molecular BioSciences, Washington State University, Pullman, WA 99164, United States*

Many time resolved techniques are continuing to be employed in stand alone and coupled

modes to discern the dynamic structure of biomembranes. Some of the recent advances will be

discussed.

COLL 49

One-pot synthesis of fluorescent hybrid nanoparticles and their assembly into transparent and multi-colored nanofilms

***Yuuka Fukui**, yuukafukui@applc.keio.ac.jp, Yui Ozawa, Keiji Fujimoto.Department of Applied Chemistry, Keio University, Yokohama, Kanagawa Prefecture 223-8522, Japan*

We developed a route for one-pot synthesis of hybrid nanoparticles and their assembly into a nanofilm by utilizing a fusion and fission-triggered nanoreactor system based on water-in-oil miniemulsion system [*J. Mater. Chem.*, 2012, 22, 3493-3499, *J. Mater. Chem. C*, 2013, 1, 1231-1237].

(a) One-pot synthesis of fluorescent hybrid nanoparticles (figure 1a)

A fluorescent nanocrystal, ZnS:Mn^{2+} was produced in a confined system via fusion and fission of nanodroplets induced by ultrasonication and subsequent polymerization allowed for encapsulation of nanocrystals inside polymer nanoparticles. The resultant hybrid nanoparticles exhibited strong light emitting under UV irradiation due to an efficient surface capping of nanocrystals with polymers. Also, hybrid nanoparticles with different colors could be created by tuning of Mn^{2+}doping into ZnS nanocrystals.

(b) Assembly of hybrid nanoparticles to create multi-colored nanofilms (figure 1b)

The hybrid nanoparticles were spin-coated to form a transparent hybrid nanofilm. The nanofilms prepared from ZnS-encapsulated and $ZnS:Mn^{2+}$-encapsulated nanoparticles showed blue and orange emission, respectively. Furthermore, we developed a simple and facile way in making diverse fluorescent colors. By mixing of hybrid nanoparticles of ZnS (blue) and those of $ZnS:Mn^{2+}$(orange) at different volume ratios, the output color of the nanofilm could be controlled from blue to orange.

We believe that our nanoreactor system would offer a viable way in one-pot synthesis of nanomaterials applicable to various devices.

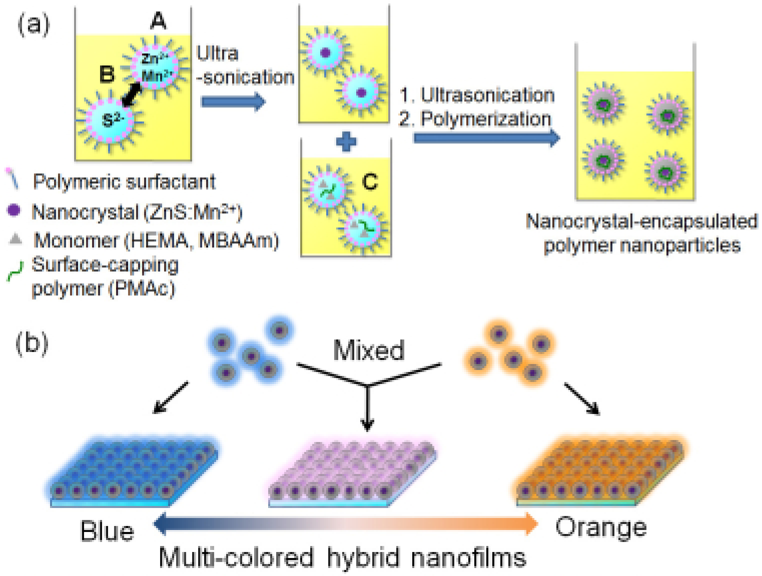


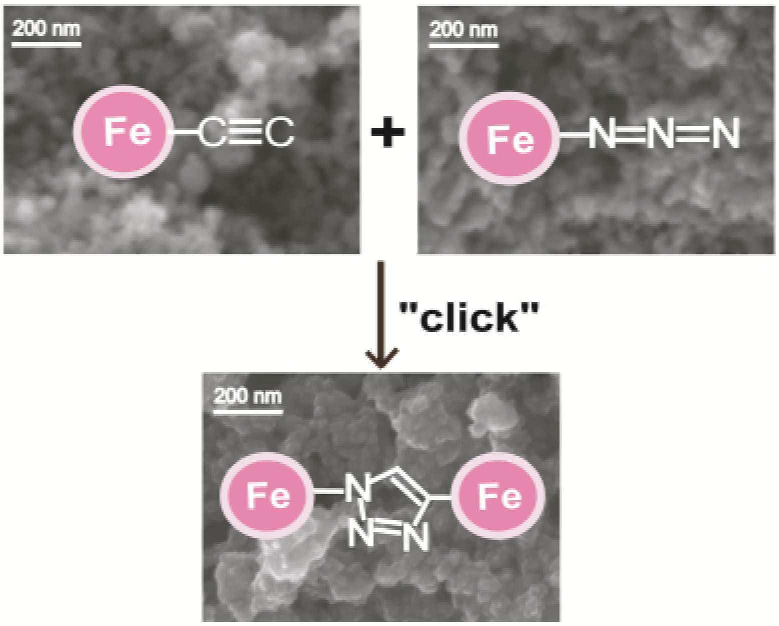
Figure 1 (a) A route to prepare $ZnS:Mn^{2+}$ nanocrystals, followed by their encapsulation by polymerization of HEMA within a nanoreactor system based on miniemulsion. (b) The resultant hybrid nanoparticles were spin-coated to form transparent and fluorescent hybrid nanofilms.

COLL 50

Application of "click chemistry" in designing new magnetic materials

Yue Liu[1]*, yueliu@udel.edu, Ramarao Neelam*[2]*, Timothy Miller*[1]*, George Hadjipanayis*[2]*, Andrew Teplyakov*[1]*.Â (1) Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716, United StatesÂ (2) Department of Physics & Astronomy, University of Delaware, Newark, Delaware 19716, United States*

Iron nanoparticles were used as a case study to apply chemical surface functionalization of magnetic nanoparticles to drive their assembly into new magnetic materials. Two batches of iron nanoparticles were functionalized with 5-azidopentanoic acid and 5-hexynoic acid, respectively. The iron nanoparticles modified with two different functionalities were then reacted through “click chemistry” by using Cu(I) catalyst in DMSO/water solvent. A combination of density function theory (DFT) calculations, Fourier- transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) were used to investigate each surface modification step as well as the result of the “click chemistry” process. This approach proved the success of this material design scheme.Scanning electron microscopy (SEM) uncovered the morphological change after “click” reaction of the iron nanoparticles modified with two different functionalities, confirming the formation of a new material. A series of control experiments ruled out the possibility of changing morphology through redox reactions and other unwanted processes. Vibrating sample magnetometer (VSM) showed that the new material retained approximately 50% of magnetization. Future work will focus on using organic solvents and faster “click”-type reactions to prevent surface oxidation and retain the magnetic properties at their original level.



COLL 51

Nonequilibrium synthesis of hierarchical nanostructures at reactive interfaces

*Eric J Nelson[1], Eric J Lochner[2], Yan Xin[3], **Jason J Pagano**[1], jpagano@svsu.edu.Â (1) Department of Chemistry, Saginaw Valley State University, University Center, Michigan 48710-0001, United StatesÂ (2) Department of Physics, Florida State University,* *Tallahassee, Florida 32306-4350, United StatesÂ (3) National High Magnetic Field Laboratory, Tallahassee, Florida 32310-3706, United States*

Chemical reactions far from equilibrium are capable of producing hollow tubes of silica-supported metal hydroxides (or oxides). The tubes are hierarchically ordered materials which grow at the molecular level into the macroscopic. In our experiments, we produce highly linear silica/cadmium hydroxide/cadmium oxide tubes that grow to decimeter lengths and have radii in the range of 40-600 µm. Scanning electron microscopy (SEM) characterizations of the outer and inner surfaces reveal qualitative differences. The walls of the tubular precipitation structures have typical widths of 3-10 µm. Results from powder X-ray diffraction (XRD) and transmission electron microscopy (TEM) of the powdered silica/cadmium hydroxide/cadmium oxide tubes are presented. Potential applications of silica/cadmium hydroxide/cadmium oxide tubes will be discussed.

COLL 52

Self-assembly of colloidal nanoparticles: The roles of shape, size, and ligand

***Zewei Quan**[1], zquan@lanl.gov, Zhongwu Wang[2], Jiye Fang[3], James Boncella[4], Hongwu Xu[1].Â (1) Earth and Environmental Science, Los Alamos National Laboratory, Los Alamos, NY 87545, United StatesÂ (2) Cornell High Energy Synchrotron Source, Cornell University, Ithaca, NY 14853, United StatesÂ (3) Department of Chemistry, State University of New York at Binghamton, Binghamton, NY 13902, United StatesÂ (4) Materials Physics and Applications, Los Alamos National Laboratory, Los Alamos, NM 87545, United States*

Self-assembly of various building blocks into macroscopic structures with desired features and functions, that is, "bottom-up" assembly, is an interesting theme that runs through chemistry, biology and material science.[1] Among them, due to the research efforts from many groups, colloidal nanoparticles can be prepared with tunable shapes, sizes and organic ligands. We have used this tunability in our investigations of the self-assembly process.

Here, I will present our recent progress on the self-assembly of colloidal nanoparticles, focusing on colloidal lead chalcogenide nanoparticles with adjustable sizes from 3 to 9 nm.[2,3] With the progressive increase in particle size, their shapes change correspondingly from octahedra to cubes. Additionally, we also use different solvents to modulate the individual particle interactions to control the final superlattice type. The use of advanced synchrotron-based small angle and wide angle X-ray scattering (SAXS and WAXS) techniques provides us with a powerful set of tools to perform this study.[4] These investigations are expected to produce deep insights into the effects that control the complex processes that determine particle and superlattice morphology

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COLL 53

Assembly of asymmetric microparticles at air/water interface

Sung-Min Kang[1]*, sungmin.kang21@gmail.com, Chang-Hyung Choi*[1]*, Byoung-Jin Lee*[1]*, Daeyeon Lee*[3]*, Bum Jun Park*[2]*, Chang-Soo Lee*[1]*.Â (1) Department of Chemical Engineering, Chungnam National University, Daejeon, Daejeon 305-764, Republic of KoreaÂ (2) Department of Chemical Engineering, Kyung Hee University, Yongin-si, Yongin-si 446-701, Republic of KoreaÂ (3) Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA 19104, United States*

Self-assembly of particles at fluid–fluid interfaces at the microscopic level has been extensively investigated. The ability to control the shape and wetting properties of anisotropic particles could provide a unique opportunity to control their surface activity.

In this work, we study self-assembly behavior of complex patched particles by using capillary multipoles. Complex patched particles with hydrophilic body and relatively hydrophobic patches can be synthesized by micromolding technique combined with photopolymerization.

At an air/ water interface, the formation of capillary multipoles induced by individual patchy results in formation of complex assembled structure. In addition, the formation of assembled structures can be manipulated by the size of controlled patchy.

We envision that the interfacial assembly of complex patched particles provides alternative and efficient tool for fundamental study about a long ranged particle-particle interaction. Based on this study, we are able to understand particle-particle interaction at fluid-fluid interface.

COLL 54

Deposition of 2D colloidal coatings from zeolite nanoplatelets by controlled convective assembly

Daniel Liu[1]*, danieljliu@gmail.com, Orlin Velev*[2]*, Benjamin Martin*[1]*.Â (1) NSF-PREM Center for Interfaces in Materials, Texas State University, San Marcos, Texas 78666,* *United StatesÂ (2) Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, United States*

Relatively monodisperse zeolite (ZSM-2) nanoparticles were synthesized by a hydrothermal reaction. The approximately 150 nm diameter zeolite nanoparticles have a well-defined hexagonal platelet-like geometry with an aspect ratio of approximately 5:1 and form a stable colloidal suspension in water. The nanoplatelets were deposited onto a substrate by a controlled convective assembly method that involved evaporation of a dilute aqueous suspension confined in a small meniscus region that was slowly drawn across the substrate surface. The deposition formed a coating of the zeolite nanoplatelets with monolayer and multilayer regions. The nanoparticles in monolayer regions are close-packed and uniformly oriented in a hexagonal arrangement, while the multilayer regions are disordered. Major process parameters such as suspension concentration and deposition speed were found to be key factors in controlling the resulting morphology and continuity of the coating. The surface energy of the substrate surface and the evaporation rate are also significant. The results make possible the rapid and facile deposition of strongly adhesive catalytic nanofilms.

COLL 55

Greener pathways for the synthesis of nanomaterials

***Rajender S Varma**, Varma.Rajender@epa.gov.Sustainable Technology Division, National Risk Management Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268, United States*

Vitamins B_1, B_2, C, and tea and wine polyphenols which function both as reducing and capping agents, provide extremely simple, one-pot, greener methods to bulk quantities of nanomaterials in water.[1] Shape-controlled synthesis of via microwave (MW)-assisted spontaneous reduction of noble metal salts using sugars or polyols will be presented. MW-assisted method has been developed for the cross-linking reaction of poly (vinyl alcohol) (PVA) with metallic systems and formation of biodegradable carboxymethylcellulose (CMC) composite films with noble nanometals. MW hydrothermal process produces magnetic nanoferrites[2] and micro-pine structured materials in water from readily available metal salts.[3] Sustainable route to nanoparticles using polyphenols from winery waste,[4a] beet juice,[4b] and biodiesel byproduct, glycerol[4c] and use of microwaves to generate uniformly smaller size particles will be highlighted.

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COLL 56

Effects of multiplexing small molecule-DNA hybrid linkers on the DNA-directed synthesis of nanoparticle superlattices

Ibrahim Eryazici[1]*, ieryazici@northwestern.edu, Robert J. Macfarlane*[1]*, Keith A. Brown*[1]*, Byeongdu Lee*[2]*, Ryan V. Thaner*[1]*, Chad A. Mirkin*[1]*, SonBinh T. Nguyen*[1]*.Â (1) Department of Chemistry, Northwestern University, Evanston, IL 60208, United StatesÂ (2) X-ray Science Division, Argonne National Laboratory, Argonne, IL 60439, United States*

The assembly of gold nanoparticles (AuNPs) into colloidal crystals via programmable DNA interactions has recently been shown to be a versatile method for creating nanoparticle-based superlattices with tunable particle compositions, lattice parameters, and crystal symmetries.[1] A broad range DNA-linked AuNP lattices, whose structures can be predicted through a phase diagram, can be formed by controlling both the hydrodynamic size and number of DNA strands on these particles. We have extended this work to include a new DNA linker system based on small molecule-DNA hybrids (SMDHs), wherein the incorporation of a small molecule core results in branched DNA building blocks. When these branched SMDHs are used as linkers in the construction of AuNP superlattices, every single hybridized junction between particles comprises multiple DNA duplex connections. This allows us to increase the total number of DNA connections between particles and tune the thermodynamics of binding between the SMDHs. In this presentation, we will discuss the thermodynamic properties of this new class of SMDH-linked AuNP structures and their implications in the formation of nanoparticle superlattices.

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COLL 57

Atomistic modeling of colloidal nanoparticles with active ligands: Solvation, electro-activity, pH-activity, and bio-activity

Petr Kral*, pkral@uic.edu.Chemistry, Physics, University of Illinois at Chicago, Chicago, IL 60607, United States*

We present our recent collaborative studies of colloidal nanoparticles with active ligands that can control the nanoparticle behavior. In particular, we show that: 1) nanoparticles of different sizes can have different solvation properties, 2) self-assembly and positioning of nanoparticles at the interfaces of different ionic solvents can be controlled

by electric fields, 3) pH can control the self-assembly of nanoparticles into exotic superstructures, and 4) ligands can determine the biological responses of nanoparticles. We use atomistic molecular dynamics simulations to capture the unique characteristics of these novel systems and explain their properties through the physical, chemical, and biological processes taking part at their ligands.

COLL 58

Controlled self-assembly of colloidal nanoparticles into finite-sized superstructures

Henry Chan*, hchan20@uic.edu, Petr Kral.Department of Chemistry, University of Illinois at Chicago, Chicago, IL 60607, United States*

Under carefully controlled conditions, our experimental collaborators have observed the self-assembly of non-spherical colloidal nanoparticles into superstructures with unique shapes, topologies, and self-limited sizes. We use precise atomistic molecular dynamics simulations and intricate Monte Carlo techniques to model the formation of these systems of nanoparticles coupled by anisotropic forces and in the presence of external fields.

COLL 59

Flexible chains of surface-modified nickel nanoparticles

Ruslan Burtovyy[1]*, rburtov@clemson.edu, James Townsend*[1]*, Yu Gu*[1]*, Jeffery Owens*[2]*, Konstantin Kornev*[1]*, Igor Luzinov*[1]*.Â (1) Department of Materials Science and Engineering, Clemson University, Clemson, South Carolina 29634, United StatesÂ (2) Air Force Civil Engineer Center, Tyndall AFB, Panama City, Florida 32403, United States*

We report on surface modification of Ni nanoparticles (NiNP) (100 nm) with polyethylene glycol (PEG) protective layer. The modification has been carried out using “grafting to” technique, where PEG (10 nm) is attached to the particles' surface through pre-grafted poly(glycidyl methacrylate) (PGMA) anchoring layer. It allows overcoming the major problem of poor colloidal stability of ferromagnetic nanoparticles. Considering “universal” solubility/affinity of PEG to media of various polarities dispersibility of the modified particles in water, ethanol or even toluene has been improved significantly. It has been demonstrated that nanochains formed by the modified NiNP in magnetic field are extremely flexible. They attain straight “rod” configuration under the field and collapse entirely to a “globular” shape at zero field. The process is completely reversible. Even more visually stunning example was observed for large chains composed of several layers of NiNP. The chains can bend to the highest degree attaining “snake-like” configuration manifesting their extraordinary flexibility. It is for the first time that such remarkable behavior was demonstrated. On contrary, once formed rigid “rod” configuration of as synthesized NiNP chains is preserved disregarding of

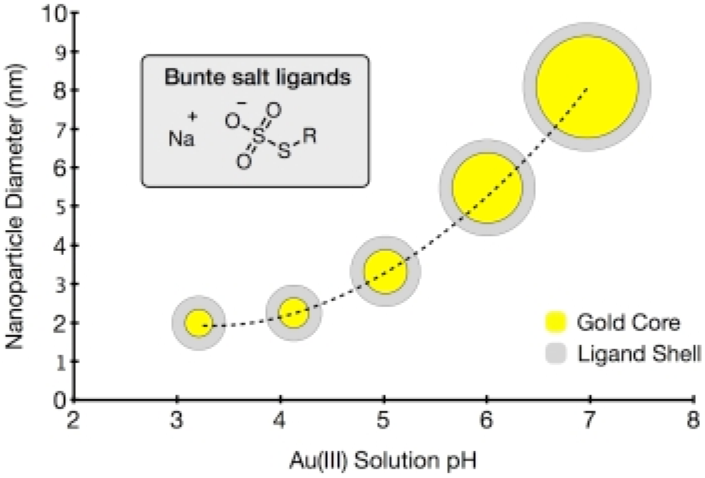
presence or absence of external magnetic stimuli. The experimental as well as theoretical aspects of the observed phenomenon of the chains flexibility will be discussed.

COLL 60

Targeted direct synthesis of water soluble functional gold nanoparticles with core diameters below 10 nm

***Edward W Elliott**, edwarde@uoregon.edu, Patick M. Haben, James E. Hutchison.Department of Chemistry, University of Oregon, Eugene, OR 97403, United States*

Stable gold nanoparticles with size-dependent optical properties functionalized with well-defined ligand shells offer utility for wide variety of applications such as sensing, imaging, and drug delivery. Thiolate stabilized gold nanoparticles (AuNPs) in the range of 2-10 nm meet these material requirements; however, targeting core sizes across this range while simultaneously controlling surface functionality proves synthetically challenging. We report a single-step direct synthesis that produces water-soluble AuNPs with targeted core sizes across this range while simultaneously controlling surface functionality using one or more ligand moieties. The reduction of Au(III) with sodium borohydride in the presence of a functionalized masked thiol yields functionalized nanoparticles in a single step. By synthesizing alkyl thiosulfates as the masked thiols, water can be used as the only solvent. The use of this class of ligands also allows core size to be controlled as a function of pH. Reaction conditions were rapidly optimized using a combination of a microreactor and automated small-angle X-ray scattering size analysis. The dependence of the core size on the pH was closely correlated but unique for each ligand or for a pair of ligands studied. For each ligand or pair of ligands a working curve was produced which made it possible to subsequently synthesize particles with specific, targeted core diameters. This method eliminates the need for ligand exchange and thus avoids complexity due to additional synthetic steps.



COLL 61

Long chained fatty acid monolayers: Influence of methyl branching

Mark W Rutland[1,2]*, mark@kth.se, Jonathan DF Liljeblad*[1]*, Eric Tyrode*[1]*, Esben Thormann*[1]*, Ann-Claude Dublanchet*[3]*, Gustavo Luengo*[3]*, C. Magnus Johnson*[1]*.Â (1) Department of Surface and Corrosion Science, KTH Royal Institute of Technology, Stockholm, SwedenÂ (2) Chemistry Materials and Surfaces, SP Technical Research Institute of Sweden, Stockholm, SwedenÂ (3) L'OrÃ©al Research and Innovation, Aulnay-sous-Bois, France*

The morphology and molecular conformation of Langmuir-Blodgett deposited and floating monolayers of a selection of straight chain (eicosanoic acid, EA), iso (19-methyl eicosanoic acid, 19-MEA), and anteiso (18-methyl eicosanoic acid, 18-MEA) fatty acids have been investigated by Vibrational Sum Frequency Spectroscopy (VSFS), AFM imaging, and the Langmuir trough. While the straight chain fatty acids form smooth, featureless, monolayers on the contrary all branched chain fatty acids display 10 – 50 nm size domains (larger for 19-MEA than the 18-MEA) with a homogeneous size distribution. No differences between the chiral (S) form and the racemic mixture of the 18-MEA are observed with any of the utilized techniques. The aliphatic chains of the straight chain fatty acids appear to be oriented perpendicular to the sample surface, based on an orientational analysis of VSFS data and the odd / even effect. In addition, the selection of the subphase (neat water or $CdCl_2$ containing buffered to pH 6.0) used for the LB-deposition has a profound influence on the monolayer morphology, packing density, compressibility, and conformational order. Finally, the orientation of the 19-MEA dimethyl moiety is estimated, and a strategy for performing an orientational analysis to determine the complete molecular orientation of the aliphatic chains of 19-MEA and 18-MEA is outlined and discussed.

COLL 62

Adventure in superomniphobic surfaces

Frederic GUITTARD*, guittard@unice.fr, Thierry DARMANIN, Elisabeth TAFFIN DE GIVENCHY, Sonia AMIGONI.CNRS, LPMC, UMR7336, Group Surface & Interface, Univ. Nice Sophia Antipolis, Nice, France*

The control of surface wettability (nano and micro roughness and chemical functions) is a major challenge for many practical applications and for new materials like superhydro/oleophobic surfaces. The biomimetism of natural surfaces allowed for the deeper understanding of our fundamental knowledge of surface wettability. The consequence is the development of many methods to reproduce this phenomenon and to conceive anti-wetting surfaces from water to oil. Hence, the study of superhydrophobic surfaces is exponential since 2004 with more than 700 publications in 2010 and in 2011, and more than 350 patents up to now in 2013. Thus, some reviews on superhydrophobic materials were reported, showing the interest of the scientific

community in this domain. However, the elaboration of superoleophobic surfaces was reported only in few works, mainly based on a fluorinated post-treatment of rough surfaces. Indeed, the lower the surface tension of the liquid probe is, the more difficult it is to prevent spreading out. Here, we report examples of the elaboration of superoleo-and-hydro-phobic surfaces by electrodeposition (one-pot build-up method). In order to consider the possible modulation of oleophobic/hydrophobic behaviour, the relation between the surface properties and the electrochemical parameters is also presented. **Advanced Materials, 2013** , 25, 1378-1394

COLL 63

Oleophobic perfluoro polyester films

Tugba Demir*, tdemir@g.clemson.edu, Yuriy Galabura, Philip J Brown, Igor Luzinov.Material Science and Engineering, Clemson University, Clemson, sc 29634, United States*

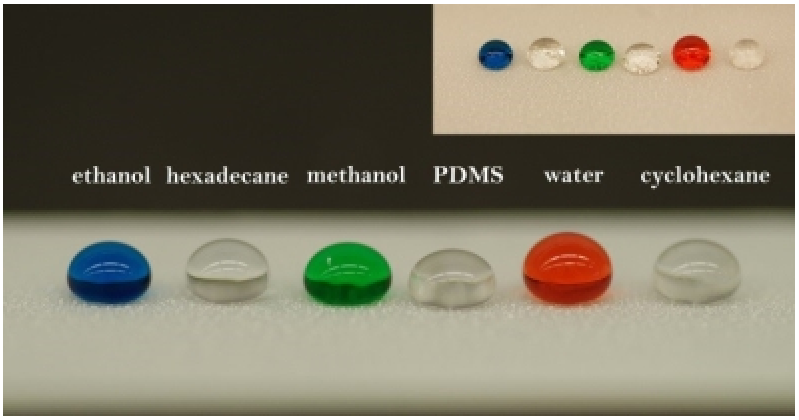
Perfluoro-ester polymers (PF-oate) were synthesized via Schotten–Baumann reaction of acid chloride with perfluoro alcohols. The polymers were characterized using ^{1}H, ^{13}C NMR, FT-IR, TGA and DSC. Next, the polymers were solvent-blended with polyethylene terephthalate (PET) at various concentrations to obtain oleophobic polyester films of different compositions. The wettability of the films with water and hexadecane was determined using contact angle measurements. The obtained PET/PF-oate films demonstrated low wettability that depended on the film composition.

COLL 64

Robust superamphiphobic inorganic-organic thiol-ene surfaces via spray-deposition and photopolymerization

Li Xiong*, li.xiong@eagles.usm.edu, Laken L Kendrick, James Goetz, Derek L Patton.School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, MS 39406, United States*

Surperamphiphobic surfaces, exhibiting high contact angles and low contact angle hysteresis to water and low surface tension liquids, have attracted a great deal attention in recent years due to the importance in many practical applications. In this work, we present a simple strategy for fabrication of superamphiphobic coatings based on photopolymerization of hybrid thiol-ene resins. Spray-deposition and UV cure of thiol-ene resins containing hydrophobic silica nanoparticles and fluorinated thiols provides a multiscale topography that endows the surface with superamphiphobicity and repellency towards several low surface tension liguids. Droplet impact and sandpaper abrasion tests indicate the coatings respectively possess a robust anti-wetting behavior and good mechanical durability.



COLL 65

Preparation of poly(α-methylen-γ-butyrolactone) and evaluation of its surface physical properties

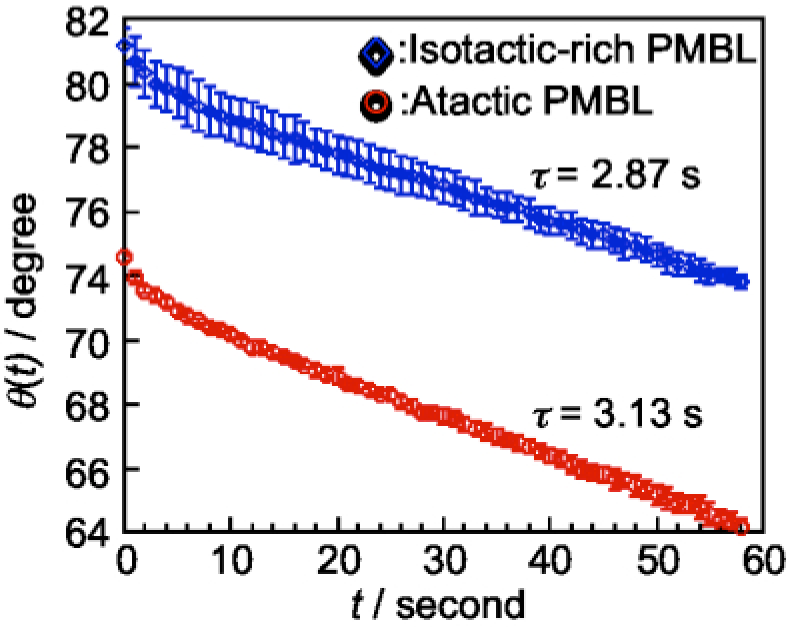
Tomoyasu Hirai[1,2], *t-hirai@cstf.kyushu-u.ac.jp, Xinyue Zheng*[2], *Masanao Sato*[2], *Yuji Higaki*[1,2], *Atsushi Takahara*[1,2]*.Â (1) institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka 744 Motooka Nishi-ku, JapanÂ (2) Graduate School of Engineering, Kyushu University, Fukuoka 744 Motooka Nishi-ku, Japan*

Poly(α-metylene-γ-butyrolactone) (PMBL) is a polymeric material, which has both high glass transition temperature (T_g) and high refractive index even though its chemical structure is similar to PMMA. In this presentation, we discuss an effect of stereoregularity on surface wettability by using PMBLs prepared by anionic polymerization, which can control the stereoregularity.

Both isotactic-rich and atactic PMBLs were synthesized on the basis of conventional anionic polymerization method. Surface wettability was evaluated by using static and dynamic contact angle measurement. Interestingly, atactic PMBL showed higher surface energy than that of isotactic-rich PMBL, nevertheless, sliding angle of atactic PMBL was lower. These results imply that the surface reorganization of atactic PMBL is more suppressed than that of isotactic-rich PMBL. In order to investigate the details of surface wettability, time dependence of static contact angle measurement was demonstrated as shown in figure1. Open symbols are experimental result, and solid lines are the best-fit curve on the basis of eq 1.

$\theta(t)=(\theta_{ini}-\theta_{ter})\exp(-t/\tau)+kt+\theta_{ter}$ (1)

Here, θ_{ini} and θ_{ter} are the initial values of θ at t=0 and the terminal vale of θ in a qusai-equilibrium state, respectively, while τ is the time corresponding to the θ decay in the initial stage. The t values obtained from PMBL were 2.87 s in isotactic-rich and 3.13 s in atactic, respectively. This result strongly supports that the surface reorganization of atactic PMBL is slightly suppressed than that of isotactic-rich PMBL.



COLL 66

Breakdown of superhydrophobicity of nanotextured surfaces

Antonio Checco[1], *checco@bnl.gov, Benjamin M. Ocko*[1], *Atikur Rahman*[1], *Charles T. Black*[1], *Mykola Tasinkevych*[2], *Siegfried Dietrich*[2].*Â (1) Brookhaven National Laboratory, Upton, New York 11973, United StatesÂ (2) Max Planck Institute for Intelligent Systems, Stuttgart, Germany*

Superhydrophobic surfaces exhibit elaborate textures designed to repel liquids and reduce adhesion by trapping air. However, they fail under conditions involving high temperature, pressure, and humidity when the air trapped in the texture is prone to escape. A current research challenge is to improve the robustness of these surfaces by delaying or preventing air escape.

Here we describe a novel, block copolymer based fabrication approach for creating robust water repellent surfaces with well-defined textures at the 10 nm scale[1]. We show that tuning the nanostructure shape and aspect ratio dramatically influences the surface wetting properties, with proper control crucial for achieving robust superhydrophobicity. Further, we characterize the robustness of the various nanotextures against forced water infiltration using transmission small angle x-ray scattering under variable hydrostatic pressure up to 50 atm. In these experiments, the infiltration filling fraction (under variable applied pressure) is obtained from the intensity of

the diffracted signal. In all structures, significant infiltration occurs irreversibly above a critical pressure depending on the texture size and geometry. The detailed adsorption isotherms are well modeled by accounting for the specific shape of the nanotexture's geometry. Further, the desorption isotherms provide insight in to the irreversible gas-liquid exchange in nano-confined systems.

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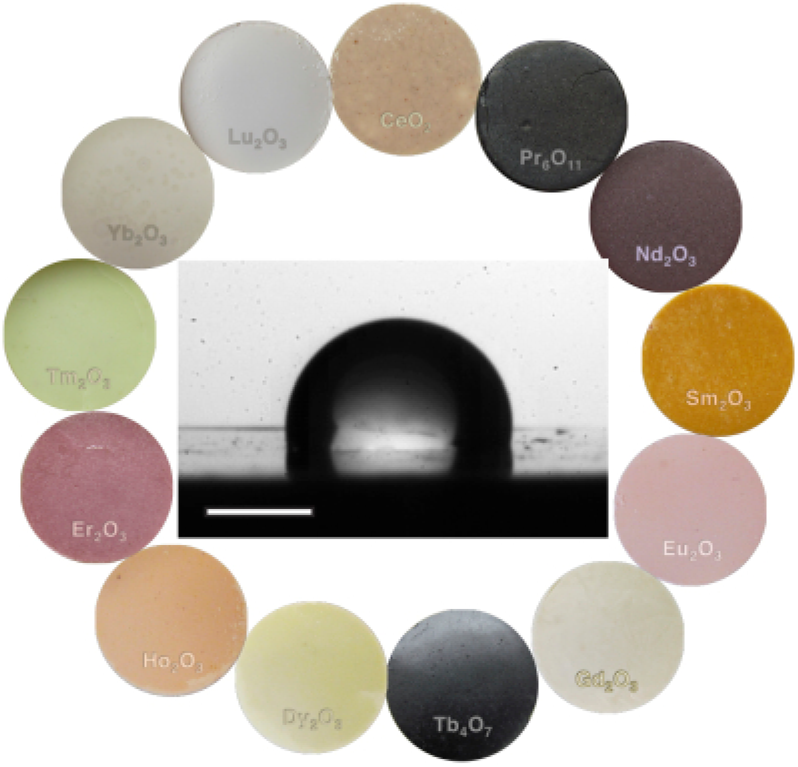
COLL 67

Hydrophobic rare-earth oxide ceramics with applications to sustained dropwise condensation

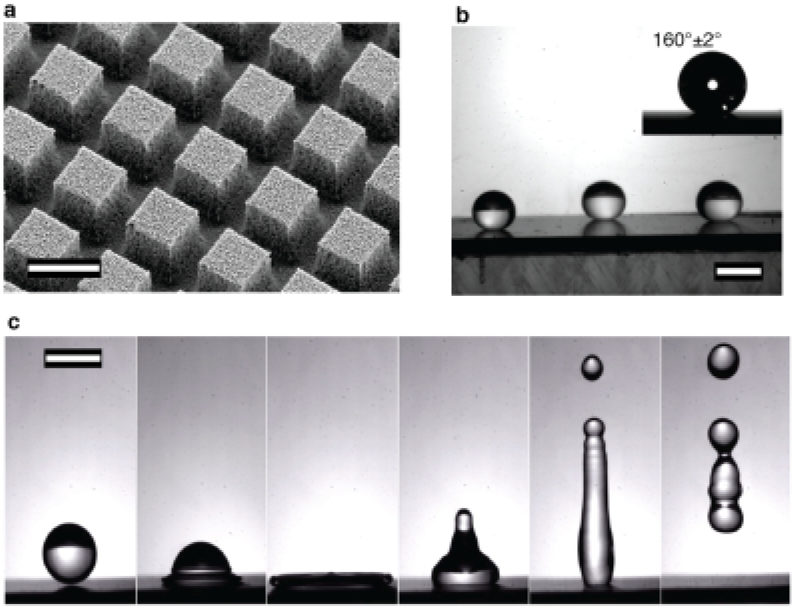
Gisele Azimi, *gazimi@mit.edu, Adam T. Paxson, Hyuk-Min Kwon, Kripa K. Varanasi.Mechanical Engineering, MIT, Cambridge, MA 02139, United States*

Hydrophobic materials that are robust to harsh environments are needed in a broad range of applications [1]-[3]. Although durable materials such as metals and ceramics, which are generally hydrophilic, can be rendered hydrophobic by polymeric modifiers [4], these materials deteriorate in harsh environments. Here we show that a class of ceramics comprising the entire lanthanide oxide series, ranging from ceria to lutecia, is intrinsically hydrophobic (see figure1)[5].



Photographs of the sintered rare-earth oxide pellets (cerium oxide through lutetium oxide). All the pellets are hydrophobic: water contact angles range between 100° and 115°. The image at the center is a goniometer snapshot of a water droplet beading up on a smooth neodymium oxide surface, as a model sample of the entire REO series; scale bar is 1 mm.

We attribute their hydrophobicity to their unique electronic structure, which inhibits hydrogen bonding with interfacial water molecules. We also show with surface-energy measurements that polar interactions are minimized at these surfaces and with FTIR/GATR that interfacial water molecules are oriented in the hydrophobic hydration structure. Moreover, we demonstrate that these ceramic materials promote dropwise condensation, repel impinging water droplets, and sustain hydrophobicity even after exposure to harsh environments[5]. These ceramics can also be used to fabricate superhydrophobic surfaces using various techniques. As an example, we fabricated superhydrophobic surfaces by sputtering a thin layer (~200-350 nm) of ceria onto nanograss-covered silicon microposts (figure2a). Water droplets display high contact angles (figure2b) and exhibit extreme mobility due to low contact angle hysteresis (<10°) on these surfaces. In addition, impinging water droplets completely bounce off the surface, leaving it dry (figure2c). Hence, we envision that this class of robust hydrophobic materials will have far-reaching technological potential in various industrial applications, where water repellency and dropwise condensation are desirable.



Superhydrophobicity and water repellency of rare-earth oxide coated textured surfaces. a) SEM of nanograss-covered microposts (side ~ 10 μm, inter-post spacing ~ 5 μm); scale bar is 10 μm; b) Photographs of water droplets on the ceria sputtered nanograss micropost surface (θ =160° ± 2°); scale bar is 2.5 mm.; c) High-speed photography images of a water droplet bouncing off the surface (impact velocity ~ 1.6 m/s); scale bar is 2.5 mm.

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COLL 68

Superhydrophobic coatings using surface-modified halloysite nanotubes

Atsushi Takahara[1,2,3], *takahara@cstf.kyushu-u.ac.jp, Wei Ma*[2]*.Â (1) Takahara Soft Interfaces Project, JST ERATO, Fukuoka, JapanÂ (2) WPI I2CNER, Kyushu University, Fukuoka, JapanÂ (3) IMCE, Kyushu University, Fukuoka, Japan*

Nanotubular materials are important building blocks for future nanotechnology and have attracted research interests over the past two decades. Among various nanotubes, an increasing attention has been being paid to the clay based ones, due to many of their great advantages, such as abundant availability, environmental friendliness, and biocompatibility. One of the most well-known clay nanotubes is halloysite, a hydrated polymorph of kaolinite consisting of silica on the outer surface and alumina in the innermost surface [1]. Halloysite has been widely used as nanocontainers for controlled release of various active agents and nanofillers for organic/inorganic hybrid materials. Other usages of halloysite include pollutant removing, catalyst supporter, and drug delivery.

Superhydrophobic surfaces with water contact angle larger than 150° have shown great significance in both scientific and industrial areas, due to their potential applications in many important areas, including self-cleaning materials, corrosion resistance, and low dragging coatings [2]. By mimicking lotus structure, a considerable amount of artificial superhydrophobic surfaces have been developed. However, most of the reported methods require special equipments, complicated process control or expensive materials. uperhydrophobic surfaces using clay nanotubes as the building blocks have not been reported.

In this work, we demonstrated the fabrication of a superhydrophobic coating using 1H,1H,2H,2H-perfluorooctyltrimethoxysilane (FOTMS) modified Halloysite nanotubes (F-HNT). A sol-gel process using tetraethoxysilane (TEOS) and F-HNT was applied for the coating preparation. Fourier transform infrared (FTIR) analysis indicated that halloysite nanotubes were successfully modified with FOTMS. SEM measurements show that the F-HNT/silica coating exhibited a micro/nano hierarchical structure, The obtained coating gives water contact angles above 150^o. Moreover, the hydrophobicity of the film can be tuned by the content of F-HNT; stick and non-sticky superhydrophobic films can also be achieved at certain F-HNT contents.

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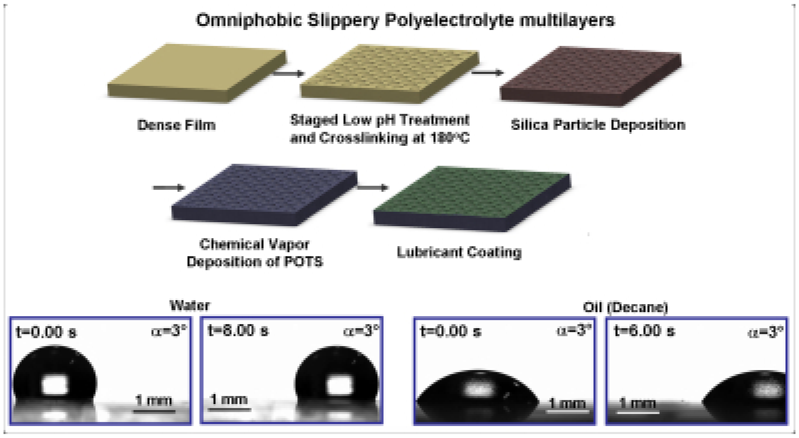
COLL 69

Omniphobic slippery coatings based on lubricant-infused porous polyelectrolyte multilayers with layer-by-layer assembly

Xiayun Huang[1], *sherry.huangxiayun@gmail.com, James D Chrisman*[1]*, Nicole S Zacharia*[1,2,3]*.Â (1) Department of Mechanical Engineering, Texas A&M University, College Station, Texas 77843, United StatesÂ (2) Department of Materials Science and*

Engineering, Texas A&M University, College Station, Texas 77843, United StatesÂ (3) Department of Polymer Engineering, The University of Akron, Akron, Ohio 44325, United States

Omniphobic and slippery coatings from lubricant infused textured surfaces have recently been shown to have superior properties including low contact angle hysteresis and low sliding angles. Here, we present a new approach to the fabrication of these omniphobic slippery surfaces by using polyelectrolyte multilayers assembled by the layer-by-layer technique. Water soluble weak polyelectrolytes, branched poly(ethyleneimine) and poly(acrylic acid), were used as the basis for the polyelectrolyte multilayer structures. Due to the responsive change density variation to the pH of surrounding environment, the honeycomb-like microporous structures can be achieved through staged acid treatment. The omniphobic slippery surface would be prepared by infusing a fluorinated lubricant into a porous polyelectrolyte multilayer. These surfaces repel water and decane with sliding angles as low as 3°. One advantage of polyelectrolyte multilayers is the ease with which they can coat non-planar surfaces, such as glass tube.



COLL 70

Novel non-fluorinated super hydrophobic surfaces

***Mani P Singh**, msingh@gelest.com, Robert C Woerner, Janis G Matisons, Joel Zazyczny, Barry Arkles.Gelest Inc., Morrisville, PA 19067, United States*

Applications of hydrophobic surfaces have a growing global market targeting automotive, health, microelectronics, and pharmaceutical industries. These hydrophobic properties are commonly achieved with perfluorinated compounds including polymers and silanes. The negative health and environmental concerns associated with these fluorinated treatments are driving the search for new alternatives with minimal effects on the environment. Formulations containing silanes, siloxanes, and inorganic particles are viable alternatives to fluorosilanes in hydrophobic applications. As Gelest, Inc. is one of

the leaders in silane chemistry, the availability of new chemistries and application techniques makes novel hydrophobic surfaces an exciting new research area.

Application of various non-fluorinated silanes and silicones in combination with inorganic particles will be presented along with the effect of application method on the resulting hydrophobicity. Characterization by static, advancing, and receding contact angles provide a direct correlation with the hydrophobic properties of these viable alternatives. While fluorinated static contact angles range from 108°-115°, non-fluorinated smooth surfaces without particles exhibit similar contact angles. Introduction of micro and nano-roughness by incorporating inorganic particles create surfaces with static contact angles leading into the super-hydrophobic region of 150°. AFM, SEM, and XPS shed light on the surface morphology and topography of the treated substrates.

COLL 71

Curvature-dependent wetting of perfluorinated monolayers

Kellen M Harkness[1], *kellen.harkness@epfl.ch, Z. Pelin Guven*[2], *Ozge Akbulut*[2], *Francesco Stellacci*[1]*.Â (1) Department of Materials Science and Engineering, Ecole Polytechnique Federale de Lausanne, Lausanne, SwitzerlandÂ (2) Faculty of Engineering and Natural Sciences, Sabanci University, Tuzla Istanbul, Turkey*

Fluorinated organic compounds have assumed an important role in green chemistry, chemical and pharmaceutical production, and surface engineering. Applications for perfluorinated monolayers have been explored for two-dimensional surfaces and ultrasmall (<3 nm diameter) nanoparticles, with general behavior being superhydrophobic as expected. We have found that an intermediate range of surface curvature produces a remarkable anomalous shift in wetting properties. Solubility in fluorocarbon solvents is lost, and solubility is gained in some organic solvents. This shift in solubility is rationalized as an effect of internal dipoles in the protecting fluorinated monolayer: at relatively low surface curvatures, the dipoles align to generate a coherent enhancement of wetting in polar organic solvents. The ability to dissolve perfluorinated nanomaterials in organic solvents, and the role of surface curvature on dipole-driven wetting effects have implications for numerous fields of research.

COLL 72

Structure and dynamics of single hydrophobic/ionic heteropolymers at the vapor-liquid interface of water

Vasudevan Venkateshwaran, *venkav2@rpi.edu, Srivathsan Vembanur, Shekhar Garde.Howard P. Isermann Department of Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, United States*

Aqueous interfaces are ubiquitous in biological and nanoscopic systems and present an ideal platform for assembly of conformationally flexible molecules. While hydrophobic

polymers collapse into globular conformations in bulk water, polymers that contain ionic/charged groups in their sequence adopt specific folded conformations depending on the position of the charged monomers in the sequence. Recent work has highlighted that primitive water--mediated interactions between small hydrophobic solutes or between oppositely charged ions can be significantly different near interfaces compared to that in bulk water. We have employed extensive molecular dynamics simulations to study the conformational stability, structure and dynamics of model polymer molecules containing hydrophobic and ionic groups, at the water vapor--liquid interface. We show that the different effects of the interfacial environment on hydrophobic and electrostatic interactions leads to very different structure and dynamics of model polymer molecules at the vapor--liquid interface compared to that in bulk water. We also show that under certain circumstances, the conformational preferences of the polymer can be predicted from our understanding of the effect of interfaces on the primitive interactions between small solutes. Collectively, our results are useful in understanding the role of various factors that influence structure, dynamics and assembly of complex biomolecules in the interfacial environment.

COLL 73

Single polymers at surfaces: Adhesion and dynamics

***Roland Netz**, rnetz@physik.fu-berlin.de.Phyiscs Department, FU Berlin, Berlin, Germany*

Single-polymer behavior at surfaces combines the fields of non-equilibrium thermodynamics, elasticity theory and hydrodynamics. Theoretical approaches thus rely on molecular simulations, continuum modeling and scaling approaches.

This is demonstrated with a few combined experimental/theoretical examples:

- Spider silk consists of polypeptides with highly repetitive motives and readily adsorbs on hydrophobic and hydrophilic surfaces. The dominant hydrophobic attraction can be quantitatively explained with classical MD simulations including explicit water. Both water structural effects and dispersion interactions contribute to this solvation attraction.

- On surfaces, the friction coefficient of bound peptides is very low on hydrophobic substrates, which is traced back to the presence of a vacuum layer between substrate and water, forming a lubricating cushion on which a polymer can glide. Conversely, friction forces on hydrophilic substrates are large. A modified Amonton´s law is introduced, which generally describes the dynamics of hydrogen-bonded matter on the nano-scale.

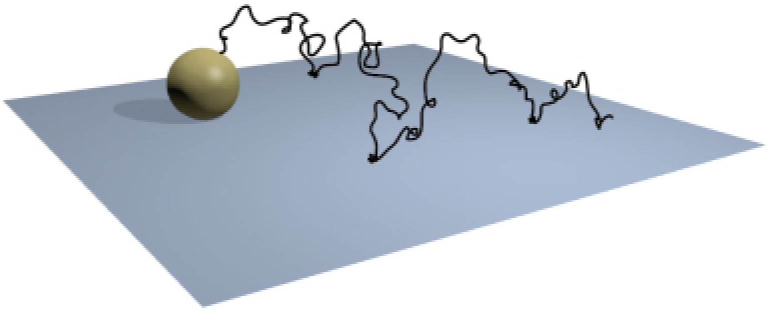
- For peptides adsorbing at surfaces, the adsorption strength depends crucially on the surface wetting properties. For hydrophilic surfaces, the interaction tends to be repulsive, for hydrophobic surfaces, the interaction is attractive. The microscopic mechanism behind this so-called Berg law is discussed.

COLL 74

Universal mechanism of molecular transport at the solid-liquid interface

Michael J Skaug, *mike.skaug@gmail.com, Joshua N Mabry, Daniel K Schwartz.Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado 80309, United States*

The mobility of molecules on a solid surface plays a key role in diverse phenomena such as friction and self-assembly and in surface-based technologies like heterogeneous catalysis and molecular targeting. To understand and control these surface processes, we need a universal model of surface transport at solid-liquid interfaces. However, unlike diffusion at a solid-gas interface, little is known about the mechanisms of diffusion at a solid-liquid interface. Using single-molecule tracking at a solid-liquid interface, we found that a diverse set of molecules, including polymers and proteins, underwent intermittent random walks with non-Gaussian displacements. This contrasts with the normal random walk and Gaussian statistics that are commonly assumed for molecular surface diffusion and has important implications for molecular targeting and molecule motion near surfaces. Our findings suggest that intermittent hopping is universal to molecular surface diffusion.



COLL 75

Modulating the mobility of surface-rolling molecules via substrate and wheels

***Lin-Yung Wang**[1]*, *linyungw@rice.edu, Saumyakanti Khatua[1], Pin-Lei E Chu[1], Jazmin Godoy[1], Anatoly B Kolomeisky[1], James M Tour[1], Stephan Link[1,2].Â (1) Department of Chemistry, Rice University, Houston, Texas 77005, United StatesÂ (2) Department of Electrical and Computer Engineering, Rice University, Houston, Texas 77005, United States*

The single-molecule imaging of inherently fluorescent nanocars on three substrates, (plasma cleaned, reactive ion etched, and amine-functionalized glass) and nanocars equipped with either *p*-carborane-wheeled or adamantane wheels are reported. The

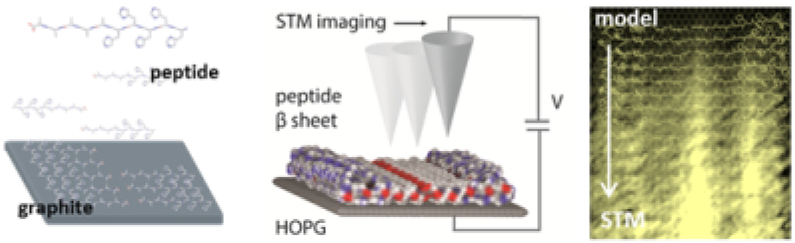
nanocars were imaged using 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) as the chromophore, which was rigidly incorporated into the nanocar chassis via Sonogashira cross-coupling chemistry that permitted the synthesis of nanocars having different geometries. Using single-molecule fluorescence imaging, the percentage of moving nanocars and their diffusion constants were determined for each substrate. We found that the nanocar mobility decreased with increasing surface roughness and increasing surface interaction strength. The mobility of four- and three-wheeled nanocars with adamantane wheels was also compared. It was found that, for the four-wheeled nanocar, the percentage of moving nanocars and the diffusion constant show a significant improvement over *p*-carborane-wheeled nanocars with the same chassis. The three-wheeled nanocar showed only limited mobility due to its geometry. These results are consistent with a wheel-like rolling motion. We furthermore developed a model that relates the percentage of moving nanocars in single-molecule experiments with the diffusion constant. The excellent agreement between the model and the single-molecule studies yields a detailed understanding of motion in these molecular machines.

COLL 76

Developing scanning probe techniques for the analysis of biomolecules

Miles A Silverman[1,2]*, miles.silverman@gmail.com, Shelley A Claridge*[4]*, John C Thomas*[1,2]*, Travis Meyer*[3]*, Joseph Woodworth*[3]*, Konstantin Dragomiretskiy*[3]*, Stanley Osher*[3]*, Andrea L Bertozzi*[3]*, Paul S Weiss*[1,2]*.Â (1) Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90024, United StatesÂ (2) California NanoSystems Institute, University of California, Los Angeles, Los Angeles, California 90024, United StatesÂ (3) Department of Mathematics, University of California, Los Angeles, Los Angeles, California 90024, United StatesÂ (4) Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, United States*

Single-molecule measurements of complex biological structures such as proteins are an attractive route for determining structures of the large number of important biomolecules that have proved refractory to analysis through standard techniques such as X-ray crystallography and nuclear magnetic resonance. We use a custom-built low-current scanning tunneling microscope to image peptide structure at the single-molecule scale. In a model peptide that forms β sheets, a structural motif common in protein misfolding diseases, we successfully differentiate between histidine and alanine amino acid residues, and further differentiate side chain orientations in individual histidine residues, by correlating features in STM images with those in energy-optimized models. We are developing the techniques to determine structures locally and understand important chemical details of biomolecules at the single-molecule level, therefore providing key insight and probing effects between single peptide structures.



COLL 77

Single polymer adhesion and friction at the liquid-solid interface

***Thorsten Hugel**, thugel@mytum.de.Department of Physics, Technical University Munich, Garching, Germany*

Polymer-solid contacts play an important role in (bio)technology, but a fundamental understanding of their interface is still missing. We developed an AFM-based method to probe single polymer adhesion [1] and friction [2] at the liquid-solid interface.

I will first summarize our results on how the hydrophobic attraction and Hofmeister effects determine single polymer adhesion and structure formation at solid substrates. Then I will explain how a combination of AFM-base constant-pulling-velocity and waiting-time experiments yields the polymer contour length and monomeric desorption rate for single polymers. Finally I will elucidate how single polymer friction is affected by solvent and solid substrate properties. Our results necessitate a new friction mechanism, which we term desorption stick, that is independent of normal force, polymer length and velocity.

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COLL 78

WITHDRAWN

COLL 79

Probing chiral pockets around a single molecule on a surface: STM experiments and DFT simulations

***Peter H McBreen**[1], peter.mcbreen@chm.ulaval.ca, Guillaume Goubert[1], Yi Dong[1], Michael Groves[2], Anton M. H. Rasmussen[2], Bjørk Hammer[2].Â (1) Department of Chemistry, Laval University, QuÃ©bec, Qc G1V 0A6, CanadaÂ (2) Interdisciplinary*

Nanoscience Center (iNano) and Department of Physics and Astronomy, Aarhus University, Aarhus, Denmark

Scanning tunneling microscopy and DFT methods were used to study individual prochiral and chiral molecules on Pt(111) in order to better understand chirality transfer reactions on catalyst surfaces (1). The chiral molecules studied were (*R*)-(+)-1-(1-naphthyl)ethylamine, (R)-NEA, and simple derivatives. The conformation dependent molecular motion of individual (R)-NEA adsorbates was studied. A number of prochiral substrates were used to probe several chiral pockets around single (R)-NEA adsorbates, determining in each case the prochiral ratio of the substrate in the chiral pocket. Stereodirecting interactions at individual chiral pockets were determined. Diffusion pathways to form bimolecular chiral molecule/prochiral surbstrate complexes were computed.

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COLL 80

Design of a multidentate oligomeric platform for biocompatible magnetic, metallic, and semiconductor nanocrystals

Hedi Mattoussi*, mattoussi@chem.fsu.edu, Wentao Wang, Xin Ji, Goutam Palui.Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FLorida 32306, United States*

We have developed a versatile surface-functionalization strategy that is applicable to metal and metal oxide nanoparticles (e.g., quantum dots and Fe_3O_4). This strategy involves the design and optimization of a set of multidentate oligomers prepared using a one-step reaction of a short polymer backbone with lateral poly(ethylene glycol), PEG, chains and selective anchoring moieties. While biocompatibility is promoted by the introduction of functionalized-PEG moieties, coordination onto the metal-rich nanocrystals depends on the particular system in question. For instance, catechol groups allow strong ligand affinity to iron oxide NPs. When substituted with lipoic acid and/or imidazole the resulting ligands are ideally suitable for ligating QDs and AuNPs. Ligand exchange with these oligomers is remarkably efficient. The resulting NPs preserve their homogenous size and distribution, exhibit high colloidal stability over a broad range of conditions, and present a controllable number of functional groups, making them compatible with common bio-orthogonal chemistries.

COLL 81

Improving biocompatibility of carbon and post-carbon nanomaterials via dispersion chemistry

***Mark C Hersam**, m-hersam@northwestern.edu.Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208-3108, United States*

Carbon nanomaterials (e.g., carbon nanotubes and graphene) hold promise for biomedical applications due to their ability to be functionalized with nucleic acids, proteins, and polymers, in addition to their strong optical absorption at near-infrared wavelengths that are well-aligned with the transmission window for biological tissue. However, due to their strong hydrophobicity, these nanomaterials have limited stability in aqueous solution, leading to aggregation and corresponding deleterious effects in vitro and in vivo. To overcome these issues, we have employed amphiphilic biocompatible block copolymers (e.g., Pluronics and Tetronics) as dispersants for single-walled carbon nanotubes, multi-walled carbon nanotubes, and graphene, resulting in substantial reduction in toxicity, particularly for pulmonary in vivo assays. In addition to delineating the details of the dispersion chemistry for carbon nanomaterials, this talk will also present preliminary results on extending this approach to post-graphene two-dimensional layered nanomaterials such as molybdenum disulfide and related transition metal dichalcogenides.

COLL 82

Metallic nanoparticles anchored on nanotubes: Functional and biocompatible materials and nanomedicine devices

***Mauricio Terrones**, mut11@psu.edu.Department of Physics, Department of Chemistry, Department of Materials Science and Engineering and Center for 2D Layered Materials, The Pennsylvania State University, University Park, Pennsylvania 16802, United StatesResearch Center for Exotic Nanocarbons (JST), Shinshu University, Nagano, Japan*

By doping carbon nanotubes it is possible to alter significantly the electronic, mechanical and chemical properties of the tubes. In this context, it will be demonstrated that Ag, ZnO, Au and TiO_2, particles could be easily anchored on the surface of N-doped nanotubes using various wet chemical approaches. The bio-applications of CN_x nanotubes will also be described in detail. In particular, comparative toxicological studies of CN_x MWNTs and pure carbon multi-walled nanotubes (MWNTs) on mice and using amoeba cells reveal that CN_x tubes appear to be far less harmful. Interestingly, pure MWNTs appeared to be lethal at all doses tested for intratracheal instilation, whereas CN_x MWNTs were not. Cellular assays using Ag-CNx MWNT systems also revealed marginal toxicity after 24h, and full cellular recovery was observed at 48h based on an MTS assay. Therefore, Ag-nanotube systems appear to be very different from isolated dispersed Ag-NPs. Finally, it will be demonstrated that microfluidic devices constructed using arrays of carbon nanotubes could be successfully used to separate plasma from blood and also as an efficient biomarker separation tool.

COLL 83

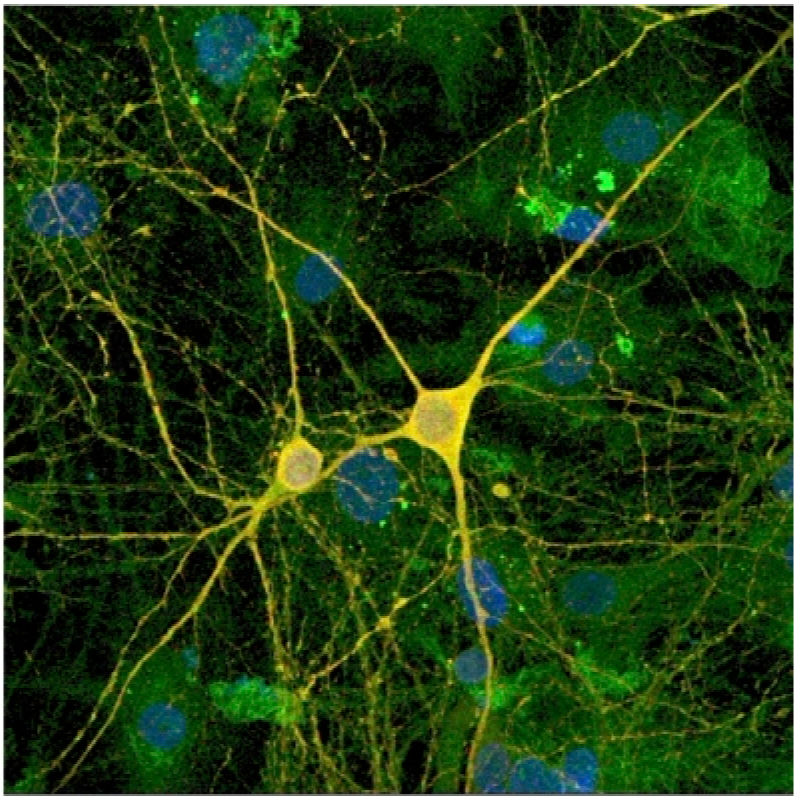
Carbon nanotubes are ideal substrates for neuronal growth

Maurizio Prato*, prato@units.it.Department of Chemical and Pharmaceutical Sciences, University of Trieste, Trieste, Italy*

Among the wide range of novel nanometer scale structures available, single-wall carbon nanotubes (SWNT) and multi-wall carbon nanotubes (MWNT) stand as unique materials for fundamental research and potential applications. However, manipulation and processing of carbon nanotubes (CNTs) has been difficult because of their intractability and insolubility in most common solvents. Considerable effort has therefore been devoted to the chemical modification of CNTs, which might open the way to many useful applications.

Our group has been involved in the organic functionalization of various types of nanocarbons, including carbon nanotubes, fullerenes and, more recently, graphene. The organic functionalization offers the great advantage of producing soluble and easy-to-handle CNTs. As a consequence, since biocompatibility of CNT is expected to improve, many functionalized carbon nanotubes may find useful applications in the field of nanomedicine.

Carbon nanotubes can act as active substrates for neuronal growth, a field that has given so far very exciting results. Nanotubes are compatible with neurons, but especially they play a very interesting role in interneuron communication. Improved synaptic plasticity is just one example.



During this talk, we will illustrate the latest advances in our laboratory of the most exciting results in these fast developing fields.

This research was financed by the ERC Grant Carbonanobridge.

COLL 84

Few-layer graphene from ball-milling of graphite with triazine derivatives: Applications

Ester Vázquez, *ester.vazquez@uclm.es.Department of Organic Chemistry, Universidad de Castilla- La Mancha, Ciudad Real, Ciudad Real 13001, Spain*

Graphene is considered the ultimate material for applications in many fields, from electronics to composites and biosensors. Biological studies on graphene and graphene oxide are also currently underway in many laboratories for two main aims: (i) the exploitation of the graphene properties in biological applications; (ii) the assessment of the potential toxicity of graphene layers.

Graphene is usually prepared by the renowned scotch tape technique or by CVD processes. As such, graphene cannot be dispersed in water of biological media, owing to its complete insolubility. Novel ways to prepare dispersible graphene in water are

very much needed. Ball milling of graphite in the presence of melamine has been found in our labs to be a method of choice to exfoliate graphite and generate dispersions of graphene in many solvents, including water.

During this talk, we will discuss (i) optimized ways to generate graphene in solvents using ball milling; (ii) the use of graphene in polymer composites for drug delivery purposes; (iii) studies of interaction of so-prepared solutions with cells.

COLL 85

Improved drug delivery efficacy with nanoscale biomaterials–based structures as carriers

***Xing-Jie Liang**, liangxj@nanoctr.cn.CAS Key Laboratory for Bioeffects of Nanomaterials and Nanosafety, National Center for Nanoscience and Technology of China, Zhongguancun, Beijing 100190, China*

Recent advances in nanotechnology have provided novel strategies to innovate drugs for pharmaceutical development and clinical applications. Bionanotechnology is to utilize the developed technologies and/or materials smaller than 100 nanometers in one dimension and takes advantages of properties that are only presented at this nano level. Nanoscale materials, with their unique size-dependent physical and chemical properties, have showed promising advantages in biological research fields such as intercellular targeted drug delivery, vehicles controlled release of payload, precisely silence of targeted genes, and so on. However, to develop efficient nanomaterials with these promising progresses, the high penetration of plasma membrane and low in vivo toxicology of engineered nanomaterials as drug carriers exist as a potential barrier and has caught much attention. Therefore, Designing nanomaterials for effectively expected effects without significant toxicity has become an important issue for clinical and pharmaceutical application of novel nanobiomaterials. It is critical to screen and identify novel nanomaterials with an exclusive biological function in vitro and in vivo. Recently, innovative materials assembled at nanosize have been developed with negligible cytotoxicity in tissue culture and without detectable side effects in vivo. The unique properties of nanostructures at pharmaceuticals still needs further study by support of scientist with cellular, molecular, materials, biochemical and pharmaceutical background. The developed nanotechnology may inspire researchers to innovate a new generation of nanoscale materials with inventive non-traditional approach to treat various of diseases. The development of nanoscale biomaterials-based structures will allow for more precise efficiently targeted delivery, extended in vivo retention and controllable release behaviors at different levels.

COLL 86

Carbon nanotubes-liposomes conjugate as a platform for drug delivery into cells

Oren Regev[1]*, oregev@bgu.ac.il, Sivan Perez*[1]*, Yechezkel Barenholz*[2]*, Faina Karchemski*[1]*.Â (1) Department of Chemical Engineering, Ben-Gurion University, Beer-Sheva, IsraelÂ (2) Department of Biochemistry, The Hebrew University, Jerusalem, Israel*

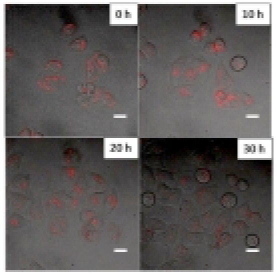
Carbon nanotubes (CNT) are widely explored as carriers for drug delivery due to their facile transport through cellular membranes. However, the amount of loaded drug on a CNT is rather small. Liposomes, on the other hand, are employed as a carrier of a large amount of drug. The aim of this study is to develop a new drug delivery system,inwhich drug-loaded liposomes are covalently attached to CNT to form a CNT-liposomes conjugate (CLC). The advantage of this novel approach is the large amount of drug that can be delivered into cells by the CLC system,
thus preventing potential adverse systemic effects of CNT when administered at high doses. This system is expected to provide versatile and controlled means for enhanced delivery of one ormore agents stably associated with the liposomes.

COLL 87

Cell penetration and dynamics of oligopeptide-modified phospholipid polymer nanoparticles embedding quantum dots

Kazuhiko Ishihara*, ishihara@mpc.t.u-tokyo.ac.jp, Yuuki Inoue, Yuriko Tsukamoto.Department of Materials Engineering, The University of Tokyo, Hongo Bunkyo-ku, Tokyo 113-8656, Japan*

To obtain a stable and highly sensitive bioimaging fluorescence probe, polymer nanoparticles with embedded quantum dots (QDs) were prepared and the surface was covered with phospholipid polymer. The QDs are promising alternative to organic dyes for bioimaging. However, their use has been strongly limited by difficulties in obtaining biocompatibility of QDs. QDs were embedding in the polylactic acid (PLA) nanoparticles and the surface was covered with biocompatible 2-methacryloyloxyethyl phosphorylcholine (MPC)-based polymer (PMBN). The octaglycine(G8) immobilized-PMBN/polylactic acid (PLA) nanoparticles embedding QDs showed resistance to cellular uptake from HeLa cells owing to the nature of the phosphorylcholine groups in the MPC units. On the other hand, when an octaarginine (R8), which was one of the cell penetrating peptide, was immobilized at the surface of the nanoparticles, they could penetrate the membrane of HeLa cells effectively. Cytotoxicty of the PMBN/PLA/QD nanoparticles was not observed even after immobilization of R8. We examined the role of R8 by changing the ratio of R8/G8, more than 0.80 of this ratio was necessary to internalization to cells. Fluorescence intensity of the nanoparticles was not bleached during 30 h observation continuously. During proliferation of cells having the R8-PMBN/PLA/QD nanoparticles, the nanoparticles distributed to daughter and grand daughter cells (Fig 1). Thus, we obtained stable fluorescent polymer nanoparticles for excellent bioimaging probe.



COLL 88

Using supramolecular nanobeacons to probe cellular uptake efficiency and enzymatic activities

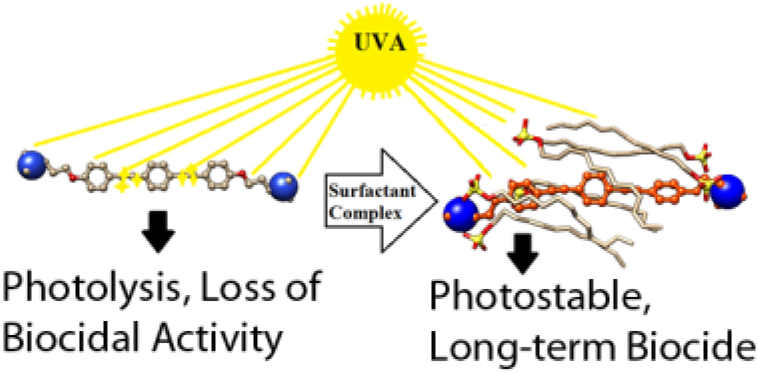
***Lye Lin Lock**, llock4@jhu.edu, Claudia Reyes, Honggang Cui.Department of Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, Maryland 21093, United States*

Shape and surface chemistry are important factors to regulate nanoparticle's cellular entry pathways. In this lecture, we report our recent effort of using nanobeacons to probe the shape and surface chemistry effect on the internalization efficiency of nanoparticles by cancer cells. We designed a series of self-assembling molecular beacons that can form either spherical or filamentous nanostructures depending on their self-assembly conditions. The surface chemistry of these supramolecular nanobeacons can be readily tuned through the incorporation of different C-terminal amino acids (for example, lysine gives a positively charged surface while glutamic acid gives a negatively charged surface). The beacons reported herein were designed to be specifically responsive to an enzyme located within the lysosomes. Only after specific cleavage by the targeted enzyme within the cells, the beacon molecule will start to fluoresce, giving a detectable optical signal. Our results show that spherical nanobeacons with a positively charged surface has the highest efficiency for cellular uptake, while filamentous nanostructures regardless of their charge status can hardly get into cells.

COLL 89

Cationic oligo-*p*-phenylene ethynylenes form complexes with surfactants for long-term light-activated biocidal applications

Eric H. Hill[1,2], *hille@unm.edu, Harry C. Pappas*[1], *Deborah G. Evans*[2], *David G. Whitten*[1].*Â (1) Center for Biomedical Engineering, University of New Mexico, Albuquerque, New Mexico 87131, United StatesÂ (2) Nanoscience and Microsystems Engineering program and Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, New Mexico 87131, United States*



Cationic Oligo-p-Phenylene Ethynylenes are highly effective light-activated biocides that deal broad-spectrum damage to a variety of pathogens, including bacteria. A potential problem arising in the long-term usage of these compounds is photochemical breakdown, which nullifies their biocidal activity. Recent work has shown that these molecules complex with oppositely-charged surfactants, and that the resulting complexes are protected from photodegradation. In this manuscript, we determine the biocidal activity of an oligomer and a complex formed between it and sodium dodecyl sulfate. The complexes are able to withstand prolonged periods of irradiation, continuing to effectively kill both Gram-negative and Gram-positive bacteria, while the oligomer by itself loses its biocidal effectiveness quickly in the presence of light. In addition, damage and stress responses induced by these biocides in both *E. Coli* and *S. Aureus* are discussed. This work shows that complexation with surfactants is a viable method for long-term light-activated biocidal applications.

COLL 90

Amino acids on metals: Chiral assembly and dynamic restructuring of copper surface

Erin V. Iski, *erin-iski@utulsa.edu.Department of Chemistry and Biochemistry, University of Tulsa, Tulsa, OK 74104, United States*

The 2D-scale study of relevant biomolecules, like amino acids, is pertinent for a variety of applications from the origin of biological homochirality and the amplification of surface

chirality to the examination of noncovalent supramolecular interactions. The need for pristine molecular resolution of these systems requires the use of ultra-high vacuum scanning tunneling microscopy (UHV STM) in the initial characterization of the systems. Importantly, it is also possible to study the assembly of these molecules with liquid or *in situ* STM in an attempt to bridge the temperature and pressure gap of ultra-high vacuum studies. In this way, these amino acid systems can be studied at more relevant conditions, and solvent choices can be made to mimic biological environments. Through the examination of the self-assembly behavior of five amino acid molecules on a Cu(111) single crystal in UHV, an unexpected phenomenon was discovered. All of the amino acids assisted in the immobilization of copper atoms on the surface. The energetic landscape of the surface as mediated by temperature and molecular coverage facilitated the growth of copper islands and clusters. The growth and size fluctuation of the islands offered an interesting snapshot of metal nanocluster diffusion that often occurs at time scales beyond the resolution of a given surface science technique. The presence of ~1 ML of molecules on the surface effectively trapped the metal atoms into localized islands. Elevated temperature were used to promote further diffusion, coalescence, and extinction of the islands. In conclusion, while these systems provide insights into the chiral assembly of amino acids as studied in both UHV and in liquid, they also provide a unique glimpse into metal surface diffusion and offer the ability to study the mass transport of metal atoms, which is important for the understanding of thin film growth and its morphological evolution.

COLL 91

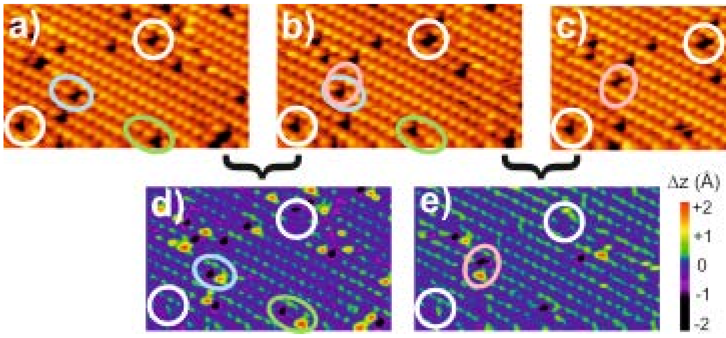
Kinetic effects in the self-assembly of organic molecules on solid surfaces

***Roberto Otero**, roberto.otero@uam.es.Dept. de FÃsica de la Materia Condensada, Universidad AutÃ³noma de Madrid, Madrid, Madrid 28049, SpainInstituto MadrileÃ±o de Estudios Avanzados en Nanociencia IMDEA-Nano, Madrid, Madrid 28049, Spain*

The self-assembly or organic species on metallic surfaces has being the subject of many recent works, due to the large field of applicability of the nanostructured systems obtained by this method. In most of the publications, the observed self-assembled structures are explained only as the result of a subtle balance between intermolecular and molecule-substrate interactions, with total disregard of possible kinetic effects during growth. This is usually so because the energies involved (diffusion barrier, intermolecular interaction, molecule-substrate interaction) are usually small, so that the system has the time to explore a large volume of the configuration space to find the minimum energy arrangement. For growth processes in which slower dynamical processes are involved kinetic effects must certainly become more important.

In this contribution we describe two dynamical processes which take place during the formation of self-assembled monolayers, and are slow enough to be followed by STM at relatively moderated temperatures. One of them involves the diffusion of vacancies in organic self-assembled monolayers, whose collective character ensures a relatively low rate. The other one is the phase-transition between two ordered phases of the organic

acceptor DCNQI deposited on Cu(100), which turns out to be associated to the isomerization reaction of the adsorbate at sufficiently high temperature conditions.



COLL 92

Self-assembled quasicrystalline monolayers

S. Alex Kandel, *skandel@nd.edu.Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, United States*

The process of molecular self-assembly relies on intermolecular interactions to create and maintain long-range order. In nearly all cases, the order created is crystalline. Here we report on the formation of a surface monolayer that has orientational order and local five-fold symmetry, but lacks translational periodicity; this is a two-dimensional quasicrystal, the first to result from small-molecule self-assembly. In this system, quasicrystallinity begins with the formation of hydrogen-bonded cyclic pentamers that. Pairwise interactions between pentamers is mediated by weaker CH-π bonds, and growth and annealing processes are then responsible for aperiodicity. These mechnisms are confirmed in a series of control experiments, and are further elucidated by comparison to density functional theory calculations. Monolayer structures are characterized using scanning tunneling microscopy at low temperature and in ultra-high vacuum.

COLL 93

New dimensions in patterning: Placement and metrology of chemical functionality at all scales

Paul S. Weiss, *psw@cnsi.ucla.edu.California NanoSystems Institute and Departments of Chemistry & Biochemistry and of Materials Science & Engineering, UCLA, Los Angeles, CA 90095, United States*

We place single molecules and larger groups into precisely controlled environments on surfaces. Monolayer matrices and inserted molecules and sub-assemblies can be

designed so as to interact directly, to give stability or other properties to supramolecular assemblies. New families of molecules are being developed to yield even greater control and are enabling determination of the key design parameters of both the molecules and assemblies. This, in turn, is enabling hierarchically controlled chemical patterning and selective functionalization from the sub-nanometer to the centimeter scales. We are simultaneously developing a suite of metrology tools for these methods to give unprecedented information on the structures and properties of these assemblies.

COLL 94

Temperature dependence and desorption kinetics of metal porphyrins on Au(111)

***K W Hipps**, hipps@wsu.edu, Ursula Mazur, Ashish Bhattarai, Bhaskar Chilukuri.Department of Chemistry, Washington State University, Pullman, WA 99164-4630, United States*

The energetics and kinetics associated with metal porphyrin adsorption on conducting surfaces from solution are of great potential importance to the formation of self assembled structures for electronic and optical applications. In this study variable temperature solid-solution interfacial scanning tunneling microscopy (STM) imaging is used to probe the self assembly of porphyrin adlayers. We demonstrate that the adsorption of cobalt octaethylporphyrin (CoOEP) and NiOEP from phenyloctane onto Au(111) are kinetically controlled and essentially irreversible below about 100°C. Above 100°C slow desorption and re-adsorption processes allow for exchange of CoOEP and NiOEP species on the surface. Temperature and relative concentration studies provide values for the relative free energies and enthalpies of activation for the desorption process. Experimental results are compared to DFT calculated values of adsorption energy.

COLL 95

Thermal and quantum tunneling driven molecular self-assembly on surfaces

***Charles Sykes**, charles.sykes@tufts.edu.Department of Chemistry, Tufts University, Medford, MA 02155, United States*

Atomic and molecular self-assembly are important phenomena that underpin many technologies. Typically, thermally enabled diffusion allows a system to sample many areas of configurational space, and ordered assemblies evolve that optimize interactions between species. I will first describe a system in which the diffusion is quantum tunneling in nature and report the self-assembly of H atoms on a Cu(111) surface into complex arrays based on local clustering followed by larger scale islanding of these clusters. We contrast the diffusion and assembly of H with D, which has a much slower tunneling rate and is not able to form the large islands observed with H over equivalent time scales. This system constitutes the first example of quantum-

tunneling-enabled self-assembly, while simultaneously demonstrating the complex ordering of H on Cu(111), a catalytically relevant surface.

In more applied work I will describe the assembly of thioethers, phosphines and selenoethers on metal surfaces. The literature contains a wealth of data about thiol-based monolayers; however, relatively little is known about the self-assembly of molecules with different head groups. By adjusting the molecule-surface interaction and using different head group elements, a vast array of new systems with novel properties may be formed. We demonstrate that the simple hard/soft rules of inorganic chemistry can be used to rationalize the observed trend of molecular interaction strengths with a soft gold surface, i.e., P > Se > S. The structure of the monolayers can be explained by the geometry of the molecules in terms of dipolar, quadrupolar or van der Waals interactions between neighboring species driving the assembly of distinct ordered arrays. As these studies directly compare one element with another in simple systems, they serve as a guide for the design of self-assembled monolayers with novel structures and properties.

COLL 96

Controlling porphyrin nanoarchitectures at solid interfaces

Jonathan P Hill[1], *Jonathan.Hill@nims.go.jp, Yongshu Xie*[2], *Misaho Akada*[1], *Yutaka Wakayama*[1], *Qungmin Ji*[1], *Katsuhiko Ariga*[1]*.Â (1) WPI Centre for Materials Nanoarchitectonics, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, JapanÂ (2) Key Laboratory for Advanced Materials, East China University of Science and Technology, Shanghai, China*

Supramolecular arrangement of porphyrins and other molecules has great potential in the fields of molecular information storage and sensing due to their ease of deposition and good chemical and thermal stabilities. In particular, porphyrins of relatively large molecular weights can be applied in thermal deposition while tetrapyrrole molecules have had an extensive synthetic chemistry developed, which enables synthesis of complex derivatives. In this work, we present complementary examples of porphyrin nanoarchitectonics. Fabrication of binary molecular monolayers using two different porphyrin molecules *tetrakis*(3,5-di-*t*-butyl-4-hydroxyphenyl)porphyrin and *tetrakis*(4-pyridyl)porphyrin by deposition in ultrahigh vacuum is demonstrated. This leads to two unusual heteromolecular monolayer structures were observed with one exhibiting good separation of molecules within the monolayer. Also, a synthetic nanoarchitectonic approach was used to prepare self-assembled molecular nanowires at a mica substrate. The nanowires could be observed growing using atomic force microscopy (AFM) and the network structures of the nanowires can be influenced by manipulation using the AFM probe tip. Formation of molecular monolayers with chromophores positioned remote from the substrate surface will also be discussed.

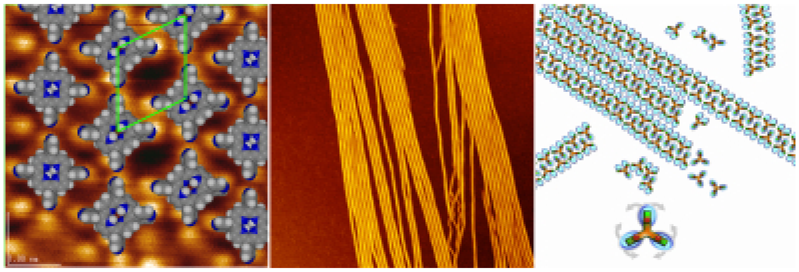


Figure 1 . (Left) Inhomogeneous molecular monolayer of *meso-tetrakis*(4-pyridyl)porphyrin. (Centre) Self-assembled nanowires of amphiphilic porphyrin trimer. (Right) Model of the structure of the nanowires.

COLL 97

Bonding at the metal-organic interface

Eva Zurek[1]*, ezurek@buffalo.edu, James Hooper*[1,2]*, Scott Simpson*[1]*.Â (1) Department of Chemistry, University at Buffalo, State University of New York, Buffalo, NY 14260-3000, United StatesÂ (2) Department of Theoretical Chemistry, Jagiellonian University, Krakow, Poland*

We have carried out van der Waals first-principles calculations in order to systematically study the perturbations of the electronic structure of various organic molecules physisorbed or weakly chemisorbed to the coinage metal surfaces copper, silver and gold. The molecules considered include: benzene, substituted benzenes, 4-fluorostyrene, tetraphenyl porphyrin, a quinonoid zwitterion, croconic acid and rhodizonic acid. We have employed a frontier orbital perspective to analyze the bonding between the substrate and the adsorbate, studied the charge redistribution at the organic-metal interface, and analyzed how this affects the self-assembly.

Our theoretical studies have helped to explain the experimental observations of STM (scanning tunneling microscopy) groups by showing that: tetraphenyl-porphyrin forms attractive networks on the Ag(111) surface and repulsive ones on Cu(111) because of the larger amount of charge transfer to Cu(111); the 10 D permanent dipole of a quinonoid zwitterion changes substantially upon adsorption to the coinage metal surfaces Cu(111), Ag(111) and Au(111) as a result of donation of charge from the molecular HOMO to the surface and back donation to the LUMO; the charge transfer which occurs between the zwitterion and Au(111) has been studied as a function of surface coverage; 4-fluorostyrene molecules form clusters of “magic” sizes that depend on the metal surface and can be understood in terms of a balance between attractive H-bonding and van der Waals interactions as well as Coulomb repulsion between the molecules; the topological organic ferroelectric molecule croconic acid forms chiral honeycomb networks on the Ag(111) surface, and spontaneous electric polarization within the 2D-sheets as well as concerted proton transfer to switch the polarization is possible. Moreover, our calculations have illustrated that classic activating groups generally increase and prototypical deactivating groups decrease the amount and direction of charge transferred from a tri-substituted benzene derivative to the Cu(111) surface.

COLL 98

Switchable static and dynamic self-assembly of magnetic droplets on superhydrophobic surfaces

*Jaakko V.I. Timonen[1], Mika Latikka[1], Ludwig Leibler[2], Robin H.A. Ras[1], **Olli Ikkala**[1], Olli.Ikkala@aalto.fi.Â (1) Department of Applied Physics, Aalto University (formerly Helsinki University of Technology), Espoo, FinlandÂ (2) MatiÃ¨re Molle et Chimie, Ecole SupÃ©rieure de Physique et Chimie Industrielles, Paris, France*

Self-assembly is a process in which interacting bodies are autonomously driven into ordered structures. Static structures such as crystals often form through simple energy minimization, while dynamic ones involve continuous energy supply and dissipation. Dynamic systems are ubiquitous in nature and biology, but have been proven to be challenging to understand and engineer. Here we bridge the gap from static to dynamic self-assembly by introducing a model system based on ferrofluid droplets on superhydrophobic surfaces (Timonen et al, *Science*, 2013, **341** , 253-257). The droplets self-assemble under a static external magnetic field into simple patterns that can be switched to complicated dynamic dissipative structures by applying a time-varying magnetic field. The transition between the static and dynamic patterns involves kinetic trapping and shows complexity that can be directly visualized.

COLL 99

Reversible adsorption of nanoparticles at the oil-water interface by controlling particle-particle interactions

*Xiaoqing Hua, Mingxiang Luo, Michael A Bevan, **Joelle Frechette**, jfrechette@jhu.edu.Department of Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, MD 21210, United States*

The driving force for the adsorption of nanoparticles (< 5nm) at the oil-water interface can be small and is particularly sensitive to wetting properties of the particles at the fluid interface. We will discuss the reversible interfacial assembly of 5 nm diameter gold nanoparticles functionalized with stoichiometric ion-pairs.[1] Using titration, and microscopy we demonstrate that the mechanism for particle desorption from the interface is the electrostatic repulsion between the nanoparticles. By controlling electrostatic repulsion we can control both the extent of adsorption at the interface and the separation between particles within the interfacial film. We also show that under some condition spontaneous emulsification is possible. Finally, we will also present a

thermodynamic model to predict the surface coverage of nanoparticles at the oil-water interface.

[1] M. Luo, G. Olivier, and J. Frechette, “Electrostatic interactions to modulate the reflective assembly of nanoparticles at the oil-water interface “, Soft Matter, 8, 11923-11932, 2012.

COLL 100

Programmed micro-bubble constructions within patterned silk film for encapsulation

***Chunhong Ye**, chunhong.ye@mse.gatech.edu, Dhaval D. Kulkarni, Vladimir V. Tsukruk.Department of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States*

We demonstrated a novel method to fabricate individually addressable “micro-bubble” constructions by confining dissolution of a polystyrene prelayer in the polystyrene-silk fibroin multilayer thin film which was patterned to specific shape and dimension by photolithography. Raman spectra revealed that the polystyrene only presented in the self-formed “micro-bubble” region, indicating the successfully “self-encapsulation” property of the “micro-bubble” structures. The count and shape of “micro-bubbles” on each silk fibroin pattern can be well controlled by the pattern thickness and geometry. Furthermore, The silk fibroin pattern with “micro-bubble” constructions also indicated the capability for “self-encapsulation” for various materials, such as hydrophobic and hydrophilic polymers, nanoparticles, which provided a novel method for the application in the field of solid-state delivery system, drug delivery and bioengineering.

COLL 101

Dip-coating deposition on chemically patterned surfaces: A mechanistic analysis and comparison with topographically patterned surfaces

***Yan Wang**, yanw@mail.pse.umass.edu, Thomas J McCarthy.Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Amherst, MA 01003, United States*

There is a significant literature that describes the deposition of particles/crystals/substances by dip-coating deposition to form arrays on chemically patterned surfaces. A chemically patterned surface containing hydrophilic features on a hydrophobic background is withdrawn from a solution (or dispersion) of the desired substance. The solution dewets from the hydrophobic background, yet pins on the hydrophilic features. Selective deposition occurs after solvent evaporation. An apparently similar approach, recently described by several groups, involves dip-coating deposition of substances from solutions onto hydrophobic topographic features (arrays of posts on superhydrophobic surfaces) that are separated by air. These two

approaches, however, differ remarkably upon analysis of the events at receding 3-phase contact lines. Tensile capillary bridge failure occurs with the post-containing superhydrophobic surfaces and sessile capillary bridge failure occurs with chemically patterned surfaces. The solvent evaporation stage, that occurs after the capillary bridge failures, varies in the two approaches as well. They depend on the receding contact angles of the hydrophobic post tops and the hydrophilic chemically patterned features. Controlling the evaporation rate (adjusting the vaporization/condensation equilibrium) by raising the partial pressure of the solvent is identified as a key factor for chemically patterned surfaces.

COLL 102

Biomolecule-mediated droplet fusion for biosensing

*Praveena Mohan, **Andrew P. Goodwin**, andrew.goodwin@colorado.edu.Department of Chemical and Biological Engineering, University of Colorado, Boulder, Boulder, Colorado 80303, United States*

In this talk, we will present our efforts in designing biomimetic, chemically-responsive nanoemulsions that can respond to the presence of specific biomolecules to generate detectable signals rapidly and without washing steps. Detection of specific biomolecules is of tremendous importance for improving patient health, identifying infectious disease transmission patterns, and many other health-related goals. Screenings are most effective when performed on large populations with wide dissemination to local clinics or point-of-care operation. While ELISA is the gold standard of biomarker detection and quantification, its high cost, lengthy operation times, and reagent instability hinder its widespread utilization, and thus many who would benefit from regular screening cannot because of difficulties in affording the procedure or traveling to a test site. To address this, we have created nanoemulsions with mimics of SNARE complexes on their surface. Under normal conditions the emulsions are stable to environmental conditions and nonspecific coalescence, but when two emulsions with matching complexes interact, they fuse together, mixing their contents. The ability of these nanoemulsions to fuse together can in turn be mediated through noncovalent interaction with sensing analytes such as thrombin. We will present in this talk our work in creating these nanoemulsions and advancing their chemical and physical properties towards biosensing.

COLL 103

Evaporation-induced shape changes in femtoliter-volume microscale droplet interface bilayers

__Pat Collier__, colliercp@ornl.gov, Jonathan Boreyko.Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37830, United States

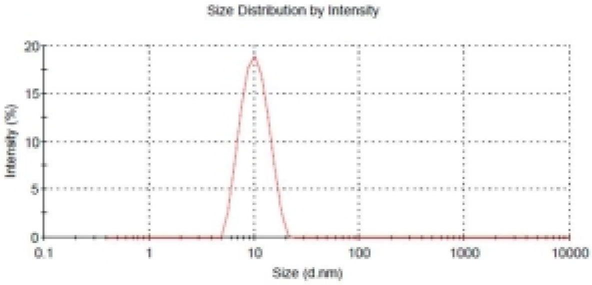
Droplet interface bilayers (DIBs) are a powerful platform for studying the dynamics of synthetic cellular membranes; however, little has been done to elucidate the unique dynamical behaviors of DIBs. Here, we generate femtoliter-volume, microscale droplet interface bilayers (μDIBs) in microfluidic devices using both lipid-in and lipid-out methods to characterize the dynamic morphology of lipid interfaces during evaporation. We identify how the transfer of lipid molecules to and from interfaces depends upon the initial locations of lipid agglomerates in the system, causing μDIBs to exhibit three distinct behaviors: (i) bilayer buckling and vesicle fission when the concentration of lipid agglomerates in the system is negligible, (ii) unzipping when lipid agglomerates are outside of the droplets in the oil, and (iii) shrinking when lipid agglomerates are inside the droplets. These findings offer a better understanding of the dynamics of lipid transfer between interfaces.

COLL 104

Mineral oil nanoemulsion exhibiting strong bactericidal activity against *Mycobacterium immunogenum* and *Pseudomonas aeruginosa*

Shu-Chi Chang[1], *shuchichang@nchu.edu.tw, Shang-Jie Lin*[1], *Tzu-Wen Chen*[1], *Yao-Tung Lin*[2]*.Â (1) Department of Environmental Engineering, National Chung Hsing University, Taichung, Taiwan 40227, Taiwan Republic of ChinaÂ (2) Department of Soil and Environmental Sciences, National Chung Hsing University, Taichung, Taiwan 40227, Taiwan Republic of China*

Mycobacterium immunogenum and *Pseudomonas aeruginosa* currently are of high health concerns in metalworking processes. To date, tank-side biocide addition is the most common microbial control measure but usually unable to prevent mycobacteria growth. This study aimed to formulate an inherently bacteria-resistant metalworking fluid (MWF) with industrial grade chemicals through nanoemulsification. Using a phase inversion temperature method, we created a low-cost mineral oil nanoemulsion (MONE) exhibiting high bactericidal activity against *M. immunogenum* and *P. aeruginosa*. A short term biocidal test showed that a 5% dilution of MONE (5% MONE) has high emulsion stability and extremely strong bactericidal effects. The first-order biocidal rate constants of 5% MONE are higher than 72% of the 32 different test combinations of commercially available MWFs with two industrial biocides. A longer term test on an aged 5% MONE showed that it achieved 100% elimination of all tested bacteria. The biocidal kinetics of MONE seemed to follow a new equation, $ln(N/N_0)= -k_0'(exp(n'C))t$, better than the widely applied Chick-Watson law equation. This new formulation may offer an inexpensive solution in sustainable utilization of MWF and a new research direction on biodeterioration prevention of MWFs.



COLL 105

Surface plasmon mediated selective deposition of Au nanoparticles on Ag nanobowtie

***Wei David Wei**, wei@chem.ufl.edu.Department of Chemistry and Center for Nanostructured Electronic Materials, University of Florida, Gainesville, FL 32611, United States*

Utilizing intrinsic surface properties to direct and control nanostructure growth on nanoscale surface is fundamentally interesting and holds great technological promise. We have developed a novel “bottom-up” approach to fabricating Au nanoparticles on a Ag nanobowtie *via* a chemical solution deposition by using localized surface plasmon resonance (SPR) excitation. Surprisingly the Au nanoparticles were founded to be selectively placed at the junction between the individual Ag nanoprisms. The deposition location is consistent with the strong SPR-enhanced EM field distribution as predicted from the numerical simulation. Moreover, how does the enhanced SPR EM field involve in molecular dissociation will be discussed.

COLL 106

Solution phase strategies for VLS-like growth on colloidal plasmonic substrates

***Jill E. Millstone**, jem210@pitt.edu, Patrick J. Straney, Lauren E. Marbella.Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, United States*

Multicomponent and composite architectures promise to synergistically combine properties of their constituent materials. One attractive class of these materials is the combination of plasmonically active nanoparticles with catalytic or magnetic materials. However, the architectures of these secondary components can be difficult to control, and is often either templated by the underlying structure (e.g. core-shell or “framed” nanoparticle colloids) or by an external template (e.g. porous anodized aluminum oxide). Here, we demonstrate the use of nanoparticle surface chemistry to create linear arrangements of discrete, 1D Pt nanoparticle alloys directly on the surface of a thin triangular gold nanoprism substrate. The synthesis of both components is accomplished in the solution phase and leverages several aspects of the growth chemistry including the supramolecular assembly of the surfactant and speciation of the platinum precursor. The reaction is followed by electron microscopy techniques, as well as X-ray photoelectron spectroscopy, inductively coupled plasma mass spectrometry, and ^{195}Pt-NMR.

COLL 107

Towards molecular control of interparticle separations in (opto)plasmonic nanoparticle clusters and arrays *via* template guided self-assembly

***Bjoern Reinhard**, bmr@bu.edu.Department of Chemistry and The Photonics Center, Boston University, Boston, Massachusetts 02215, United States*

Template guided self-assembly is a versatile fabrication technique for plasmonic nanoparticle clusters and their arrays. The approach also facilitates the integration of

metallic and dielectric nanoparticles at defined lattice sites into extended optoplasmonic hetero-nanoparticle arrays that provide a rich spectrum of localized and delocalized electromagnetic modes. Although template guided self-assembly strategies facilitate the generation of electromagnetically strongly coupled nanoparticles with truly nanoscale interparticle separations, it remains, challenging to control the interparticle separation within the assembly. One potential control strategy is provided by the ligands (HS-(CH2)11-(EG)6-OCH2−COOH) grafted onto the nanoparticle surface. We investigated the influence of the ligand density and the buffer conditions used during the assembly on the average gap width (*g*) between the nanoparticles. The overall size (*n*) and shape of the individual clusters was determined through an electron-beam-lithography defined template. Through correlation of scattering spectroscopy and scanning electron microscopy we achieved a systematic comparison of the spectral cluster response as function of *n* for different assembly conditions and ligand densities. The recorded size-dependent spectra revealed a systematic spectral shift for clusters obtained with different ligand density and/or buffer, indicative of significant differences in *g*. These differences were independently confirmed through high resolution transmission electron microscopy performed with nanoparticle chains assembled on Si_3N_4 membranes. We shifted the far-field resonance of the superradiant mode in the assembled nanoparticle chains by up to 250 nm through variation of *n* between *n* = 1 and 7 (at constant *g*) and up to 100 nm through variation of *g* between 0.37 nm and 1.08 nm (at constant *n*). Overall, these studies confirm a measurable level of tunability for *g* on molecular length scales.

COLL 108

Biodegradable gold nanoclusters which exhibit high-NIR absorbance for biomedical imaging

Robert J Stover[1]*, stover@utexas.edu, Avinash Murthy*[2]*, Sai Gourisankar*[2]*, Golay Nie*[2]*, Miguel Martinez*[2]*, Thomas Truskett*[2]*, Konstantin Sokolov*[1,3]*, Keith Johnston*[1,2]*.Â (1) Texas Materials Institute, University of Texas at Austin, Austin, TX 78712-1591, United StatesÂ (2) Chemical Engineering, University of Texas at Austin, Austin, TX 78712-1591, United StatesÂ (3) Biomedical Engineering, University of Texas at Austin, 200 E. Dean Keeton St., Stop C0400, Austin, TX 78712-1589, United States*

Gold plasmonic nanoparticles are receiving attention for a variety of types of NIR optical biomedical imaging including photoacoustic spectroscopy. Herein we present a novel method to assemble equilibrium gold nanoclusters from 5 nm primary gold nanospheres, which exhibit high near-infrared (NIR) absorbance and have the capability to fully dissociate back to primary particles, which are capable of efficient renal clearance. The equilibrium assembly is manipulated via controlling colloidal interactions, specifically electrostatic repulsion and depletion attraction. The charge on the primary ~5 nm gold nanospheres is tailored via either pH of the dispersion solution or place exchange reactions with a variety of biocompatible ligands such as lysine, cysteine, or glutathione to help increase biocompatibility. Afterwards, the addition of a biodegradable polymer, PLA(1k)-b-PEG(10k)-b-PLA(1k), followed by controlled solvent evaporation results in depletion attraction which mediates the formation of dense clusters between 20-40 nm in diameter depending on gold and polymer concentration. In some cases, salt is also added to the mixture for greater control over nanoclusters size. The adsorption of the polymer onto the cluster surface effectively quenches the particles in the cluster state. At this stage the clusters show high NIR absorbance suitable for biomedical optical techniques such as photoacoustic imaging. In response to cellular pH environments, the quenching polymer degrades thus causing the clusters to dissociate back to primary constituents which are ideal for efficient renal clearance.

COLL 109

Role of etching in the formation of Ag nanoplates with straight, curved, and wavy edges and comparison of their SERS properties

Dong Qin, *dong.qin@mse.gatech.edu, Yin Yang.Materials Science and Engineering, Georgia Institute of Technology, United States*

In this talk, we report the systematically investigation on the role of oxidative etching in the formation of Ag nanoplates with different morphologies. By monitoring the reduction of AgNO3 with poly(vinyl pyrrolidone) (PVP) in an aqueous solution under hydrothermal condition, we confirmed that etching plays an essential role in promoting the growth of Ag triangular nanoplates with straight edges at the expense of multiple twinned particles (MTPs) via Ostwald ripening. Ultimately, the etching resulted in the formation of enneahedral nanoplates with curved edges that have not been reported previously. For the first time, we also observed selective etching on the side edges in ethanol under a solvothermal condition for the generation of Ag nanoplates with wavy edges. A comparison study of surface-enhanced Raman scattering (SERS) indicates that, at the same particle concentration, Ag nanoplates with wavy edges showed an enhancement at least 6 and 13 times stronger than those with straight and curved edges, respectively. The finite difference time domain (FDTD) calculation results support our experimental observations that the sharp features on nanoplates with wavy edges made them the most active SERS substrates.

COLL 110

Mechanism-based design of precursors for the deposition of inorganic films and nanostructures

Lisa McElwee-White, *lmwhite@chem.ufl.edu.Department of Chemistry, University of Florida, Gainesville, FL 32611-7200, United States*

A chemistry-based approach to designing precursors for the deposition of inorganic materials requires consideration of the physical properties of the precursor compound and its probable decomposition pathways. We have been using Chemical Vapor Deposition (CVD) of tungsten carbonitride (WN_xC_y) films from tungsten imido, hydrazido and nitrido complexes as a model system to investigate the relationship between conventional organometallic mechanistic study of the precursors and the deposition results. An analogous approach can be applied to designing precursors for other techniques such as Surface Plasmon Mediated Chemical Deposition (SPMCD) of nanoparticles and Electron Beam Induced Deposition (EBID) of nanostructures.

COLL 111

Strategies to prepare $CuIn_xGa_{x-1}S_2$ and $Ag_xCu_{x-1}InS_2$ nanoparticles from molecular single source precursors

***Joshua J Pak**, pakjosh@isu.edu.Department of Chemistry, Idaho State University, Pocatello, ID 83209, United States*

Over the years, the use of molecular single source precursors (SSPs) has been an effective strategy to prepare binary and ternary nanoparticles. By decomposing molecular SSPs containing all requisite elements, one can produce nanoparticles with controlled stoichiometry, size, and phase. However, the same strategy is not always readily applicable to the preparation of quaternary and more complex compositions. We have been interested in tuning nanoparticle properties such as bandgap by judicious control of the stoichiometry among a variety of component elements. In this presentation, we will discuss the synthesis of complex molecular precursors designed for this purpose and their decomposition to prepare novel I-III-VI multinary nanoparticles such as $CuIn_xGa_{x-1}S_2$ and $Ag_xCu_{x-1}InS_2$.

COLL 112

Electron beam induced deposition of nanostructures: A surface science perspective

***Howard Fairbrother**[1], howardf@jhu.edu, Samantha Rosenberg[1], Josh Wnuk[2], Mike Barclay[1], Cornelis Hagen[3].Â (1) Department of Chemistry, Johns Hopkins University, Baltimore, MD 21218, United StatesÂ (2) Intel Cooperation, Hillsboro, Oregon, United StatesÂ (3) Faculty of Applied Sciences, Delft University of Technology, Delft, The Netherlands*

Electron beam induced deposition (EBID) is a minimally-invasive, lithographic strategy that uses the electron stimulated decomposition of volatile organometallics under low vacuum conditions to fabricate and prototype three-dimensional metallic nanostructures. One of the limitations of EBID lies in the often unacceptably high level of organic contamination in the deposits which adversely affects properties and restricts their value (e.g. as catalysts and biosensors). At the heart of EBID are the electron stimulated reactions of the surface bound organometallic precursors which are responsible for deposition and the ultimate chemical composition of the deposit. In this presentation I will describe the current status of EBID and in particular how surface analytical techniques have been used to provide mechanistic and kinetic insights into the

influence that ligand architecture, substrate temperature and electron fluence have on the surface reactions and molecular level processes that underpin EBID.

By studying the electron stimulated reactions of monodentate FEBIP precursors ($MeCpPtMe_3$, $W(CO)_6$, $Pt(PF_3)_4$, $Co(CO)_3NO$) we have shown that deposition is often initiated by electron stimulated ejection of a single ligand. For example, in the case of $Pt(PF_3)_4$, deposition is initiated by Pt-P bond cleavage but subsequent electron stimulated reactions of the $Pt(PF_3)_3$ intermediate occur exclusively as a result of P-F rather than Pt-P bond cleavage. For precursors such as $MeCpPtMe_3$ that do not form intermediates during EBID, substrate temperature and electron fluence do not influence the film's chemical composition. In contrast, for precursors such as $Pt(PF_3)_4$ and $W(CO)_6$ where deposition creates an intermediate, ligand eject from the intermediate can occur at sufficiently high substrate temperatures, improving the film's metal content. However, higher electron fluxes promote ligand decomposition within surface intermediates, retarding desorption of intact ligands and negatively impacting the film's metal content.

COLL 113

Spontaneous nanostructure assembly with new focused charged particle beam-induced processes

Aurelien Botman[1]*, aurelien.botman@fei.com, Steven J. Randolph*[1]*, Alan Bahm*[1,2]*, Marcus Straw*[1]*, Milos Toth*[2]*.Â (1) FEI, Hillsboro, OR 97124, United StatesÂ (2) School of Physics and Advanced Materials, University of Technology Sydney, Sydney, New South Wales 2007, Australia*

Two new room temperature processes for spontaneous nanostructure formation by focused charged particles in reactive gaseous environments will be presented. Both processes are fundamentally different from conventional gas mediated focused charged particle beam deposition. Firstly, the growth of complex 3D Ga-filled micropillars formed via a bottom-up self-ordering process will be described. These micropillars arise from a number of distinct physical and chemical interactions occurring during focused ion beam bombardment of III-V solids in a reactive gaseous environment. A pre-seeding step allows the formation of micropillar arrays. Secondly, a method for the synthesis of highly porous, nanocrystalline platinum films based on fluorine-mediated decomposition of Pt(PF3)4 adsorbates will be discussed. Pure platinum deposition results from a spontaneous reaction in the presence of the gas phase precursors. Spatial localization is achieved by functionalizing substrate surfaces via charged particle beam induced pre-fluorination.

COLL 114

Osmotic stress induced stochasticity in *E.coli* synthetic gene network

Subra Muralidharan, *subra.murali@wsu.edu, Narayanan Srividya, Austin Peasley, Gayathri Balandaram.School of Molecular Biosciences, Washington State University, Pullman, WA 99164, United States*

A focus of our research efforts is to discern the influence of mechanical and osmotic stress that build up in tumor microenvironments being causal in metastatic phenotype formation. Osmotic stress is due to differences in the activity of water between the cell interior and the microenvironment. We have investigated how the difference in water activity causes stochasticity in a synthetic gene network in *E.coli* as a model. A synthetic gene network consisting of three genes in a cascade that are sequentially downregulated and reported by CFP and YFP, and fourth independent gene reported by RFP was subjected to osmotic stress with varying concentrations of NaCl and sucrose (0 – 3 M). The fluorescence intensities and self-correlation parameters for CFP, YFP, and RFP expression, and intrinsic, and extrinsic noise parameters and transfer functions for *cfp-yfp, cfp-rfp, and yfp-rfp* gene pairs determined from the respective protein expression exhibit a combined repression and activation depending on activity of water. Stochasticity in gene expression is very sensitive to changes in water activity and almost entirely due to intrinsic noise which decreases in the order *cfp-yfp>yfp-rfp>cfp-rfp*. The transfer functions provide information on the directionality of noise propagation in the gene network. Differences between NaCl and sucrose as solutes were observed and could indicate the participation of mechanosensitive ion channels on the membrane wall. Significant aspects of these studies will be discussed.

COLL 115

Phosphoinositol lipid phase separations in Amot-membrane association

Merrell Johnson[2], Horia Petrache[2], Millicent Firestone[3], Thomas D Hurley[1], Clark D Wells[1], ***Ann C Kimble-Hill[1]****, ankimble@iu.edu.Â (1) Department of Biochemistry & Molecular Biology, Indiana University School of Medicine, Indianapolis, IN 46202, United StatesÂ (2) Department of Physics, Indiana University Purdue University Indianapolis, Indianapolis, IN 46202, United StatesÂ (3) Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, NM 87545, United States*

The Angiomotin (Amot) family of adaptor proteins binds core polarity proteins involved in polarization of the apical membrane and transcriptional co-activators as a regulator of cell growth and migration. The Amot coiled-coil homology (ACCH) domain has the unique property to selectively bind phosphatidylinositols (PI) in a similar manner as FYVE, PX and PH domains. We endeavored to understand the physical properties associated with various levels of phosphorylation on PI containing membranes as an interface between the ACCH domain and the lipidic environment for membrane association. As a result, we suggest that the presence of the PI lipid induces a phase separation thereby creating an enriched nano- to micro- scaled ordered lipid domain that can be further stabilized by cholsterol. It is under this context that we then are able to discuss ACCH domain activity as a function of lipid content, as well as further design

assays to ascertain the contributions of selected lysines and arginines toward lipid head-group binding.

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COLL 116

Important role of saccharides in the preservation of lipid bilayer structure in dehydration probed by sum frequency generation (SFG) spectroscopy

Zhang Ya[1]*, zhang.ya@nims.go.jp, Noguchi Hidenori*[1,2]*, Uosaki Kohei*[1,2]*.Â (1) International Center for Materials Nanoarchitectonics (WPI-MANA), Nation Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0044, JapanÂ (2) Department of Chemistry, Hokkaido University, Sapporo, Hokkaido 060-0081, Japan*

Saccharides are found in many plants and animals. They play important role in keeping many organisms active even in extreme life conditions such as complete dehydration as they have ability to prevent headgroup of lipid membrane to pack when water is removed. However, the mechanism of stabilization of lipid membrane in dry state by saccharides is still not well understood due to the lack of effective experimental probes. Sum frequency generation (SFG) spectroscopy is an interface-sensitive technique, based on a second-order nonlinear optical effect, in which a photon is generated at a frequency equal to the sum of the frequencies of the two incident photons, and is effective for the study of interfacial molecular structure. In this work, the role of saccharides for the preservation of DMPC bilayer structure in dry state was studied using SFG spectroscopy, atomic force microscopy (AFM) and attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy.

Although the DMPC bilayer was stable in D_2O, it was broken and formed an ordered monolayer when D_2O was removed. The stability of the DMPC bilayer increased when saccharide was introduced. Moreover, the size of the saccharide was found to be an important factor in stabilizing the DMPC bilayer structure in dry state. ATR-FTIR measurements showed hydrogen bond formation between saccharide and phospholipid headgroups was minimal. From these results, we concluded that the volumetric effect play a main role in preserving bilayer structure in dry state.

COLL 117

Lipid tilt regulates ripple phase behavior in lipid bilayer

Padmini Rangamani[1]*, Padmini.rangamani@berkeley.edu, Shachi Katira*[2]*, Berend Smit*[2]*, George Oster*[1]*.Â (1) 1Department of Molecular and Cell Biology,, University of California,, Berkeley, CA 94720, United StatesÂ (2) Department of Chemistry and Chemical Engineering, University of California,, Berkeley, CA 94720, United States*

Continuum modeling of lipid bilayers provides insight into the physics underlying geometric changes to the shape of the membrane in response to biological processes. The Helfrich model has been the gold standard for many years and applies only to length scales larger than that of the thickness of the bilayer. For small length scale processes, orientation of the lipid, characterized by 'lipid tilt', is a suitable fundamental degree of freedom. In this work, we develop a continuum model with lipid tilt as the key degree of freedom. Using local force balance, we derive the equations of motion associated with the membrane. We use this model to study the characteristics of ripple phases in bilayers. Comparing the continuum model to coarse-grained simulations, we find that the tilt degree of freedom is important to allow for ripple formation in bilayer membranes.

COLL 118

Terpenoids: Their effect on biological membranes

Vivien Jagalski[1]*, vivien@chem.ku.dk, Björn Hamberger Hamberger*[2]*, Maritè Càrdenas*[1]*.Â (1) Department of Chemistry, University of Copenhagen, Copenhagen, DenmarkÂ (2) Department of Plant and Environmental Sciences, Faculty of Science, Copenhagen, BÃ¼lowsvej 17 1870 Frederiksberg C, Denmark*

Terpenoids are the largest group of natural compounds with a high structural diversity. Synthesized out of five- carbon building blocks they are highly lipophilic, implying a potential effect on the physical and chemical properties of the biological membrane, which are proved to be crucial for each living cell. They are synthethized by enzymes at the cell membrane and are accumulated in lipophilic environments including lipid bodies.

Terpenoids are secondary metabolites produced by plant cells. They have versatile biological activities and hence the research focused on these low weight compounds the past decades. Nowadays, terpenoids find pharmaceutical applications for instance in cancer therapy, or in food industry as flavor enhancer. Despite their importance, terpenoid effects on biological bilayers have not been investigated yet. The biological membrane as the largest cell component has, besides its barrier function, an essential role in many cell processes like cell metabolism, energy storage and communication. The vitality of a cell can rise and fall with its membrane´s properties and can be crucially effected by lipophilic molecules, for example sterols and terpenoids. Sterols are molecules known for accumulating in the hydrophobic part of the lipid bilayer changing the formation of the lipids within it. Due to the chemical structure of terpenoids we hypothetize that these molecules also have an effect on lipid packing and the thermotropic phase behavior that could further effect biological pathways of the cell.

The aim is to analyze these potential effects by establishing a membrane model that mimics the biological bilayer by its lipid composition. With a combination of modern methods like Atomic Force Microscopy (AFM) in liquid and Fluorescence microscopy as well as classical methods such as differential scanning microscopy (DSC) and Langmuir Balance, changes in the lipid bilayer properties can be studied and visualized on the nanoscale. We present here initial data on lipid membrane physicochemical properties with compositions closer to the plant cell key organelles and terpenoid effects on it.

COLL 119

Investigations of Cu^{2+}-phosphatidylserine (PS) binding

Xiao Cong[1]*, xiao.cong@mail.chem.tamu.edu, Paul S Cremer*[2]*.Â (1) Department of Chemistry, Texas A&M University, College Station, TX 77843, United StatesÂ (2) Department of Chemistry, Pennsylvania State University, State College, PA 16802, United States*

Using a novel fluorescence quenching assay, phosphatidylserine (PS) lipids in supported lipid bilayers (SLBs) were found to bind Cu^{2+} with sub-picomolar affinity. The trapped Cu^{2+} is chelated by two PS lipids and the resulting Cu^{2+}-2PS complex can quench a broad spectrum of lipid-bound fluorophores in a reversible and pH-dependent fashion. At acidic pH values, the fluorophores are almost completely unquenched while at basic pH, significant quenching (85-90%) is observed. Besides, as Cu^{2+} assists deprotonation of the amine groups on PS and binds carboxylate and amine groups from two adjacent PS molecules, the Cu^{2+}-2PS complex preserves the negatively charged character on membranes. This quenching assay can be used to determine the equilibrium dissociation constants between Cu^{2+} and SLBs containing different PS concentrations, since the PS concentration on cell surfaces varies during different biological events such as apoptosis and blood clotting.

COLL 120

Time-resolved differential scanning calorimetry and small angle neutron scattering studies on the lipid transfer of phospholipid nanodiscs

Yan Xia[1], *yan.xia@uconn.edu, Mu-Ping Nieh*[1,2,3]*.Â (1) Department of Chemical & Biomolecular Engineering, University of Connecticut, Storrs, Connecticut 06269, United StatesÂ (2) Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269, United StatesÂ (3) Department of Biomedical Engineering, University of Connecticut, Storrs, Connecticut 06269, United States*

Phospholipid-based nanodiscs are fragments of biomimic membranes composed of long- and short- chain phospholipids. Their stability can strongly depend on the lipid transfer rate, which can be evaluated by time-resolved differential scanning calorimetry (DSC) and small angle neutron scattering (SANS). This presentation will focus on the lipid transfer of a mixture of zwitterionic long-chain 1,2-dihexadecanoyl-*sn*-3-phosphocholine (DPPC), charged long-chain 1,2-dihexahecanoyl-*sn*-glycero-3-phospho-(1'-rac-glycerol) (DPPG), and zwitterionic short-chain 1,2-dihexanoyl-*sn*-glycero-3-phosphocholine (DHPC), at 20 ºC, 25ºC and 30 ºC [under the melting temperature of DPPC (41ºC) to ensure stable single nanodiscs]. The lipid transfer rate can be expressed by a single exponential decay and the activation energy E_a was estimated using temperature-dependent Arrhenius equation. The energy (thermodynamic properties) that involves into the lipid transfer were further discussed using Eyring-Polanyi equation. The half-life of lipid exchange for nanodiscs was found around 40 days at 20 ºC, in contrast to that of the DPPC/DPPG liposomes (several months). One of the possible factors that causes the significant difference, the DHPC content, will be investigated and correlated with the lipid transfer rate of the nanodiscs.

COLL 121

Molecular dynamics simulation of bitumen recovery from oil sands using nanoparticle suspensions

Oleg A Mazyar, *Oleg.Mazyar@bakerhughes.com, Gaurav Agrawal, Valery N Khabashesku.Center for Technology Innovation, Baker Hughes Incorporated, Houston, TX 77040, United States*

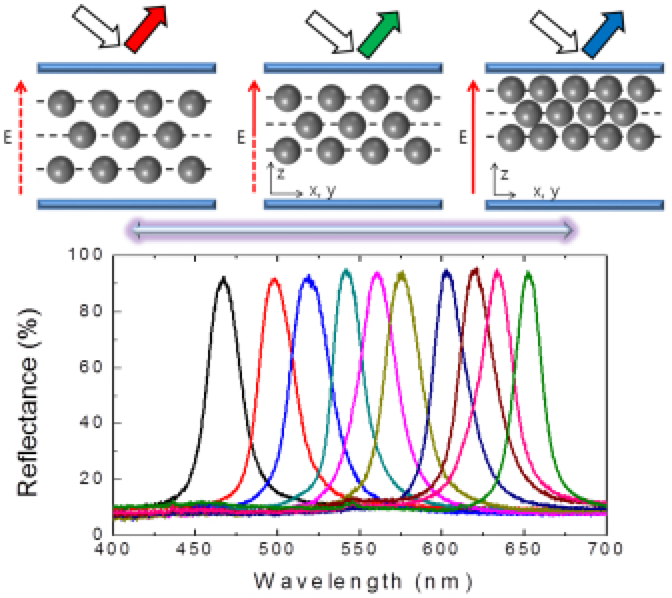
Recently, nanoparticle dispersions were suggested for improving the efficiency of enhanced oil recovery, well remediation and formation damage removal processes. These improvements are thought to be due to the effect of disjoining pressure arising from the ordering of nanoparticles in the confined three-phase contact region. In this work, we discuss the use of molecular dynamics simulations to demonstrate that nanoparticle suspensions can also enhance the recovery of bitumen from oil sands in processes like Clark's hot water process and low-temperature bitumen recovery process, where the formation of ordered structures of nanoparticles is highly unlikely.

COLL 122

Structural color manipulation using tunable photonic crystal: Important role of colloids

***Moon Gyu Han**, moongyu.han@samsung.com, Chul-Joon Heo, Hongshik Shim, Chang Gyun Shin, Jung Woo Kim, Yong Wan Jin, Sangyoon Lee.Emerging Materials Center, Samsung Advanced Institute of Technology, Yong-in, Gyenggi 446-712, Republic of Korea*

Due to recent growing interest in mobile and e-book devices, new demand for a display with excellent outdoor readability, low power consumption, and reduced eye-fatigue, has led to research on reflective displays. Crystalline colloidal arrays (CCAs) composed of monodisperse copolymer colloids investigated in this study offer great potential for a tunable photonic crystal to the application on the display technology, owing to its high reflectance and colour purity as well as easy controllability of the photonic colour in a full visible regime. With the help of easy controllability of the particle size and the surface charge, structural colour with improved viewing angle were produced by mixing colloids with different particle sizes. In addition, the stop-band tuning mechanism under electric field was systematically investigated. We also report a significant improvement of the tuning stability of the colloidal photonic crystal composed of long-range ordered crystalline colloidal arrays through modifying the ITO electrode with ion exchange resins. Thin layer of over-coating on ITO resulted in significantly improved number of switching of stable colour tuning from red to green over 800 times, which is reported best result for tunable photonic crystal with more than 100 nm of Δλ.



COLL 123

Chemotaxis of catalytic silica-manganese oxide "matchstick" particles

***Stefan A. F. Bon**, s.bon@warwick.ac.uk, Adam R. Morgan, Alan B. Dawson, Holly S. Mckenzie, Thomas S. Skelhon, Richard Beanland, Henry P.W. Franks.Department of Chemistry, University of Warwick, Coventry, United Kingdom*

Particles that can undergo directed self-propulsion are desirable for colloidal cargo delivery and self-assembly. We will describe the synthesis of silica-manganese oxide "matchstick" shaped colloids that undergo catalytic self-propulsion by consumption of hydrogen peroxide. Chemotaxis is observed when these particles are placed in a fuel gradient.

COLL 124

Sedimentation of aqueous sodium hydroxide drops in vegetable oils

***Hyaquino Hyacinthe**, thomasw@iastate.edu, Andrew R. White, Thomas Ward.Department of Aerospace Engineering, Iowa State University, Ames, Iowa 50011-2271, United States*

Adding water droplets to diesel is known to dramatically decrease NOx and smoke emissions. Furthermore water-diesel emulsions have been shown to have a higher reduction in these emissions than water injection into the intake manifold. Unfortunately the shelf-life of such an emulsion is limited by its kinetic stability. The presence of surfactants can significantly modify the sedimentation rate with the introduction of Marangoni stresses. In the case of a vegetable oil-based fuel drops of aqueous sodium hydroxide can yield sodium-carboxylate salt surfactants through saponification. Aqueous sodium hydroxide drops with pH between 11 and 13 are allowed to settle in several oils such as corn, canola, soybean and olive. The deceleration, and in some cases acceleration, of the drops compared to a clean water drop is observed.

COLL 125

Stirring of inhomogeneous fluids in a tilted-rotating tank

***Andrew R. White**[1], thomasw@iastate.edu, David C. Swan[2], Hyaquino Hyacinthe[1], Thomas Ward[1].Â (1) Department of Aerospace Engineering, Iowa State University, Ames, Iowa 50011-2271, United StatesÂ (2) Department of Mechanical and Aerospace Engineering, North Carolina State University, Raleigh, NC 27695-7910, United States*

Experiments for the inhomogeneous fluid mixing in a tilted-rotating tank is discussed at O(1-10) Reynolds and small capillary numbers. At low Reynolds numbers the flow exhibits two large vortices. As the Reynolds number increases to the laminar regime, the two vortices exhibit interactions with the bottom wall and begin a cascading effect that is similar to the well known Moffatt (J. Fluid Mech., 1964) vortices. The additional vortices aid in transporting material from the the walls to the bulk of the region between them. They are also efficient in breaking up large droplets into much smaller ones with the addition of surfactants. The vortices also intensify in magnitude with increasing

rotation rate leading to the appearance of KAM surfaces, which are barriers to efficient mixing. Experiments are performed to study dispersing water in vegetable oil (5-10% water by volume) and using laser fluorescence to illuminate the vortices via experimental Poincare mapping. The resulting images are analyzed to determine the mixed cross sectional area versus elapsed time as a function of the system parameters which are the tilt angle, surfactant concentration and Reynolds number.

COLL 126

Novel route to the formation of Pickering emulsions

Amitesh Saha[1]*, sahaa@egr.uri.edu, Vijay T John*[2]*, Arijit Bose*[1]*.Â (1) Department of Chemical Engineering, University of Rhode Island, Kingston, Rhode Island 02881, United StatesÂ (2) Department of Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana 70118, United States*

Particles that are partially wettable in two immiscible liquids are usually required to form stable emulsions. Here, we begin with completely hydrophilic and highly hydrophobic particles that do not, by themselves, form emulsions. When these particles are suspended in aqueous and organic phases respectively, and the two suspensions mixed, attractive Van der Waals forces between these types of particles cause them to assemble physically into entities that are partially wettable in both phases. These entities are very effective at stabilizing emulsions. Particle material, size, shape and concentration in suspension, as well as the choice of dispersed and continuous phase are all important for creating the physically assembled particulate entities that stabilize emulsions. This provides an interesting platform for the development of new emulsifier systems with particles bearing different physical and chemical properties assembling at oil-water interfaces to stabilize either oil in water or water in oil emulsions.

COLL 127

Extremely stable oligomer grafted silica nanoparticle stabilised oil-in-concentrated brine emulsions

Jing Li[1]*, jl906@ic.ac.uk, Milo Shaffer*[2]*, Alexander Bismarck*[1]*.Â (1) Polymer and Composite Engineering (PaCE) Group, Department of Chemical Engineering, Imperial College London, London, United Kingdom SW7 2AZ, United KingdomÂ (2) Nanostructured Hierarchical Assemblies and Composites (NanoHAC) , Department of Chemistry, Imperial College London, London, UK SW7 2AZ, United Kingdom*

Emulsions have long been of great interest due to their widespread use in everyday life and majors industries, including the pharmaceutical and petroleum sectors. Particle-stabilised emulsions have received a considerable revival of attention recently. Many studies have demonstrated that the surface properties of nanoparticles (NPs) can be tailored by grafting polymers, such as poly(*N*-isopropylacrylamide) to their surface. Furthermore, these modified NPs can be responsive and yet efficient emulsifiers.

However, high salinities have always been a critical problem to emulsifiers, especially for polymer grafted NPs. In fact, concentrated brine has been traditionally used to break emulsions. At high ionic strength, electrostatic repulsion between particles is effectively screened leading to NP aggregation. Additionally, it may cause grafted polymers to collapse and entangle, removing steric stabilisation. These effects all contribute to a change in the hydrophilicity of NPs, resulting in lower emulsion stability and/or complete emulsion destabilisation. Steric stabilisation of sulfonated copolymer grafted iron oxides NPs in brine has been recently reported but successful emulsification has yet to be demonstrated.

Here, we report the functionalisation of silica NPs by grafting a specific oligomers covalently. These oligomer-graft-NPs were characterised using Dynamic Light Scattering and zeta potential measurements, which indicated stable dispersions. Furthermore, oligomer-graft-NPs and commercially available Wacker silica NPs can act as efficient emulsifiers in both water and standard American Petroleum Institute (AP1) brine (1.8 M total ionic strength, NaCl and $CaCl_2$). Stable decane-in-brine emulsions were prepared. In higher brine concentration, the stability of Wacker stabilised emulsions decreased, but oligomer-graft-NPs stabilised emulsions showed improved stability with smaller droplet size. The effect of temperature on emulsion stability with brine as continuous phase and the responsiveness of modified NPs are being studied.

COLL 128

Giant charge reversal and charge amplification with monovalent ions in highly size-asymmetric colloidal suspensions

Guillermo I. Guerrero-Garcia[1], *ivan-guerrero@northwestern.edu, Niels Boon*[1], *Monica Olvera de la Cruz*[1,2]*.Â (1) Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, United StatesÂ (2) Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States*

In previous works, we have shown that the ionic excluded volume and the ionic size-asymmetry may promote an overcompensation of the bare colloidal charge of a single macroion by counterions, or the so-called charge reversal, and may also induce a local augment of the net charge near the surface of a single macroion exceeding its bare colloidal charge, which is the so-called surface charge amplification, in concentrated supporting electrolytes. In this work, we show that large values of local charge reversal and charge amplification may appear in a suspension of big macroions and small monovalent ions with particle size-asymmetries of 250:1. A novel theoretical approach to describe the corresponding effective interactions between the macroions is also presented.

COLL 129

Tip induced crystallization lithography

***Xin Zhang**, zhx-1985@163.com, Brandon L. Weeks.Department of Chemical Engineering, Texas Tech University, Lubbock, Texas 79409, United States*

The preparation of uniform large-area organic crystal arrays on substrates plays an important role for producing high quality organic thin film based devices, such as organic semiconductors, solar cells, light-emitting diodes, and sensors. To date, various techniques have been applied to fabricate organic crystal arrays on substrates, such as soft-lithography, ink-jet printing and templated growth.Here we demonstrate a new technique for efficiently fabricating large-area organic crystal arrays on substrates using tip induced crystallization lithography (TICkLe). The methodology depends on coating an organic amorphous thin film on a substrate and then inducing crystallization using an Atomic Force Microscope (AFM) tip. In this report, the size of the smallest feature made using TICkLe was around 2μm.

COLL 130

Nanoscale surface properties of frost during formation

***Niklas Nordgren**, niklas.nordgren@sp.se, Mikael Järn.SP Technical Research Institute of Sweden, SP Chemistry, Materials and Surfaces, Stockholm, Sweden*

Frost formation at the nanoscopic level was studied in situ by means of atomic force microscopy (AFM). The results obtained on mica at low surface temperature conditions displayed a slow directionally growing frost layer. The propagating ice layer was found to be only a few nanometers thin. Conversely, when increasing the temperature rapid melting occurred uniformly across the layer. Moreover, AFM quantitative nanomechanical analysis revealed a significant difference in the adhesion behavior of the frost layer and the bare mica substrate demonstrating the role of chemistry and topography on the interfacial properties of the hydrophilic surfaces. The presented metrological approach sets the stage for studying many important surface phenomena of ice at various interfaces with the aim to for example develop new nanomaterials and surfaces with tailored anti-icing properties.

COLL 131

Genomic studies of elastomeric materials for asymmetric wetting, adhesion, and transport properties

***Melik C Demirel**, mdemirel@engr.psu.edu.Materials Research Institute, Penn State, University Park, PA 16802, United States*

We developed an integrative approach for the understanding and engineering of asymmetric wetting, transport and adhesion properties of elastomeric materials extracted from squid ring teeth. Materials properties of elastomers extracted from biological samples vary significantly between the species within the same genus due to the differences in structure and composition. The gain or loss of materials physical

properties between different squid species sheds light into not only the molecular structure but also the integration of the hierarchy of systems that serves at morphological length scales. Therefore, understanding the functional transitions of biomimetic systems, both computationally and experimentally,helps us to design, fabricate and synthesize materials resilient to environmental factors, as well as eco-friendly advanced materials for their novel asymmetric wetting, adhesion and transport properties.

COLL 132

Biomimetic surfaces with switchable and adaptive hydrophobic behavior

***Sergiy Minko**, sminko@clarkson.edu.Department of Chemistry and Biomolecular Science, Clarkson University, Potsdam, NY 13699, United States*

Living systems demonstrate examples of surfaces and interfaces with tunable and adjustable hydrophobic properties to adapt changes in their environment. In this talk we demonstrate several examples of synthetic materials that mimic biological systems and demonstrate hydrophobic-hydrophilic transitions via adapting changes in their environment in air, in liquids or by remote signals. Such systems could find a number of applications from engineering to biology when synthetic materials could adjust their interactions with living systems or stimulate the living system response.

COLL 133

Hydrophobic and “switchable” cellulose nanocrystals

*Kevin H. M. Kan, Tiffany Abitbol, Lexa Graham, **Emily D. Cranston**, ecranst@mcmaster.ca.Department of Chemical Engineering, McMaster University, Hamilton, Ontario L8S 4L7, Canada*

By learning from nature and using bio-components, we can engineer high-performance materials with improved functionality. Cellulose nanocrystals (CNCs) stand out due to their mechanical and optical properties but are limited by their hydrophilicity and interfacial compatibility with hydrophobic polymers. I will present recent advances in surface modification routes to achieve hydrophobic CNCs through polymer grafting and surfactant adsorption. The resulting materials are characterized by contact angle, turbidity, mass spectrometry, surface plasmon resonance spectroscopy and various microscopies. Hydrophobically-modified CNCs disperse in organic solvents which opens new avenues for composite processing including solvent ball milling and melt mixing and extends the range of potential applications for these bio-based nanoparticles. Surfactant-modified CNCs effectively stabilize oil-in-water and water-in-oil emulsions which can be controlled through surfactant type and concentration. Finally, a water based “grafting-from” polymerization method can be used to graft hydrophobic polymers or responsive polymers which switch surface charge, colloidal stability and

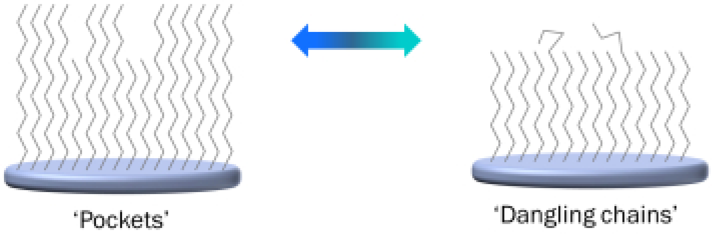
hydrophobicity with temperature, pH or by bubbling carbon dioxide through the nanoparticle suspension.

COLL 134

Thin fluid film and droplet behavior on tunably disordered self-assembled monolayer surfaces

***Scott K Shaw**, scott-k-shaw@uiowa.edu.Department of Chemistry, University of Iowa, Iowa City, Iowa 52242-1294, United States*

The molecular structure and organization of a substrate's surface layers are important to control wetting, fouling, and other important processes. Advanced materials and new fabrications methods for tailored surfaces are urgently desired. This work explores properties of fluid droplets and films supported on substrates modified by tunably disordered self-assembled monolayer (SAM) systems. By creating mixed monolayers of varying chain length, the top-most region of the monolayer is changed from crystalline to one of several disordered phases. This affects the hydrophobicity and surface energy of the SAM layer, leading to changes in the fluid's chemical structure and contact angle. Fluid layers are introduced on SAM-modified surfaces by a highly controlled emersion process. Characteristics of the fluids and SAM surfaces are probed using vibrational spectroscopy, ellipsometry, and contact angle goniometry. Results are correlated with expectations from chemical interactions i.e. hydrophobic forces, hydrogen bonding, van der Waals, electrostatics, etc.



COLL 135

Protein resistance and surface restructuring of PEG-silane amphiphiles with variable PEG segment lengths

***Marc A Rufin**[1], rufinm@tamu.edu, John A Gruetzner[1], Matthew J Hurley[1], Melissa L Hawkins[1], Melissa A Grunlan[1,2].Â (1) Department of Biomedical Engineering, Texas A&M University, College Station, Texas 77843, United StatesÂ (2) Department of Materials Science and Engineering, Texas A&M University, College Station, Texas 77843, United States*

Protein adsorption on blood-contacting medical devices leads to thrombosis and infection. Therefore, protein-resistant biomaterials have the potential to improve device safety and efficacy. Poly(ethylene glycol) (PEG) has been incorporated into biomaterials (e.g. silicones) to confer protein resistance, but its performance in vivo is limited. To improve protein resistance, we prepared PEG-silane amphiphiles with a siloxane tether and variable PEG segment length (m) (Figure 1). Surface-grafted coatings having similar graft densities were prepared on silica wafers to eliminate restructuring effects and compared to those based on “PEG-controls” (i.e. no siloxane tether) as well as “siloxane controls” (i.e. no PEG segment). While surface hydrophilicity of PEG-silane amphiphile coatings increased with PEG segment length, the “PEG-control” surface-grafted coating was the most hydrophilic and exhibited the greatest resistance to fibrinogen adsorption. Next, medical-grade silicone was bulk-modified with PEG-silane amphiphiles as well as the controls. While silicones modified with the “PEG-control” were hydrophobic, those modified with PEG-silane amphiphiles were more hydrophilic and demonstrated a high capacity to restructure at aqueous interfaces. These results indicate that the siloxane tether imparts PEG with an important ability to restructure to the surface of polymeric networks. It was also found that PEG segment length influenced surface restructuring, where silicones modified with PEG-silane amphiphiles of m=8 were the most hydrophilic.

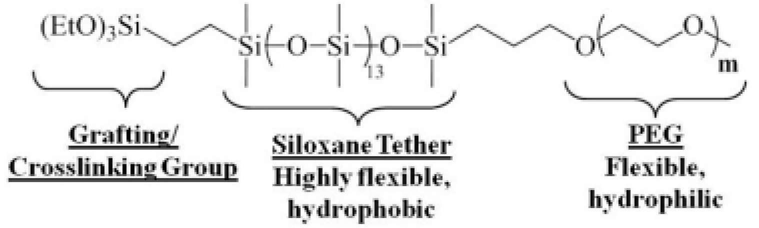


Figure 1: PEG-silane amphiphile chemical structure with variable PEG segment repeat unit length (m = 3, 8, & 16).

COLL 136

Canna indica seedpod: An inspiration to fabricate high aspect ratio hierarchical superhydrophobic surfaces

Chandra Shekhar Sharma, *cssharma@iith.ac.in, Srinadh Mattaparthi.Chemical Engineering, Indian Institute of Technology Hyderabad, Hyderabad, AP 502205, India*

Introduction

Materials, objects and processes found in nature functions from macro-scale to the nano-scale. Bio-inspiration or biomimetics is a tool to mimic these natural objects to develop functional materials which provide desired properties such as superhydrophobicity. There are a large number of examples found in nature such as plants, bacteria, land animals, aquatic animals and insects which provide an inspiration to mimic some structural and functional properties owned by them. For example some plant leaves and flower petals like lotus leaf, rice leaf, taro leaf and rose petal are well known for their superhydrophobic and self-cleaning properties due to the multiscale structural patterns present on their surfaces. Most of these examples as reported in literature are based on low aspect ratio structures.

India canna, a species of the Canna genus that belongs to the family Cannaceae, has been chosen here as a model plant. Unlike its leaves and petals which show ultra hydrophobic nature due to low aspect ratio multiscale surface structures, Canna Inica seedpod possesses high aspect ratio hierarchical structures and also also shows superhydrophobic nature. We not only successfully mimicked these high aspect ratio hierarchical structures into a number of polymers like PDMS and an organic (resorcinol formaldehyde) gel by replica molding but also showed that these biomimicked polymer surfaces exhibit superhydrophobicity. These high aspect ratio biomimicked hierarchical structures may find potential applications in self cleaning surfaces, low friction surfaces in microfluidics and in MEMS.

Experimental

Materials: Canna Indica seedpod of red color was chosen from a local garden. Polydimethoxysilane (PDMS) (Parts 1 and B) was purchased from Dow corning. Resorcinol, formaldehyde, potassium carbonate and chloroform were purchased from Merck India.

Method: Replica molding is one of example of soft lithography techniques to fabricate sub-micron structures over a large area. We cut the seedpod into small pieces and poured the PDMS solution onto it followed by curing at 120 ºC for 2 hours. PDMS mold was swollen in chloroform for easy release of bio-template giving a negative replica containing holes in PDMS. Once the PDMS negative replica having holes was prepared after swelling it into chloroform for its easy release, we poured resorcinol-formaldehyde (RF) sol into it. After controlled drying, we were able to fabricate positive RF gel replica with high aspect ratio hierarchical structures as similar to original seedpod.

Characterization: SEM was used to observe the morphology of the original seedpod and its negative PDMS and positive RF gel replicas. The 3-D confocal microscopy was used to measure the aspect ratio of individual spike present in seedpod structure. Contact angle was measured using goniometer to study the wettability characteristics of these biomimicked polymer surfaces.

Results and Discussion

Figures 1 and 2 summarizes the results on structural characterization and wettability characteristics of original and biomimicked high aspect ratio hierarchical polymer surfaces as discussed above.

Figure 1: The digital camera and 3-D confocal microscopy image of original Canna Indica seedpod

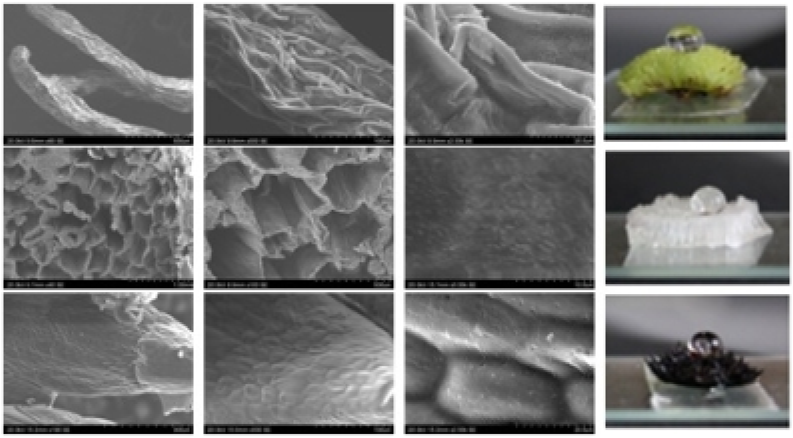


Figure 2: SEM images (first three rows) of original seedpod (first row); negative PDMS replica (second row) and positive RF gel replica (third row) followed by digital image of water droplet last row)

Conclusions

Biomimicking has been depicted as a powerful tool for the microfabrication of high aspect ratio hierarchical structure in polymers. These biomimicked polymer surfaces retained the superhydrophobic behavior as of their original biotemplates.

Acknowledgement: Research grant of Indian Institute of Technology, Hyderabad is acknowledged.

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COLL 137

Anti-fouling silicone coatings prepared with PEO-silane amphiphiles

Melissa L. Hawkins[1], *gies67@tamu.edu, Bagrat Grigoryan*[1], *Samantha M. Schott*[1], *Melissa A. Grunlan*[1,2]*.Â (1) Department of Biomedical Engineering, Texas A&M University, College Station, TX 77843, United StatesÂ (2) Department of Materials Science & Engineering, Texas A&M University, College Station, TX 77843, United States*

Silicones are commonly used for blood-contacting medical devices as well as marine and industrial coatings. However, due to their extreme hydrophobicity, silicones exhibit poor resistance to biological adhesion, including blood proteins and microorganisms. To reduce adhesion events, silicone surfaces have been hydrophilized by various physical and chemical strategies including modification with poly(ethylene oxide) (PEO; or poly(ethylene glycol) (PEG)). In this study, linear PEO-silane amphiphiles containing a flexible, hydrophobic siloxane tether of variable length (n) were used to prepare bulk-modified silicones (acetoxy cure RTV silicone, 20% silica) as well as model surface-grafted coatings on silicon wafers (Figure 1). Contact angle measurements were recorded and compared to the adsorption of fibrinogen protein solutions via QCM-D. Surface-grafted coatings confirmed that increased siloxane tether length produced an increase in surface hydrophobicity and, hence, reduced protein resistance. However, for bulk-modified silicones, reconstruction of the amphiphiles to the surface and the resulting increase in surface hydrophilicity was generally enhanced with a longer siloxane tether. Thus, restructuring of the PEO-silane amphiphile in a bulk coating and the resulting surface wettability is impacted by siloxane tether length.

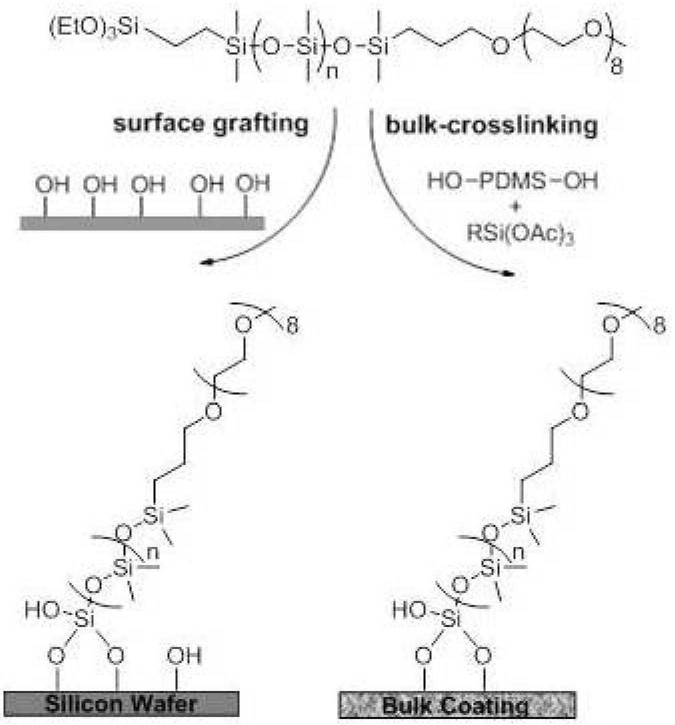


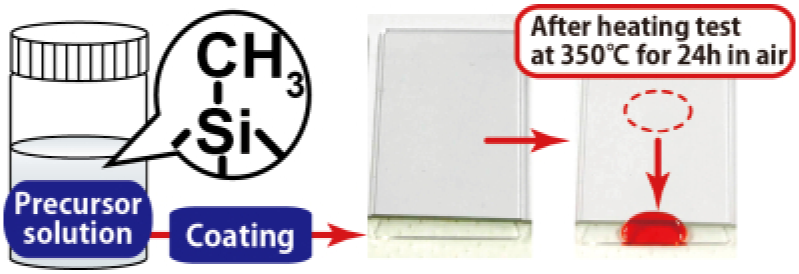
Figure 1. Surface and bulk modification of silicones with PEO-silane amphiphiles.

COLL 138

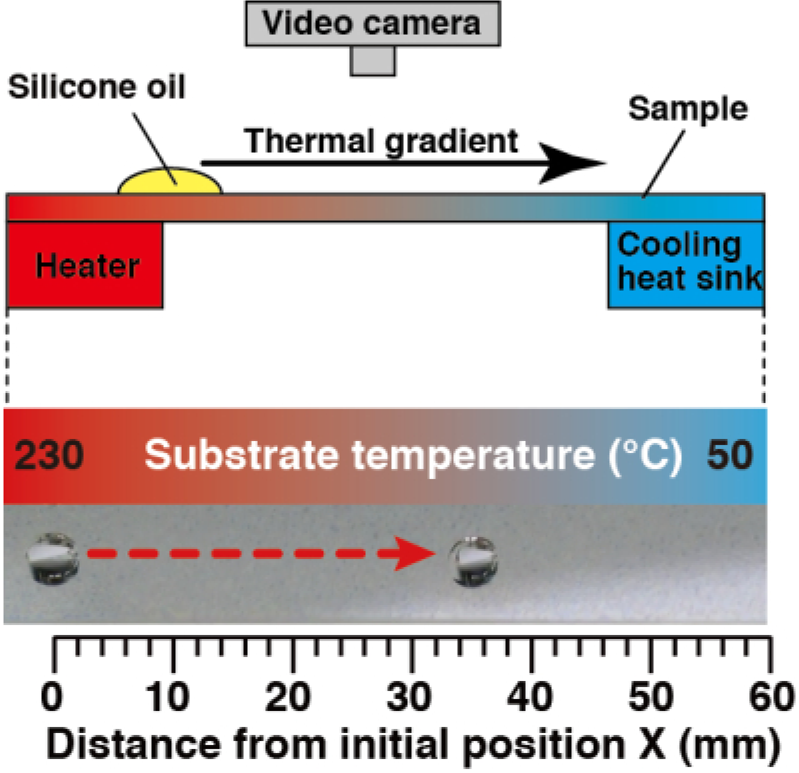
Thermally-responsive, durable, water/oil repellent coating using polymethylsilsesquioxane

***Chihiro Urata**, chihiro-urata@aist.go.jp, Benjamin Masheder, Cheng F Dalton, Atsushi Hozumi.Department of Materials Research Institute for Sustainable Development, National Institute of Advanced Industrial Science and Technology (AIST), 2266-98, Anagahora, Shimo-Shidami, Moriyama-ku, Nagoya 463-8560, Japan*

A thermally stable/durable, water/oil repellent coating composed of polymethylsilsesquioxane (PMSQ) was successfully fabricated through a simple sol-gel reaction of methyltriethoxysilane.(1) SEM and AFM confirmed that the resulting coating was visibly transparent and smooth ($R_{\mathrm{rms}} < 0.3$ nm). This PMSQ surface showed statically hydrophobic (θ_S= *ca.* 85°) and oleophilic (θ_S= *ca.* 35°) properties, but unusually, had excellent dynamic dewettability. Small volumes of probe liquids such as water and *n*-hexadecane can be easily set in motion to move across the surface when the substrate tilt angle is ~10° at room temperature. Thanks to a thermally stable Si-CH_3 bond, this excellent water/oil repellency remained even after the thermal treatment up to 350°C for 24 h in air



, which exceeds decomposition temperature of conventional perfluorinated surfaces. Investigation of the repellent properties of PMSQ surfaces at high temperatures (~300°C) using thermally stable probe liquids, such as silicone oil and polyphenylether, revealed that static contact angles (CA's) exhibited a positive temperature coefficient, i.e a comparable increase in static CAs of these probe liquids at elevated temperatures. Based on this fundamental surface property, we have successfully manipulated probe liquids to migrate from higher temperature regions to lower regions through a thermally-induced gradient of surface tension



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COLL 139

Modification of gas hydrate interfacial energy and wettability with corrosion inhibitors

***Zachary M Aman**, zachary.aman@uwa.edu.au, Michael L Johns, Eric F May.Centre for Energy, The University of Western Australia, Crawley, WA 6009, Australia*

Gas hydrates represent a critical risk in subsea flow assurance, as particle aggregation and deposition may lead to complete flowline blockage. Anti-agglomerants are strong surfactants that may be injected to stabilize a non-aggregating particle slurry, but continuous dosage may be cost-prohibitive. Corrosion inhibitors are structurally similar to anti-agglomerants, but their effect on hydrate particle aggregation has not been established. This study deploys high-pressure differential scanning calorimetry to measure the effect of model corrosion inhibitors on the stability of a hydrate dispersion in crude oil. The results indicate that corrosion inhibitors adsorb to hydrate-oil interfaces, and may effectively stabilize a hydrate-in-oil dispersion. The threshold adsorption concentration is quantitatively similar to previously-established behavior of carboxylic and sulfonic acid surfactants. These results are compared to established techniques, including interfacial tensiometry, and represent the first deployment of high-pressure calorimetry to detect surfactant adsorption at the hydrate-oil interface.

COLL 140

Lubrication and wet adhesion in the presence of draining channels

*Charles Dhong, Rohini gupta, **Joelle Frechette**, jfrechette@jhu.edu.Department of Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, MD 21218, United States*

We will discuss our efforts to understand the mechanisms behind the adhesion of tree frog under wet conditions. Central to the adhesion and locomotion of tree frogs is their structured toe pads, which consist of hexagonal arrays of epithelial cells separated by a network of interconnected channels. It has been proposed that the channels facilitate the drainage of excess fluid trapped between the toe pads and the contacting surface, and thus reduce the hydrodynamic repulsion during approach. We present direct force measurements of the normal and peeling hydrodynamic interactions during the drainage of fluid from the gap between a structured and a smooth surface. We find that the structured surfaces lead to faster time to contact due to the reduction of drainage forces and can display stronger adhesion. We compare to our results with that of Reynolds theory modified for structured surfaces.

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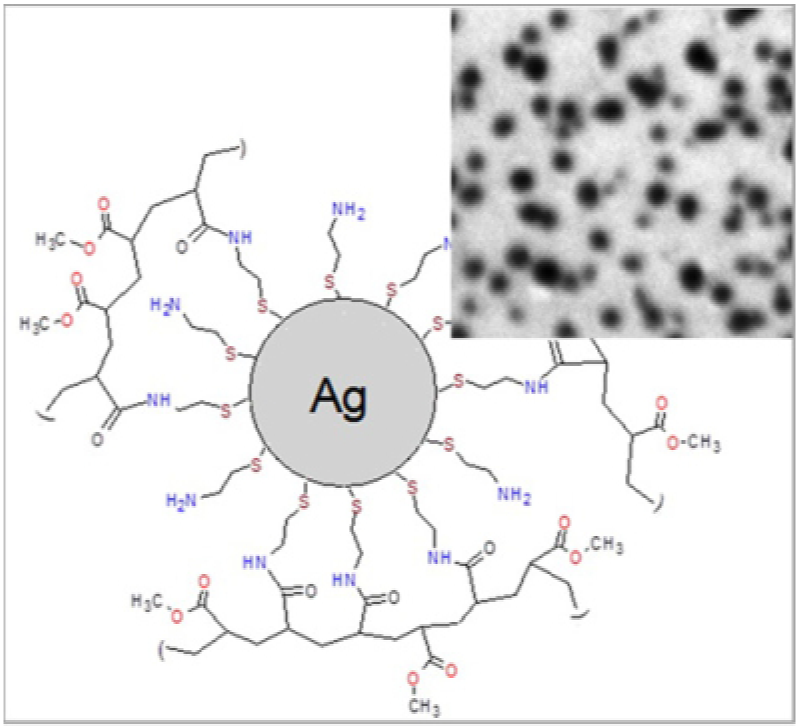
COLL 141

Silver-polymer nanocomposite material

*Jordan Ellison, Greg Wykoff, Anita Paul, Ray Mohseni, **Aleksey Vasiliev**, vasiliev@etsu.edu.Department of Chemistry, East Tennessee State University, Johnson City, TN 37614, United States*

Silver-polymer composite material containing highly dispersed silver nanoparticles was obtained from bare nanosilver. This nanocomposite was prepared in three steps. On the first step, a self-assembled monolayer with terminal amino groups was formed on the surface of nanoparticles by treatment with 2-aminoethanethiol. Then polyacrylic acid (MW=1,800) was bonded to the amino groups of the surface silver 2-aminoethanethiolate with the use of diisopropylcarbodiimide. Intermediate product formed large agglomerates in polyacrylic acid due to the presence of unreacted carboxyl groups. Finally these groups were esterified by methanol. On this step, silver nanoparticles formed a stable colloidal dispersion in the polymer matrix. The average particle size of nanosilver calculated from XRD and TEM data was 27 nm. The structure of the product was confirmed by FT-IR and NMR spectroscopy.

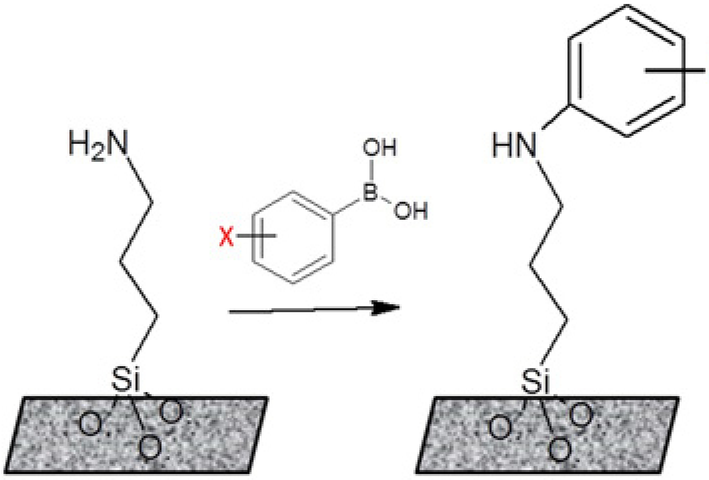


COLL 142

Functionalization of surface by catalytic N-arylation

*Kenneth Seaton, George Kubi, **Aleksey Vasiliev**, vasiliev@etsu.edu.Department of Chemistry, East Tennessee State University, Johnson City, TN 37614, United States*

Surface of mesoporous silica gel was functionalized by the reaction of catalytic N-arylation. 3-Aminopropyl-functionalized silica gel was used as a starting material. The reaction was carried out in the presence of copper acetate as a catalyst. Optimal conditions of the synthesis were determined for the reaction of terminal amino groups with phenylboronic acid. Then Br, Cl, CH_3, OCH_3, SCH_3, $CH=CH_2$, and CHO groups were introduced to the surface with the use of para- and meta-substituted phenylboronic acids.



In addition to aromatic compounds, heterocyclic and vinylboronic acids were also used in this reaction. The presence of the functional groups was confirmed by elemental analysis and characteristic reactions. Obtained functionalized materials were studied by BET adsorption of nitrogen, DSC and TGA methods.

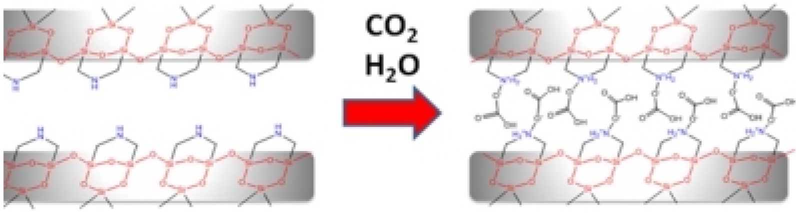
COLL 143

Mesoporous silsesquioxane for post-combustion capture of CO_2

*Odette Esam, **Aleksey Vasiliev**, vasiliev@etsu.edu.Department of Chemistry, East Tennessee State University, Johnson City, TN 37614, United States*

The objective of this work was the synthesis of stable mesoporous adsorbent for reversible adsorption of CO_2 from industrial emissions. A functionalized silsesquioxane material with high contents of surface amino groups was prepared from a bridged precursor, bis[3-(trimethoxysilyl)-propyl]amine, by sol-gel method in acidic media in the presence of a surfactant. In contrast to non-bridged organic trialkoxysilanes, no cross-linker (e.g., tetraethoxysilane) was necessary to provide mesoporous structure of the material. Thus the adsorbent had increased concentration of surface basic sites for CO_2

adsorption. Adsorption was carried out at the room temperature in CO_2 flow. The adsorption capacity of the material was particularly high in the presence of water vapor in the gas. Then physically adsorbed CO_2 was removed by nitrogene purging. On the desorption step, the temperature was increased up to 120 °C where surface complexes of CO_2 with amino groups decomposed.



Chemically adsorbed CO_2 was removed from basic sites of the adsorbent and captured by a saturated solution of $Ba(OH)_2$. Adsorption capacity of silsesquioxane was determined from the mass of formed $BaCO_3$. Structure and composition of the adsorbent was studied by elemental analysis, solid state NMR and FT-IR spectroscopy, DLS and BET adsorption of N_2.

COLL 144

Experimental study of absorbance and fluorescence spectra of colloidal dispersion of Au nanoparticles in solid solutions of organic dyes in polysiloxane

Nikolay Barashkov[1]*, nikolay.microtracers@gmail.com,* ***Irina Irgibayeva***[2]*, irgsm@mail.ru, Anuar Aldongarov*[2]*, Artur Mantel*[2]*, Alexander A. Ishchenko*[3]*.Â (1) R&D, Micro-Tracers, Inc, San Francisco, CA 94124, United StatesÂ (2) Eurasian National University, Astana, Astana Region, KazakhstanÂ (3) Institute of Organic Chemistry NAS Ukraine, Kiev, Ukraine*

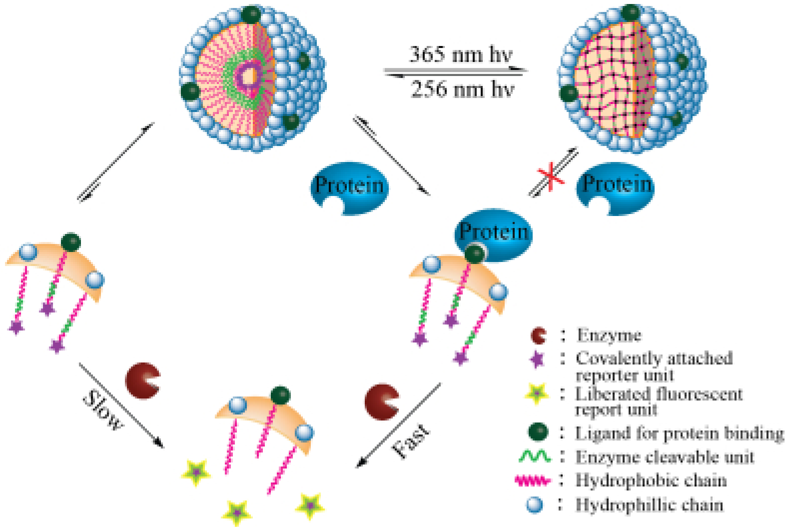
Colloidal dispersions of Au nanoparticles in polysiloxane (PSi) were prepared by mixing chloroauric acid dissolved in acetone with the vinyl-terminated Psi precursor, following by addition of Si-H containing precursor and in-oven curing at 60^oC for 24 hrs. During the curing procedure, reduction of Au(III) to the zero-valent Au takes place. Absorbance and fluorescence spectra of prepared Au/PSi nanocomposites are investigated and compared with the spectra of colloidal dispersion of Au nanoparticles in PSi containing different concentrations of four polymethine dyes, introduced in vinyl-terminated Psi precursor before curing. In several cases it was found that the presence of Au nanoparticles is able to enhance the emission efficiency of dye molecules, probably due to resonance energy transfer process. The influence of the nature of dyes, as well as their concentration and concentration of nanoparticles on the fluorescence properties of investigated nanocomposites are discussed.

COLL 145

Dual protein stimuli triggered dendritic nanocarrier disassembly

Jing Guo, *jingg@chem.umass.edu, Jiaming Zhuang, Feng Wang, Krishna R. Raghupathi, S. Thayumanavan.Chemistry, University of Massachusetts Amherst, Amherst, MA 01003, United States*

An amphiphilic dendrimer-based nanocarrier was designed and synthesized to study the collaboration of two protein stimuli triggered disassembly. On each amphiphilic unit of dendron was attached a hydrophilic pentaethylene glycol (PEG) moiety and a hydrophobic coumarin ester moiety, which allows for the formation of micelle-type assemblies in aqueous milieu with an equilibrium between assembly and its dendron state through hydrophilic-lipophilic balance (HLB). High stability of dendritic assembly makes the equilibrium favor the assembly state, which makes the hydrophobic interior difficult to be accessed by outside trigger. To overcome this, a protein-specific ligand is attached on the terminus of one PEG moiety. This design results in a dendron-protein complex, thus breaking the HLB and shifting the equilibrium to favor the monomer state, and leading to an increased accessibility of hydrophobic ester moiety by outside triggers. An enzyme can liberate a fluorescent form of coumarin that can be detected and quantified. Dye release results have shown that dual triggers boost the initial rate dramatically. We present herein a method of designing a dual stimuli responsive system which will respond with significant dye release only when both stimuli are present. Advantages such as assembly stability and response to primary biological changes, coupled with efficient targeting and faster and complete guest release make this system a promising candidate for applications such as sensing and drug delivery.



COLL 146

“Cyborg” cells as vehicles for nanoparticle delivery inside of *Caenorhabditis elegans*

***Renata Minullina**, mirenata1612@gmail.com, Gölnur Däwlätşina, Rawil Fakhrullin.Department of microbiology, Kazan (Idel buye/Volga region) Federal University, Kazan, Repubic of Tatarstan 420008, Russian Federation*

Caenorhabditis elegans is a free-living microscopic round worm, its biology, ecology and behaviour has been thoroughly studied during the recent decades. Therefore the nematode has attracted the huge attention of scientists studying the toxicity of nanoparticles (NPs).

The typical procedure of nanomaterial toxicity assessment consists of the exposition of microworms onto the solid agar-based Nematode Growth Media covered by bacterial lawn, containing certain amount of nanoparticles, or introduction of the microworms into liquid media supplemented by nanoparticles followed by the subsequent incubation for the certain periods of time. However, nanoparticles hardly can be evenly distributed in solid nematode media which leads to the undesired aggregation of nanoparticles. Therefore, a new approach which would secure the direct and straightforward delivery of nanoparticles into *C. elegans* worms is required.

In this study, we showed for the first time the application of nanoparticle-coated “cyborg cells”as delivery vehicles for controllable administration of a range of NPs into *C. elegans*. Our approach is based on direct deposition of polycation-coated magnetite NPs onto microorgnisms (*E. coli, Chlorella pyrenoidosa Saccharomyces cerevisiae*) or via the layer-by-layer assembly of polyelectrolyte multilayers doped with anionic Ag NPs.Next, the nanomodified cells are used as the food source for nematodes, which uptake the cell walls attached nanoparticles while feeding. This results in the uniform and controllable delivery of nanoparticles into *C. elegans* nematodes. The delivery of NPs into the transparent microworms can be directly monitored using optical and fluorescence microscopies.

“Cyborg” cells-mediated NPs delivery can be applied for monitoring of nanotoxicity of engineered materials, as shown here using toxic silver nanoparticles. In addition, the delivery of magnetic nanoparticles allows for the magnetic manipulation and spatial separation of NPs-labelled nematodes.

This study was supported by RFBR 12-03-93939-G8 and RFBR 12-04-32054 grants.

COLL 147

Synthesis and application of modified silver nanoparticles with high yield as anticorrosion self-assembled nanoparticles films on the surface of carbon steel alloys

***hamad a. Al-Lohedan**, hlohedan@ksu.edu.sa.department of chemistry, king saud university, riyadh, Saudi Arabia*

A new developed method is described to prepare monodisperse silver nanoparticles to enhance yield by adding a trace amount of Fe^{3+} ions into the reaction of $AgNO_3$ with oleic acid and oleylamine to produce monodsiperse nanoparticles. The core-shell silver nanoparticle coated with copolymers of styrene acrylamide nanogels with controllable particle size produced via emulsion polymerization at room temperature. The crosslinking polymerization was carried out in the presence of N,N`-methylenebisacrylamide (MBA) as a crosslinker, N,N,N`,N`-tetramethylethylenediamine (TEMED) and potassium peroxydisulfate (KPS) as redox initiator system. The structure and morphology of the silver nanogels were characterized by Fourier transform infrared spectroscopy (FTIR), transmission and scanning electron microscopy (TEM and SEM). The effectiveness of the synthesized compounds as corrosion inhibitors for carbon steel in 1 M HCl was investigated by various electrochemical techniques such as potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Monolayers of silver nanoparticles and oleic oleyl amine were self-assembled on the fresh active surface of the carbon steel electrode. The self-assembled monolayers of Ag nanoparticles have more effective corrosion inhibition for carbon steel as indicated by the high charge-transfer resistance shown in cyclic voltammetry (CV) and EIS. The results showed the nanogel particles act as mixed inhibitors. Adsorption of nanogel particles was found to fit the Langmuir isotherm and was chemisorption.

Email: hlohedan@ksu.edu.sa

Division of colloid and surface chemistry, fundamental research in colloids, surfaces and nanomaterial (poster).

COLL 148

Study of bismuth nanoparticle stability using NMR

Kathryn L. Corp[1,2]*, kcorp@linfield.edu, Marlène Branca*[1]*, Karine Philippot*[1]*, Diana Ciuculescu-Pradines*[1]*, Catherine Amiens*[1]*.Â (1) UniversitÃ¨ Paul Sabatier - Laboratoire de Chimie de Coordination, Toulouse, FranceÂ (2) Department of Chemistry, University of Florida, Gainsville, Florida 32611, United States*

Bismuth nanoparticles specifically have become interesting for their electric properties and use for thin films. Bulk bismuth has very unique electrical properties. For instance it has a very low carrier density and is a highly anisotropic Fermi surface. In addition, bismuth nanoparticles have shown potential for having even larger thermoelectric effects than bulk bismuth. This study focuses on the synthesis, characterization and stabilization of bismuth nanoparticles made from $Bi(N(SiMe_3)_2)_3$. The reproducible synthesis makes nanoparticles ranging from 1-4 nm where most of the stabilization is done by Li or Na -HMDS, along with a byproduct of the reaction. We note the strength of the diamagnetism of bismuth by observing a shift of ligands present in the nanoparticles solution. Any additional shift is due to a particular ligand helping stabilize the nanoparticles. By this method we can tell which ligand stabilizes the bismuth nanoparticles.

COLL 149

Stimuli-responsive elastomeric opal films

***Daniel Scheid**, m.gallei@mc.tu-darmstadt.de, Christian G. Schäfer, Markus Gallei.Department of Chemistry, Technische UniversitÃ¤t Darmstadt, Darmstadt, Hessen 64287, Germany*

Convenient semicontinuous emulsion polymerization protocols were applied to yield monodisperse core-interlayer-shell (CIS) particles featuring a soft shell and a hard core. Obtained particles were processed be using the melt shear technique to gain highly ordered, reversibly stretch-tunable elastomeric opal films after subsequent thermal or UV cross-linking reactions.[1,2] The resulting films revealed distinct angle-dependent reflection colors due to Bragg's law. External triggers such as strain, solvents, change of pH, but also the presence of redox reagents or by applying electric current can be used to change the reflection colours in a wide range making these films excellent candidates for a plethora of sensing applications. Furthermore, CIS particles featuring non-cross-linked hard cores embedded in a cross-linked matrix undergo a shape transition from soft spheres to oblates by applying pressure.[3] Deformation of the spherical cores led to hexagonally arranged spheroid oblates. Optical characterization shows that bead deformation provokes a tremendous photonic band gap shift of about 160 nm. Fully reversible shape transition from the form-anisotropic shape back to the original spheres is accompanied with a full recovery of the original photonic band gap making these films suitable for enhanced impact sensing applications. The multi-stimuli-responsiveness of herein investigated opal films turns them unambiguously to functional materials with a wide range of applications in fields of optical sensing, rewriteable photonics and actuation systems. Recently, functional CIS spheres based on inorganic magnetic core shell nanoparticles were used in such opal films, which unambiguously extend the range of potential applications of the opal films towards nanophotonics, nanoelectronics, plasmonics and metamaterials.

[1] Schäfer, C. G.; Gallei, M.; Rehahn, M. et al. *Chem. Mater.* 2013, *25*, 2309.

[2] Schäfer, C. G.; Gallei, M. *et al. Langmuir* 2013, *29*, 11275.

[3] Schäfer, C. G.,Gallei, M.; Rehahn, M. ACS *Appl. Mater. Inter.* **2013,** under revision.

COLL 150

Modeling of the solvent processing dynamics of aerogel/gold nanoparticle composites using modified Maxwell-Garnett theory

***Kelsey Mengle**, km9506@ship.edu, **John Richardson**, jnrich@ship.edu, Jeb Kegerreis.Department of Chemistry, Shippensburg University, Shippensburg, Pennsylvania 17257, United States*

The optical properties of gold nanoparticles are studied widely since they differ from those of the bulk metal. Gold nanoparticles were encapsulated in silica aerogels and analyzed with visible spectroscopy. Maxwell-Garnett (MG) theory was modified and used to model the behavior of aggregating gold nanoparticles to better understand the dynamics of the gelling process in different solvents. Our modification to MG theory was to include several weighted filling factors (*f*) instead of only one *f* in the MG equations to better fit the experimental data. When 1-octanethiol was added to protect the gold nanoparticles in the aerogel matrix, there was decreased aggregation. An unexpected blue shift in the surface plasmon resonance from 558 nm to 529 nm occurred between the solvent exchange to cyclohexane from acetone. This shift did not occur in the spectra of aerogel/nanoparticle composites without thiol protection. The results of our models and experiments, which will be presented, suggest that the physical and structural changes that take place during the solvent exchanges of silica gel/gold nanoparticle composites can be modeled with our modified version of MG theory.

COLL 151

Gold nanocage assembly for selective second harmonic generation imaging

sudarson Sekhar sinha, *sudarson.sinha@gmail.com, Avijit Pramanik, Paresh Ray.Chemistry & Biochemistry, Jackson State University, Jackson, MS 39217, United States*

Optical microscopy has been an important tool in biology for about a century. Here we report the development of two-photon SHG imaging of live cancer cells selectively by enhancement of the nonlinear optical response of gold nanocages assemblies. Experimental results show that values of the first-order microscopic hyperpolarizability β can be increased by up to three orders of magnitude by just developing nanoparticles self assembly. Theoretical modeling indicates that the field enhancement values for the nanocage assembly can explain, in part, the enhanced b values. Our experimental data also shows that the A9 RNA aptamer conjugated gold nanocage assembly can be used for targeted SHG imaging of the LNCaP prostate cancer cell. Experimental results with the HaCaT normal skin cell line show that bio-conjugated nanocage-based assemblies demonstrate SHG imaging that is highly selective and will be able to distinguish targeted cancer cell lines from other non-targeted cell lines. After optimization, this reported SHG imaging assay could have enormous application for biology.

COLL 152

Indentation and imprinting by core-shell particles to create nanostructures over the polymer surface

Keiji Fujimoto, *fujimoto@applc.keio.ac.jp, Yuuka Fukui, Hideaki Watanabe, Midori Nishimura.Department of Applied Chemistry, Keio University, Yokohama, Kanagawa 223-8522, Japan*

We developed a facile nano-fabrication method to generate nanostructures by the nano-indenting and the nano-imprinting of core-shell particles on a polymer surface. The particle array was achieved by spreading and compressing the particles over the water surface and transferring the particle monolayer onto the substrate with the LB technique. Then, heat-treatment of the particle-arrayed substrate was carried out by the UV irradiation or the incubation in a temperature-controlled incubator. This heat-treatment caused denting of particles into the substrate without any pressing. Then, this nanostructured substrate was immersed into ethanol and treated by ultrasonication to remove the particles from the substrate. Nanoholes were produced and their size and depth were tunable by controlling particle arrangement and heat-treatment. Next, we investigated the relation between the annealing temperature and the depth of the particle denting to elucidate a mechanism of the particle nano-indenting. The height of bumps, which is the distance from the polymer surface to the top of the particle, was measured with AFM at different temperatures**.** With increasing the incubation time at a constant temperature, the average height gradually decreased and leveled off. The initial change of the height, which reflects the rate of indenting, became steeper with increasing the temperature. It is thought that the plastic flow of the polymer substrate was induced by annealing above its *T*g and thereby the arrayed particles could undergo denting into the substrate through surface deformation. This also suggests that the gravitational force, which is proportional to the particle mass, and intermolecular forces, which reflects the affinity between the substrate surface and the particle surface, are important to determine the shear stress. We hope that the nanostructures generated by this nano-fabrication method would be applied for advanced materials and devices such as antireflection film, micro flow channels, biochips and novel tissue cultured substrates.

COLL 153

Polyethyleneimine based ionic liquid colloids

Nurettin Sahiner[1,2]*, sahiner71@gmail.com, Sahin Demirci*[1]*,* ***Nahit Aktas***[3]*, cinar49@gmail.com.Â (1) Department of Chemistry, Canakkale Onsekiz Mart University, Canakkale, Canakkale 17100, TurkeyÂ (2) Nanoscience and Technology Research and Application Center (NANORAC), Canakkale Onsekiz Mart University, Canakkale, Canakkale 17100, TurkeyÂ (3) Chemical Engineering Department, Yuzuncu Yil University, Van, Van 65080, Turkey*

Poliethyleneimine (PEI) particles weresynthesized by using micro emulsion polimerization/crosslinking method [1]. The synthesized PEI has wide size distribution and can be modified with different modifying agents such as CH_3I and alkyl halide with different chain length. The modified PEI particles were shown to be applicable in biomedical field as antibacterial materials, and drug delivery devices. Additionally, modified PEI particles were anion changed with sodium dicyanamide, sodium tetrafluoroborate and ammonium hexafluorophosphate to form ionic liquid colloids. Particle based on PEI were also used as template for in situ metal nanoparticle preparations such as Co, Ni, and Cu, and used as catalysis medium for the reduction of

4-nitrophenol (4-NP) to 4-amino phenol (4-AP), and for hydrogen generation from the hydrolysis of $NaBH_4$.

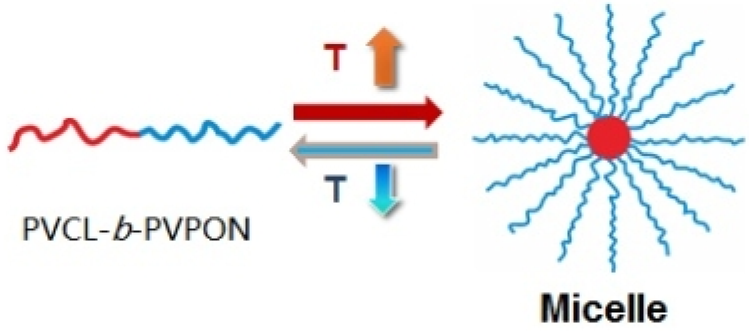
[1]. Nurettin Sahiner “Preparation of poly(ethylene imine) particles for versatile applications” Colloids and Surfaces A: Physicochem. Eng. Aspects 433 (2013) 212–218.

COLL 154

Synthesis and self-assembly of thermosensitive poly (N-vinylcaprolactam)-b-poly (N-vinyl-2-pyrrolidone) diblock copolymers

Xing Liang*, xliang@uab.edu, Veronika Kozlovskaya, Christopher Parker Cox, Yun Wang, Eugenia Kharlampieva.Department of Chemistry, University of Alabama at Birmingham, Birmingham, Alabama 35294, United States*

Amphiphilic block copolymers capable of self-assembly into various nanoscale structures are attractive candidates for applications in sensing, controlled delivery and as nanoreactors. We report on synthesis of temperature-responsive copolymers of water-soluble poly(vinylcaprolactam) (PVCL) and poly(vinylpyrrolidone) (PVPON) blocks and their assembly into temperature-sensitive nanostructures in aqueous solutions. The PVCL-*block*-PVON copolymers were synthesized by RAFT polymerization. The copolymers became amphiphilic upon increase in solution temperature due to the reversible coil-to-globule transition of PVCL blocks. The LCST of the diblock copolymers ranged from 35 to 43°C depending on PVCL molecular weight and the ratio of PVCL to PVPON lengths. Remarkably, the PVCL-*block*-PVPON copolymers underwent temperature-induced self-assembly into nanostructures of 70 nm to 200 nm in size with hydrophobic PVCL blocks shielded by hydrophilic PVPON. The effects of the block lengths ratio, PVCL molecular weight, and the copolymer concentration on the temperature-triggered formation and disassembly of the nanostructures were examined by NMR, light scattering, and TEM.



COLL 155

Temperature-responsive behavior of poly(N-vinylcaprolactam) hydrogels in the presence of Hofmeister anions

Oleksandra Zavgorodnya*, ozavgoro@uab.edu, Veronika Kozlovskaya, Xing Liang, Eugenia Kharlampieva.Department of Chemistry, University of Alabama at Birmingham, Birmingham, AL 35294, United States*

The temperature responsive behavior of hydrogels in the presence of Hofmeister ions has attracted considerable attention due to their potential applications in drug delivery and biosensing. We report on the effect of Hofmeister series anions on the phase-transition and shrinkage/swelling behavior of multilayer-based hydrogels composed of poly(N-vinylcaprolactam) (PVCL). The PVCL hydrogels were derived from hydrogen-bonded poly(vinylcaprolactam)-co-(aminopropyl)methacrylamide)/poly(methacrylic acid) (PVCL/PMAA) multilayer films cross-linked with glutaraldehyde. We found that the presence of SO_4^{2-}, $H_2PO_4^{-}$ and Cl^{-} decreased the phase transition temperature of PVCL hydrogel and suppressed its temperature-induced volume transitions due to decrease in LCST of the polymer. Br^{-} had no significant effect on the film properties at any investigated concentrations. In contrast, hydrogel swelling was increased in the presence of iodide at high concentration of ions; however, the shrinkage of the film was steadily decreasing with increasing of I^{-} concentration. We believe that our findings provide new prospects for understanding the effect of Hofmeister anions on confined thin non-ionic polymeric hydrogels.

COLL 156

Fabrication of close-packed hexagonal self-assembled PS-b-PMMA block copolymer nanodevice patterns

Dahye Lee[1]*, ldahye@uh.edu, Dmitri Litvinov*[1,2]*, T. Randall Lee*[3]*.Â (1) Materials Engineering, University of Houston, Houston, TX 77204, United StatesÂ (2) Center for Integrated Bio and Nano Systems, University of Houston, Houston, TX 77204, United StatesÂ (3) Departments of Chemistry and Chemical Engineering and the Texas Center for Superconductivity, University of Houston, Houston, TX 77204, United States*

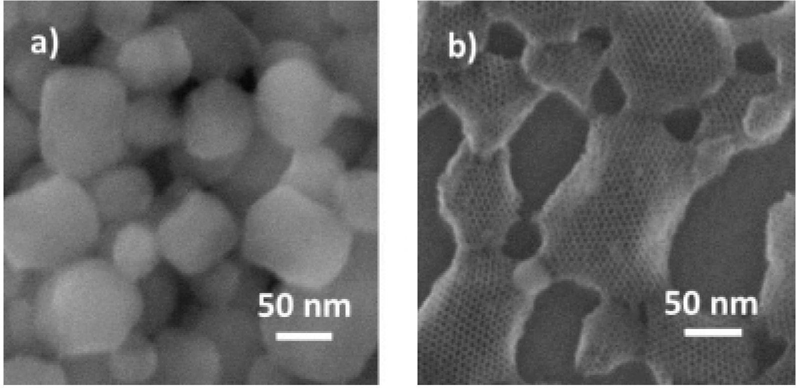
This presentation describes the fabrication and manipulation of polymeric materials to produce nanoscale devices. Polystyrene-block-polymethyl methacrylate (PS-b-PMMA) block copolymer thin films were spin-coated on a silicon wafer substrate. Upon annealing, the polymer blocks self-assemble on the surface in a hexagonal array, where the PMMA is within the PS matrix. A helium ion beam was used to degrade the PMMA polymer, enhancing the pattern on the surface. The PS templates were also strengthened by the helium ion beam by inducing crosslinking within the film. After removal of the degraded PMMA, we modified the templates to convert the cylindrical pores to hexagonal-shaped openings using an Ar^{+} milling process. The resulting thin films were analyzed by atomic force microscopy (AFM), scanning electron microscopy (SEM), and optical ellipsometry.

COLL 157

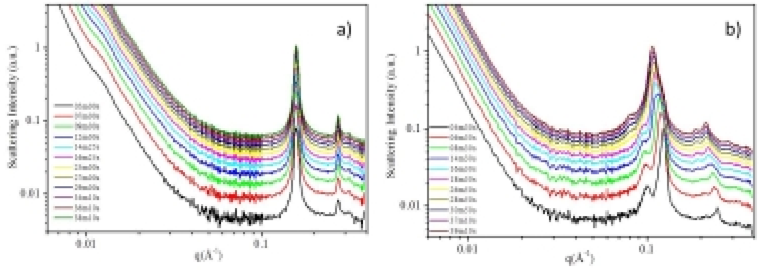
Time-resolved pore expansion upon growth of mesoporous silica nanoparticles via in situ small-angle X-ray scattering

*Cheng-Han Lin[1], Zi-Yin Chen[1], Yi-Qi Ye[3], Yi-Chia Luo[1], Kun-Che Kao[1], **Yi-Hsin Liu**[1], frfkimo@gmail.com, Chung-Yuan Mou[1,2].Â (1) Department of Chemistry, National Taiwan University, Taipei, No. 1, Sec. 4, Roosevelt Road 106, Taiwan Republic of ChinaÂ (2) Center for Condensed Matters and Sciences, National Taiwan University, Taipei, No. 1, Sec. 4, Roosevelt Road 106, Taiwan Republic of ChinaÂ (3) BL23A, National Synchrotron Radiation Research Center, 010 Hsin-Ann Rd,, Hsinchu 300, Taiwan Republic of China*

Pore-expanded mesoporous silica nanoparticles (MSNs) have demonstrated promising applications for imaging, catalysis, sensing, and drug and enzyme delivery due to distinct biocompatible and biodegradable advantages. However, previous formation mechanism for MSNs without a swelling agent may not explain a similar pathway for pore-expanded MSNs due to additional molecule interactions during cooperative self-assemblies. Our recent data reveal slower nucleation and growth rates for the pore-expanded MSNs in which manipulation of morphologies



and pore sizes via composition formulas is highly possible in a facile colloidal synthesis. We employ X-ray scattering technique



to understand such important formation variations upon pore expansion and

morphology tailoring that can apply additional benefits toward loading and catalytic efficiencies toward biomedical applications.

COLL 158

Adsorption of energy-relevant gases by nanoporous ZIF-8 films

Andrew M. Cerro, *acerro@sandiego.edu,* ***Amber M. Mosier***, *amosier@sandiego.edu, Aileen Park, Elizabeth R. Webster, Ryan S. Shine, Andres Gomez, Fangyuan Tian, Lauren Benz.Department of Chemistry and Biochemistry, University of San Diego, San Diego, CA 92110, United States*

The adsorption of energy-relevant gases including carbon dioxide, water, and methanol by thin nanoporous zeolitic framework (ZIF-8) films has been studied using a combination of X-ray photoelectron spectroscopy and temperature programmed reaction spectroscopy. Differences in gas uptake, binding location, and desorption activation energies are determined by examining the interaction of these gases with supported nanoparticle films. For example, we demonstrate how the hydrophobic nature of the films prevents water from adsorbing within the pore structure under low pressure/temperature conditions, while carbon dioxide is readily adsorbed. These results highlight the role that surface science techniques can play in uncovering properties of complex porous materials.

COLL 159

Interfacial tension of complex coacervated mussel adhesive protein according to the Hofmeister series

Seonghye Lim, Dustin Moon, Jeong Hyun Seo, ***Hyo Jeong Kim***, *khjkye@postech.ac.kr, In Seok Kang, HyungJoon Cha.Department of Chemical Engineering, Pohang University of Science and Technology, Pohang, Gyeongbuk 790-784, Republic of Korea*

Complex coacervation is a liquid-liquid phase separation in a colloidal system of two oppositely charged polyelectrolytes. The interfacial tension of the coacervate phase is the key parameter for micelle formation and interactions with the encapsulating material. However, the relationship between interfacial tensions and various salt solutions is poorly understood in complex coacervation. In the present work, the complex coacervate dynamics of recombinant mussel adhesive protein (MAP) with hyaluronic acid (HA) were determined in the presence of Hofmeister series salt ions. Using measurements of absorbance, hydrodynamic diameter, capillary force, and receding contact angle in the bulk phase, the interfacial tensions of complex coacervated MAP/HA were determined to be 0.236, 0.256, and 0.287 mN/m in NaHCOO, NaCl, and NaNO3 solutions, respectively. The sequences of interfacial tensions and contact angles of the complex coaceravates in the presence of three sodium salts with different anions were found to follow the Hofmeister ordering. The tendency of interfacial tension between the coacervate and dilute phases in the presence of different types of

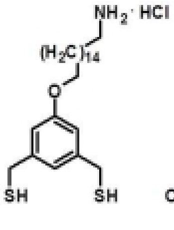
Hofmeister salt ions could provide a better understanding of Hofmeister effects on complex coacervated materials based on the protein-polysaccharide system. This information can also be utilized for microencapsulation and adsorption by controlling intramolecular interactions. In addition, the injection molding dynamics of mussel byssus formation was potentially explained based on the measured interfacial tension of coacervated MAP.

COLL 160

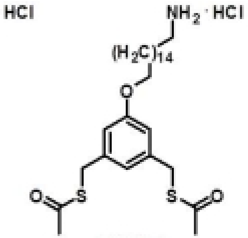
Robust amine-terminated self-assembled monolayers on evaporated gold

***Han Ju Lee**, hlee32@uh.edu, T. Randall Lee.Departments of Chemistry and Chemical Engineering and the Texas Center for Superconductivity, University of Houston, Houston, Texas 77204-5003, United States*

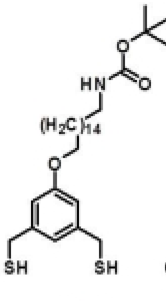
Four distinct bidentate adsorbates having either ammonium or Boc-protected amino termini, and either dimethanethiol or diethanethioate headgroups, were designed and synthesized to form thermally stable amine-terminated self-assembled monolayer (SAM) films on evaporated gold surfaces. These specialty adsorbates utilized a phenyl-based headgroup with hexadecyloxy chains positioning the amino functionality away from the surface of gold; specifically, the adsorbates were (i) 5-(16-aminohexadecyloxy)-1,3-phenylene)dimethanethiol hydrochloride (AHPDT), (ii) *S,S′*-(5-(16-aminohexadecyloxy)-1,3-phenylene)bis(methylene) diethanethioate hydrochloride (AHPDTA), (iii) *tert*-butyl 16-(3,5-bis(mercaptomethyl)phenoxy)hexadecylcarbamate (Boc-AHPDT), and (iv) *S,S′*-(5-(16-(*tert*-butoxycarbonylamino)hexadecyloxy)-1,3-phenylene)bis(methylene) diethanethioate) (Boc-AHPDTA). The structural features of the SAMs were characterized by ellipsometry, X-ray photoelectron spectroscopy (XPS), and polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS). Solution-phase thermal desorption tests were performed to evaluate the thermal stability of the films.



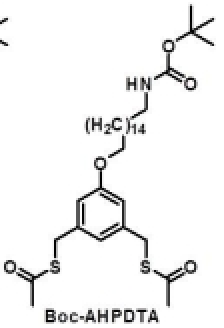
AHPDT



AHPDTA



Boc-AHPDT



Boc-AHPDTA

COLL 161

Alkyl-capped partially fluorinated alkanethiols: Unique adsorbates for generating self-assembled monolayers on gold

*Oussama Zenasni, **Maria D Marquez**, mdmarquez2@uh.edu, T Randall Lee.Departments of Chemistry and Chemical Engineering and the Texas Center for Superconductivity, University of Houston, Houston, TX 77204-5003, United States*

Abstract: The interfacial properties of monolayer films formed from ω-alkylated partially perfluorinated alkanethiols adsorbed on gold are described. These films were investigated to shed light on the overall influence of the dipole residing at hydrocarbon-fluorocarbon (HC–FC) junction. Wettability studies using contact angle goniometry revealed the interfacial energies for these fluorinated self-assembled monolayers (FSAMs), while polarization modulation infrared reflection-absorption spectroscopy (PM-IRRAS) studies suggested the packing densities of the adsorbed chains and the alignment of the terminal alkyl moiety within these films. The films were also characterized using optical ellipsometry and X-ray photoelectron spectroscopy (XPS).

Keywords: FluorinatedSelf-Assembled Monolayers (FSAMs), Alkyl-terminated Fluoroalkanethiols, Gold, Wettability, Odd-Even Effects**.**

COLL 162

Effect of shape and crystallinity on magnetic properties of Fe_3O_4 nanocubes and nanospheres

Arati G. Kolhatkar[1]*, akolhatkar@uh.edu, Chamath Dannongoda*[5]*, Ivan Nekrashevich*[2]*, Irene Rusakova*[3]*, Karen Martirosyan*[5]*, Dmitri Litvinov*[1,2,4]*, Richard C. Willson*[4]*, T. Randall Lee*[1]*.Â (1) Department of Chemistry and Texas Center for Superconductivity, University of Houston, Houston, TX 77204, United StatesÂ (2) Department of Electrical and Computer Engineering, Univerity of Houston, Houston, TX 77204, United StatesÂ (3) Department of Physics and Texas Center for Superconductivity, University of Houston, Houston, TX 77204, United StatesÂ (4) Department of Chemical and Biomolecular Engineering, University of Houston, Houston, TX 77204, United StatesÂ (5) Department of Physics and Astronomy, University of Texas at Brownsville, Brownsville, TX 78520, United States*

We synthesized monocrystalline Fe_3O_4 nanocubes and polycrystalline nanospheres with tunable body diagonals and diameters via solvothermal and thermal decomposition reactions. The dimensions of the spherical MNPs were tuned to obtain samples such that (i) for one set of spherical MNPs, the volume was equivalent to that of a targeted cubic MNP volume, and (ii) for a second set of spherical MNPs, the diameter was equivalent to the body diagonal of a
targeted batch of cubic MNPs. We used the vibrating sample magnetometer (VSM) to compare the magnetic properties of the synthesized spherical and cubic Fe_3O_4 MNPs on a volume
and diameter/body diagonal basis. As compared to the polycrystalline nanospheres, higher saturation magnetization for monocrystalline nanocubes make them more attractive for biosensing applications. Our nanocubes also have a significantly higher coercivity as compared to their nanospherical counterparts of same volume or same

diameter, which makes them more suitable for hyperthermia applications. We demonstrate that both shape and crystallinity are important parameters that we can use to manipulate nanoscale magnetism in Fe_3O_4 MNPs in order to tailor them for a particular application.

COLL 163

Functionalized gold nanoshells with thermally-labile linkers for controlled drug release

***Chien-Hung Li**, chienhung25@hotmail.com, T Randall Lee.Departments of Chemistry and Chemical Engineering and the Texas Center for Superconductivity, University of Houston, Houston, Tx 77004, United States*

Gold nanoshells in various forms continue to garner attention due to their potential use in biomedicine for photothermal therapies. This presentation describes the incorporation of a thermally-labile Diels-Alder linker in custom-designed monodentate and bidentate thiol-based adsorbates, which were used to functionalize the surfaces of gold nanoshells. The thiol moieties readily formed sulfur-gold bonds on the surface of the nanoshells, allowing the attached model drug to reside at the outer interface of the resulting self-assembled monolayer films. Since the retro-Diels-Alder reaction occurs at a temperature slightly above physiologic temperature, drug release was initiated by exposure to near-infrared (NIR) laser radiation, which caused local heating on the surface of the gold nanoshells via excitation of the surface plasmon resonance. The functionalized gold nanoshells were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), and UV-vis spectroscopy.

COLL 164

Gene silencing with functionalized gold nanoshells using click chemistry

***Amin Shakiba**[1], ashakiba@uh.edu, Preethi Gunaratne[2], T.Randall Lee[1].Â (1) Departments of Chemistry and Chemical Engineering and the Texas Center for Superconductivity, University of Houston, Houston, Texas 77204-5003, United StatesÂ (2) Department of Biology and Biochemistry, University of Houston, Houston, Texas 77204-5001, United States*

Functionalized gold nanoshells (AuNSs) are frequently cited as potential carriers for the targeted delivery of drugs to cancer cells. Prior research by our team has produced several multidentate adsorbate structures that provide a means of both stabilizing and modifying these AuNSs. In the present study, click chemistry was used in conjunction with a short-chain dithiol surfactant to attach functional groups and/or model drugs on these surfaces. Upon binding to gold, azide groups on the end of the surfactant are covalently bound to a succinimide-terminated linker via an azide**-** alkyne [3+2] cycloaddition reaction. Cysteine-based peptides are then attached to the succinimide-terminated surfactant, followed by loading with small interfering RNA (siRNA); consequently, the oligonucleotides temporarily bind to these surfaces by electrostatic interaction and can subsequently be released upon exposure to thermal energy generated upon exposure of the gold nanoshells to near-infrared (NIR) light.

Keywords: Gold Nanoshells, Bidentate Adsorbates, Click Chemistry, Small Interfering RNA (siRNA)

COLL 165

Synthesis of unique adsorbates for the preparation of self-assembled monolayers having an inverted surface dipole

***Oussama Zenasni**, zenasni_sam@hotmail.com, Maria D. Marquez, T. Randall Lee.Departments of Chemistry and Chemical Engineering and the Texas Center for Superconductivity, University of Houston, Houston, TX 77204, United States*

This presentation describes the synthesis of unique partially fluorinated alkanethiol adsorbates and the characterization of their associated thin films on gold. These fluorinated self-assembled monolayers (FSAMs) utilize a new class of fluorinated amphiphile that offers an inverted HC–FC dipole at the film interface. This study compares the properties of these films to an analogous series of CF_3-terminated SAMs of comparable film thickness formed from terminally fluorinated thiols of the form $CF_3(CH_2)_nSH$ (F1HnSH, where n = 16–19), and to CH_3-terminated SAMs formed from $H(CH_2)_mSH$, where m = 17–20 (HmSH). The properties of these films were characterized using optical ellipsometry, contact angle goniometry, polarization modulation infrared reflection-absorption spectroscopy (PM-IRRAS), and X-ray photoelectron spectroscopy (XPS).

Keywords: FluorinatedSelf-Assembled Monolayers (FSAMs), Fluoroalkanethiols, Gold, Wettability, Surface Dipole**.**

COLL 166

Photothermal destruction of *Enterococcus faecalis* using gold nanoshells

***Orawan Khantamat**, okhantamat@uh.edu, Chengzhi Cai, T Randall Lee.Departments of Chemistry and Chemical Engineering and the Texas Center for Superconductivity, University of Houston, Houston, Texas 77204-5003, United States*

Enterococcus faecalis causes nosocomial infections, including catheter-associated UTI, central line-associated bloodstream infection, and surgical site infections. It is one of the most antibiotic-resistant bacteria in existence. Innovative approaches are required to limit the exposure to and proliferation of this organism. One possible method involves the use of gold nanoshells, which are biologically inert at physiologic temperature and can be engineered for photothermal ablation of cells and tissues. In this study, gold

nanoshells were prepared and attached to model catheter surfaces, which were then subjected to *E. faecalis* growth. The properties of the gold nanoshells were characterized by scanning electron microscope (SEM), dynamic light scattering (DLS), and X-ray photoelectron spectroscopy (XPS). The bacterial survival studies were conducted on modified surfaces under near-infrared (NIR) irradiation using a colony-formation assay. These studies demonstrate that gold nanoshell-modified surfaces, when illuminated with NIR light, can effectively kill *E. faecalis*. These findings should prove useful in future applications involving medical devices.

Keywords: Gold Nanoshells, Photothermal Effect, *Enterococcus faecalis*.

COLL 167

Thermally-responsive PNIPAM-coated pocket nanoparticles

***Chulsoon Park**[1], ppccss0426@gmail.com, David Shakarisaz[2], Paul Ruchhoeft[2], T Randall Lee[1].Â (1) Department of chemistry, University of Houston, Houston, TX-Texas 77204, United StatesÂ (2) Department of Electrical and Computer Engineering, University of Houston, Houston, TX-Texas 77204, United States*

This presentation describes the synthesis of our surface polymerization initiator, the production process for creating pocket nanoparticles, and the successful coating of the resulting gold pocket nanoparticles (AuPNPs) with N-isopropylacrylamide (NIPAM). We synthesized the framework of the initiator using 4.4'-azobis(4-cyanovaleric acid) and 1,6-hexanedithiol, attaching poly(ethylene glycol)methyl ether to this assembly using DCC/DMAP. The AuPNPs were assembled through a layering procedure that involved spin coating of a sacrificial polymer layer on a silicon wafer, the vapor deposition of metal layers (e.g., gold and copper), and helium ion beam lithography through a mask to establish the nanoparticle shape. The polymerization initiator was immobilized on the resulting AuPNPs by the formation of thiolate bonds to the gold particles, and the hydrogel polymer (PNIPAM) was generated by the radical polymerization of a mixture of NIPAM monomer, acrylic acid (AAc), and N,N'-methylenebisacrylamide (BIS). The size and morphology of the resulting PNIPAM-coated AuPNPs were characterized by scanning electron microscopy (SEM), while the elemental compositions were characterized by X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (EDX). The optical properties were evaluated by UV-Vis spectroscopy. These PNIPAM-coated AuPNPs are promising carriers for drug delivery.

Keywords: Thermally and pH Responsive Hydrogel, Gold Pocket Nanoparticles, Ion-beam Lithography, Drug Delivery.

COLL 168

Self-assembly and growth of new polyamine-polyphenol conjugates for biological applications

***Ipsita A Banerjee**, bispsita@hotmail.com, Kathryn Callahan.Chemistry, Fordham University, Bronx, New York 10458, United States*

In this work, we have prepared nanoassemblies comprised of the polyphenols such as gallic acid conjugated with a series of natural polyamines. The goal of this work was to develop a new family of nanoassemblies with potent antioxidant properties. It was observed that the assembly process was dependent upon not only the type of polyphenol utilized but also the length of the polyamine moiety. While short chained polyamine moieties mostly yielded a mix of fibers and vesicular structures, larger polyamine chains tended to form fibrillar structures. The growth was monitored over a period of two weeks by both dynamic light scattering as well as by turbidity measurements. We also examined the thermal properties of the assemblies by differential scanning calorimetry. Radical scavenging assays were conducted by standard DPPH as well as FRAP assays at varying concentrations of the nanoassemblies. Furthermore, we also examined the antimicrobial properties of the formed nanoassemblies by examining the inhibition of growth of the fungus rhizopus.

COLL 169

Simple macroscopic tailoring of 2D layered hexagonal materials using redox-liquid exfoliation

***Vikram K. Srivastava**[1], vsrivast@utk.edu, Ronald A. Quinlan[2], Alexander L. Agapov[1], Kimberly M. Nelson[1], Alexei P. Sokolov[1,3], Gajanan S. Bhat[4], Jimmy W. Mays[1,3].Â (1) Department of Chemistry, University of Tennessee, Knoxville, TN 37996, United StatesÂ (2) Materials and Power Systems Branch, Naval Surface Warfare Center Carderock Division, West Bethesda, MD 20817, United StatesÂ (3) Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United StatesÂ (4) Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN 37996, United States*

The isolation of monolayer graphene from graphite has spurred development of exfoliation techniques for producing large quantities of pristine material. The liquid exfoliation of two-dimensional layered (2-D) powders using ultrasonication has emerged as a viable technique and can be further exploited to induce chemical reactions by simply adding reagents. To determine macroscopic effects using a systematic approach, we employed a simple redox exfoliation process of 2-D hexagonal layered graphite, molybdenum disulfide, and boron nitride powders. Our method demonstrates the exfoliation process can allow for production of macroscopically tunable 2-D layered materials in nearly quantitative yields. Thorough characterization of the exfoliated products displayed the addition of antioxidants greatly changed chemical, structural, and solution properties. The presence of certain antioxidants with specific precursor powders generated organic residues and various absorption characteristics, and as a result, the properties of the materials were affected at the macroscopic level. The exploration of reagents added during sonochemical exfoliation could allow for tailoring of materials with unique macroscopic properties viable in numerous applications

including reinforced polymer composites, electrical devices, lithium–ion capacitors, and chemical sensing.

COLL 170

Surface modified aggregation of perylene tetracarboxylic diimide derivatives

*Ngoc H Vu, Anthony S Ormandy, **Dana M Alloway**, dalloway@concord.edu.Department of Physical Science, Concord University, Athens, WV 24712, United States*

Functionalized perylene tetracarboxylic diimide molecules (PTCDI) are a common class of organic semiconductor molecules of interest as n-type semiconductors. The packing structure of the molecules depends on the imide functionalization and can affect the conductivity and absorbance spectra of thin films of these molecules. Fluorescence and Atomic Force Microscopy results will be presented on the effect of PTCDI alkane tail length and deposition on unmodified silica surfaces, alkane-modified surfaces, and surfaces with covalently linked PTCDI molecules as potential nucleation sites.

COLL 171

Architectural effects on surface mechanical properties of polystyrene: Surface softening and stiffening at different temperatures

***Taskin B Karim**[1], tbkarim@olemiss.edu, Gregory B McKenna[2].Â (1) Chemical Engineering, University of Mississippi, Oxford, Mississippi 38677, United StatesÂ (2) Chemical Engineering, Texas tech University, Lubbock, Texas (TX) 79415, United States*

In the present work, we have used the particle embedment technique [1] with submicron and nanometer size particles to study the effect of architecture on surface mechanical properties of polystyrene (PS). To accomplish this, we have explored the surface mechanical responses of a linear polystyrene (PS), a 3-arm star PS, and an 8-arm star PS emphasizing the range of temperature from T_g – 10 °C to T_g + 10 °C. The embedment of the particles was determined using atomic force microscopy (AFM) measurements and the embedment data was used in the Lee and Radok (LR) [2] model to estimate the surface shear compliances. The work of adhesion between submicron/nano particles and the polymer surface was considered as the driving force for particle embedment. We observed both surface softening and stiffening for the linear PS and 3-arm star PS for the studied temperature range. However, surface softening was observed at all temperatures in this study for the 8-arm star PS.

COLL 172

Dihydrorhodamine-123 as a sensitive indicator of oxidation caused by aqueous nano-C_{60} suspensions

Rangika S Hikkaduwa Koralege[1]*, rangika@okstate.edu, Befrika Murdianti*[2]*, Martha E Hilburn*[1]*, Randall D Maples*[3]*, Kevin D Ausman*[1]*.Â (1) Chemistry, Oklahoma State University, Stillwater, OK 74074, United StatesÂ (2) Department of Chemistry, University of the Ozarks, Clarksville, AR 72830, United StatesÂ (3) Department of Science & Mathematics, Eastern Oklahoma State College, Wilburton, OK 74578, United States*

Due to wide spread applications and commercializations of fullerene (C_{60}) systems, both human and environmental systems become increasingly exposed to these materials. As a result there is concern of the biological and environmental effects of these systems. Even though fullerene has negligible solubility in water, the ability to form stable aqueous C_{60} colloids (known as nano-C_{60} or nC_{60}) and the availability of these in natural systems at environmentally-relevant concentrations led to the studies of its toxicity. Previous studies have indicated that fullerene in colloidal form can induce oxidative stress in living systems. This research is focusing on the oxidation caused by fullerene colloidal suspensions. Stable aqueous fullerene colloidal suspensions are demonstrated to rely on the [6,6]-closed epoxide derivative of the fullerene ($C_{60}O$) for stability and this derivative is present in small quantities in nearly all nC_{60} preparations due to a reaction with air. Presence of $C_{60}O$ in these colloidal suspensions considered to have increased ability of oxidation. For this work nC_{60} samples prepared by enrichment of $C_{60}O$ in the colloidal particles and regular nC_{60} preparations have been used as a comparative study to monitor oxidation. Fluorescent assays for monitoring oxidative behavior of these suspensions with the probe molecule dihydrorhodamine-123 (DHR123) as the indicator of oxidation have been investigated.

COLL 173

Aggregation behaviors of Gemini cationic surfactants in alkylammonium nitrate protic ionic liquids

*Qintang Li, Xudong Wang, **Xiao Chen**, xchen@sdu.edu.cn.Key Laboratory of Colloid and Interface Chemistry, Shandong University, Jinan, Shandong 250100, China*

The aggregation behaviors of a series of symmetric and dissymmetric cationic Gemini surfactants, $[C_mH_{2m+1}(CH_3)_2N\text{-}(CH_2)_2\text{-}N(CH_3)_2C_nH_{2n+1}]Br_2$, designated as m-2-n (m = n with m = 10, 12, 14; or m ≠ n with a fixed m + n = 24, m = 16, 14, 12) have been investigated in three protic ionic liquids, ethyl-, propyl- and butyl-ammonium nitrates (EAN, PAN and BAN). Surface tension, polarized optical microscopy (POM), small-angle X-ray scattering (SAXS), and rheological measurements were adopted to investigate the micellization and lyotropic liquid crystal (LLC) formation. Compared to LLCs formed in aqueous environment, the normal hexagonal (H_I) and lamellar (Lα) phases are found to disappear with a new reverse hexagonal (H_{II}) phase instead in EAN. The structure dissymmetry plays an important role in aggregation process of m-2-n. With increasing degree of dissymmetry, the critical micellization concentration, the maximum reduction of solvent surface tension, and the minimum area occupied per surfactant molecule at the air/EAN interface all become smaller. The thermostability of

formed LLCs is therefore improved because of the more compact molecules. These characteristics can be explained by the enhancement of solvophobic effect due to the increased structure dissymmetry of Gemini surfactants. In PAN and BAN, however, their better hydrocarbon solubility due to longer chain length and penetration capability into the space between surfactants will induce the formation of aggregates with lower critical packing parameter, H_I and the biscontinuous cubic phase (V_I) in 12-2-12/PAN, H_I, V_I and Lα in 12-2-12/BAN systems.

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COLL 174

Self-assembled structures of amphiphilic asymmetric molecular brushes

***Hanying Luo**, hluo7@jhu.edu, Jose L Santos, Margarita Herrera-Alonso.Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland 21218, United States*

We report on a variety of self-assembled structures obtained by a combination of the amphiphilic character of a series of PLA/PEG-grafted molecular brushes and the assembly method. Amphiphilic asymmetric macromolecular brushes with both hydrophobic and hydrophilic side chains attached to each repeat unit of the backbone were synthesized by combining “graft from” and “graft on” strategies. Poly(D,L-lactide) (PLA) and poly(ethylene glycol) (PEG) were grafted onto a derivatized poly(glycidyl methacrylate) backbone by ring-opening polymerization and “click” chemistry. Brush hydrophilic ratio, expressed in terms of the weight fraction of PEG (*wPEG*), was varied by adjusting the length of the PLA block. Self- assembly of brush amphiphiles was accomplished by: (1) rapid mixing against a non-solvent for the PLA block and, (2) following the dialysis method. The morphological transitions of amphiphilic molecular brushes were shown to parallel those of linear diblock amphiphiles. More importantly, we report on the first known example of toroid formation from the self-assembly of molecular brush amphiphiles and the molecular and process parameters involved in their formation. Lastly, we demonstrate how the assemblies formed under rapid assembly conditions were distinct from equilibrium structures.

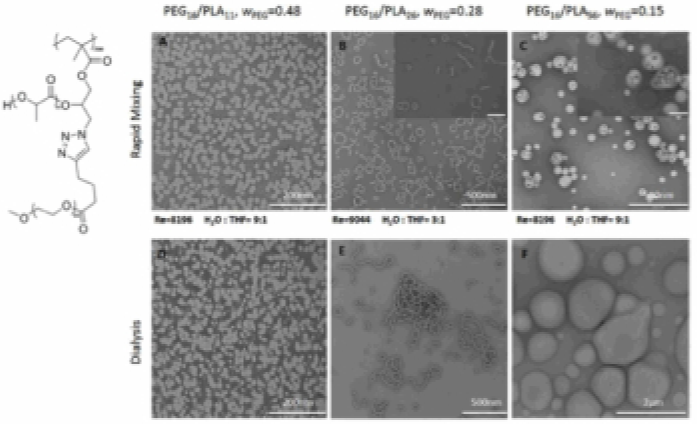


Figure 1. Structure (left) and transmission electron micrographs of aggregate morphologies (right) of amphiphilic branched brush copolymers, prepared by a rapid mixing process (top row) and by dialysis (bottom row). Differences in aggregate structure reflect the molecular characteristics of the block copolymers, with decreasing hydrophilic content from left to right, as well as the effect of processing conditions

COLL 175

Dynamic observation of cell adhesion behaviors on binary self-assembled monolayers modified gold surfaces with tunable surface potential

Wei-Lun Kao, *leokao101@gmail.com, Jing-Jong Shyue.RCAS, Academia Sinca, Taipei, Taiwan Republic of China*

Cell adhesion is crucial to cell behaviors including survival, growth and differentiation. In recent years, cell behaviors on the artificial bio-surfaces have gained great attention in medical and bio-material studies. In these studies, optical microscope (OM) based observations are the most common methods to study the cell behaviors. However, optical information has its limitation on evaluating cell-surface interactions. Thus, to get further knowledge on cell adhesion process, quartz crystal microbalance with dissipation monitor (QCM-D) can be applied to examine the real-time viscoelastic changes of cell-surface interactions. Self-assembled monolayers (SAM) are known for its convenience and versatile to modify surface. To achieve subtle control of surface properties, two functional groups are introduced to gold surface, namely 6-amino-1-hexanethiol and 6-mercaptohexanoic acid, and a series of zeta potential can be obtained with different ratios of functional groups on the gold surfaces. HEK-293T cells were then cultured on the binary-SAM modified gold-coating quartz crystal in the QCM-D window chamber at 37 degree-C. Simultaneously, OM with differential interference contrast prism was used to obtain time-lapse images for observing the change in cell morphology. In addition, after 4-hour in situ examination of cell attachment, cells were fixed by glutaraldehyde and then dehydrated with a critical point dryer. The specimens were observed by a scanning electric microscope (SEM) in low vacuum mode without conductive over-coat to investigate finer features. The QCM-D results show that with stronger positive potential, less mass and looser structure were observed. Moreover,

more cells were attached on the positive potential surface than negative ones and insignificant difference was observed between surfaces of negative potential. Furthermore, flattener and dendritic cell morphology are observed with stronger positive surface potential.

COLL 176

Effect of surface potential on cell adhesion and proliferation

***Yu-Ting Kuo**, r01527011@ntu.edu.tw.Research center of applied science, Academia Sinica, Taipei, Taiwan 11529, Taiwan Republic of China*

Surface properties are known to be one of the key factors in cell adhesion and proliferation because eukaryotic cells have to adhere through the extra-cellular matrix to function properly. Using a homogeneously mixed amine and thiol functional group on self-assembled monolayers (SAMs) anchored on glass, surfaces with a series of zeta potential from about +30 to -150 mV at pH 7.4 are obtained. Furthermore, it is found that amine and thiol SAMs on glass poses low cytotoxicity. Thus, this binary-SAM modified glass is ideal for studying the effect of surface potential on cell behaviors including adhesion and proliferation. The surface chemical composition of binary SAM is quantified using x-ray photoelectron spectroscopy (XPS) and the actual zeta potential of surfaces in physiological condition is measured with an electro-kinetic analyzer. NIH3T3 cells are chosen to culture on these binary-SAM modified glass and incubated for several different time period. The coverage and shape of cells adhered to surfaces of various potential are examined by fluorescence optical microscopy and scanning electron microscopy. It is expected that the positive surface potential promotes cell adhesion and proliferation until contact inhibition occurred.

COLL 177

Platinum drug loaded holmium iron garnet nanoparticles enhance combination chemotherapy and radiation therapy

***Imalka Munaweera**[1], msm110020@utdallas.edu, Shi Yi[2], Anthony J Di Pasqua[2], Kenneth J Balkus Jr.[1].Â (1) Department of Chemistry and the Alan G. MacDiarmid Nanotech Institute, University of Texas at Dallas, Richardson, Texas 75080, United StatesÂ (2) University of North Texas System College of Pharmacy, University of North Texas Health Science Center, Fort Worth, Texas 76107, United States*

There is strong interest in radioactive ^{166}holmium nanoparticles in radiation therapy for the treatment of cancer. The preparation of lipid coated/uncoated platinum drug loaded ^{165}holmium iron garnet magnetic nanoparticles will be described. These nanoparticles were explored as a carrier material for the stable isotope ^{165}Ho and, after neutron capture, its subsequent therapeutic radionuclide, ^{166}Ho (half-life, 26.8 h), for use in radionuclide therapy of cancer. The initial materials were characterized using PXRD, SEM, EDX, TEM, ICP-MS, Zeta potential measurements and neutron activation.

Stability, dilution studies and cells studies of neutron activated lipid coated/uncoated platinum drug loaded nanoparticles confirm the biocompatibility of the prepared materials.

COLL 178

Synthetic routes to highly active nickel phosphide hydrotreating catalysts

Andrea I. d'Aquino, *mark.bussell@wwu.edu, Boris Ilic, Richard H. Bowker, Mark E. Bussell.Department of Chemistry, Western Washington University, Bellingham, WA 98225, United States*

This project focuses on the development of nickel phosphide catalysts for the hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) of crude oil feedstocks. Molybdenum disulfide (MoS_2) based catalysts are currently used in the petroleum industry for removing heteroatom impurities, but more efficient catalysts are needed in order to meet increasingly strict environmental standards. In this research, new methods for synthesizing nickel phosphide (Ni_2P/SiO_2) catalysts have been investigated. The catalysts were synthesized via incipient wetness impregnation followed by temperature programmed reduction (TPR) in flowing hydrogen. Several synthetic routes were explored by varying the nickel salt, the phosphorus source, the pH of the impregnation solution, the precursor pretreatment (e.g. calcination) and the reduction conditions. The resulting nickel phosphide catalysts were characterized using X-ray diffraction to determine phase purities and average crystallite sizes. CO and O_2 chemisorption were used to estimate the number of active sites, and the BET method was used to determine catalyst surface areas. The observed trends in Ni_2P crystallite size and chemisorption capacities will be discussed and related to the Ni_2P/SiO_2 synthesis method.

COLL 179

Extreme thixotropic behavior in pH-responsive gels of metal oxide nanoparticles

Javen S Weston, *javen@ou.edu, Jeffrey H Harwell, Daniel E Resasco, Chandler Osbourne.Chemical, Biological, and Materials Engineering, University of Oklahoma, Norman, Oklahoma 73019, United States*

A gelation phenomena has been observed in systems of two different fumed metal oxide nanoparticles that will form an extremely viscous thixotropic gel when mixed together in aqueous solutions. The thixotropic gels are formed only within certain pH ranges and at certain particle ratios. These gels form at relatively low concentrations of solids; between 1.5-2.5 vol%. It is currently theorized that these gels only form when the pH is between the two particle types' isoelectric points (also known as the point of zero charge or PZC), so that one type of particle has an overall positive charge and the other type of particles has an overall negative charge. The gels are broken when either particle crosses its PZC and switches its overall surface charge, creating a nanoparticle dispersion that behaves much like a dispersion of only a single type of nanoparticle at that total concentration and a viscosity very close to that of water. These gels form at relatively low volume percent solids, as low as 1.75 vol%, and have extremely short time constants for relaxation back from the liquid state to the gel state.

The gels are stable against settling and do not flow under gravitational forces, behaving as a pseudo-solid under low stress conditions. Above a certain stress-level, however, the nanoparticle network is broken and the fluid's viscosity drops dramatically from its pseudo-solid state to a viscosity near that of water, i.e. between 1-10 cP. The gels' visco-elastic behavior can also responds to relatively small changes in solution pH, allowing for external control of the fluid's rheological properties via acid or base titration. The region of gelation can also be controlled by varying the type of metal oxide nanoparticles, nanoparticle size, size ratio, and solids concentration.

COLL 180

Sacrificial agents for preventing ionic and nonionic surfactant adsorption on metal oxides

***Javen S Weston**, javen@ou.edu, Jeffrey H Harwell, Mahfuz Kabir.Chemical, Biological, and Materials Engineering, University of Oklahoma, Norman, Oklahoma 73019, United States*

Surfactant adsorption on metal oxides is extremely important for a variety of practical applications from detergency to surfactant-aided environmental remediationto industrial materials processing. In this study, the adsorption of ionic and nontionic surfactants was measured on high-surface area silica and alumina nanoparticles. After characterizing the adsorption behavior for the surfactant-only systems and creating adsorption isotherms, solutions were made with varying concentrations of surfactant and varying mass ratios of different sacrificial polymers. Polystyrene sulfonate (PSS) and Polydiallyl dimethyl ammonium chloride (DADMAC) were tested as potential sacrificial agents on alumina and silica, respectively. Each surfactant/polymer system

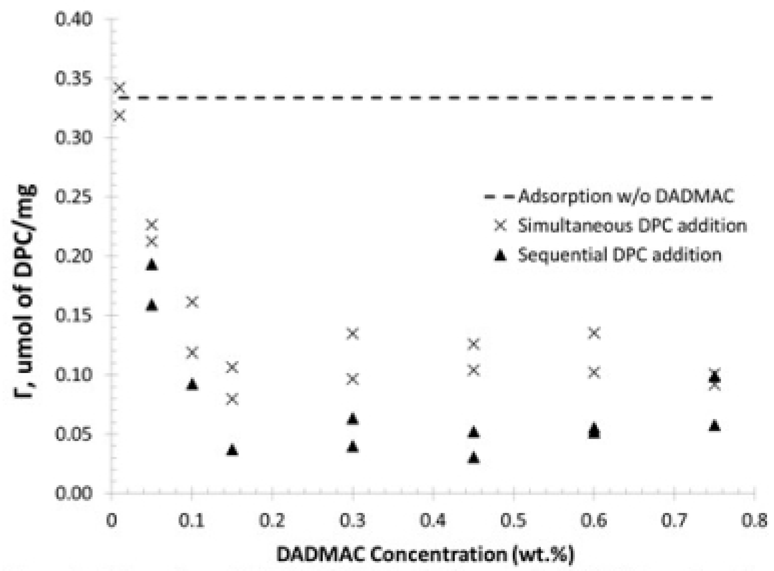


Figure 1. Adsorption of 50,000uM DPC solutions on Aerosil 200 as a function of PDADMAC concentration for sequential and simultaneous addition of DPC

was allowed to reach an equilibrium adsorption on the same high surface area metal oxide that was used in creating the adsorption isotherm. The equilibrium concentrations of the surfactants were measured and surfactant adsorption as a function of polymer concentration were determined. This data was then analyzed in order to determine what, if any, effect the proposed sacrificial agent had on the equilibrium adsorption. Results indicate that both of these polymers can have a large effect on total surfactant adsorption.

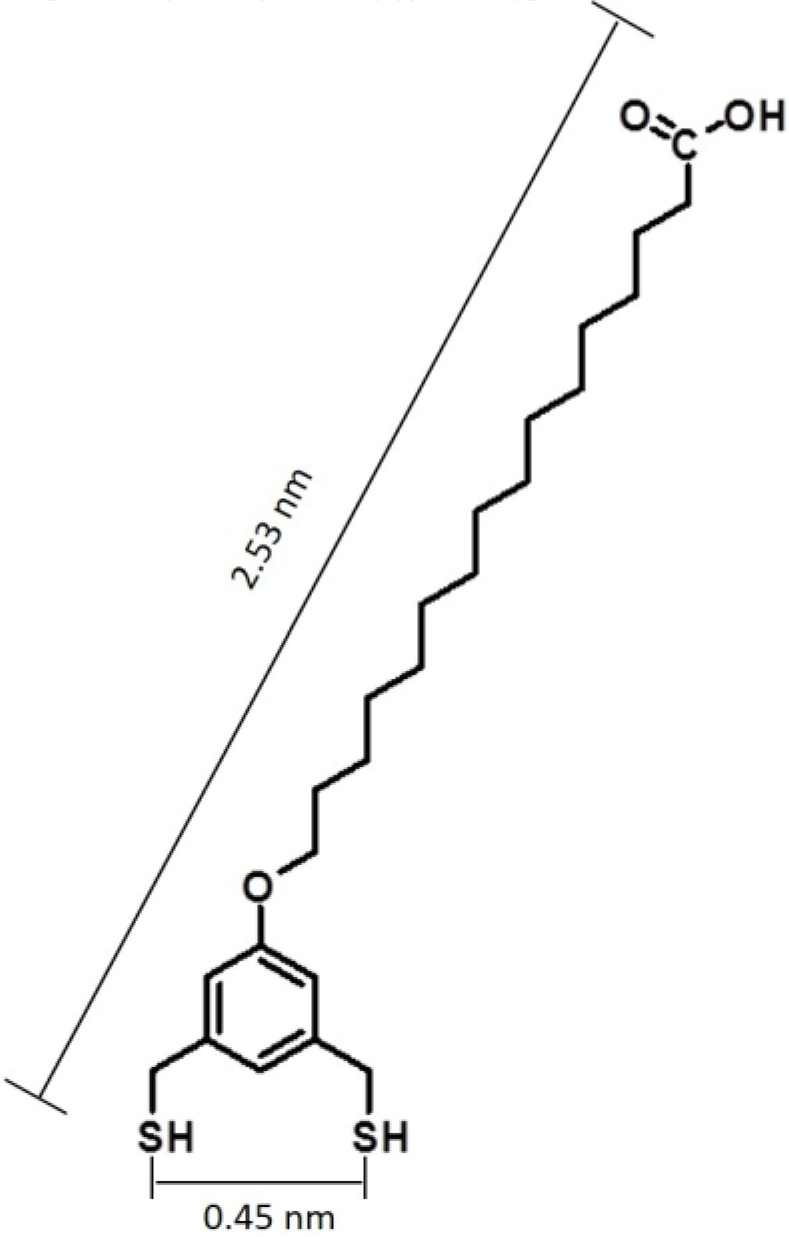
COLL 181

Self-assembly of 16-[3, 5-bis(mercaptomethyl)phenoxy]hexadecanoic acid on Au(111) studied with atomic force microscopy

Xianglin Zhai[1]*, xzhai1@lsu.edu, Han Ju Lee*[2]*, T Randall Lee*[2]*, Jayne C Garno*[1]*.Â (1) Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, United StatesÂ (2) Department of Chemistry, University of Houston, Houston, TX 77204, United States*

Although detailed investigations of monothiolated self-assembled monolayers (SAMs) have been reported, there are few studies for films of bidentate or tridentate thiol adsorbates. In comparison to monothiol SAMs, bulkier multidentate adsorbates should exhibit differences for the kinetics, stability and surface organization. Results for atomic force microscopy (AFM) studies of a bidentate adsorbate will be disclosed. Scanning probe-based nanolithography was applied to investigate the surface self-assembly of

16-[3, 5-bis(mercaptomethyl)phenoxy]hexadecanoic acid



in liquid media. The objectives are to obtain molecular-level information of designed multidentate thiols compared to reference molecules of *n*-alkanethiols. Approaches with scanning probe lithography enable side-by-side views of the surface structures, comparing the film thickness and surface properties. Experiments with AFM were accomplished in a liquid sample cell, by introducing fresh reagents to the system for *in-situ* studies. Surface structures comprised of multidentate adsorbates were inscribed within a matrix SAM by applying force to the AFM probe to graft nanopatterns. Returning to a low force for imaging, the step-wise surface changes before and after nanofabrication were captured with time-lapse AFM imaging. Nanoshaving and nanografting protocols were used to investigate the orientation of adsorbed molecules. Since the dimensions of *n*-alkanethiols are well-known, the thickness of the multidentate film was evaluated by referencing the heights of *n*-alkanethiols as an *in situ* molecular ruler. Multidentate adsorbates attach to surface through multiple linkers which should provide enhanced stability compared to monothiolated SAMs.

COLL 182

Unique bonding properties of the Au36(SR)24 nanocluster with FCC-like core

*Daniel M Chevrier[1], Amares Chatt[1], **Peng Zhang**[1], peng.zhang@dal.ca, Chenjie Zeng[2], Rongchao Jin[2].Â (1) Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H4R2, CanadaÂ (2) Department of Chemistry, Carnegie Mellon University, Pittsburg, Pennsylvania 15213, United States*

The recent discovery on the total structure of $Au_{36}(SR)_{24}$, which was converted from biicosahedral $Au_{38}(SR)_{24}$, represents a surprising finding of a face-centered cubic (FCC)-like core structure in small gold−thiolate nanoclusters. Prior to this finding, the FCC feature was only expected for larger (nano)crystalline gold. Herein, we report results on the unique bonding properties of$Au_{36}(SR)_{24}$ that are associated with its FCC-like core structure. Temperature-dependent X-ray absorption spectroscopy (XAS) measurements at the Au L3-edge, in association with ab initio calculations, show that the local structure and electronic behavior of $Au_{36}(SR)_{24}$ are of more molecule-like nature, whereas its icosahedral counterparts such as $Au_{38}(SR)_{24}$ and $Au_{25}(SR)_{18}$ are more metal-like. Moreover, site-specific S K-edge XAS studies indicate that the bridging motif for $Au_{36}(SR)_{24}$ has different bonding behavior from the staple motif from $Au_{38}(SR)_{24}$. Our findings highlight the important role of “pseudo”-Au_4 units within the FCC-like Au28 core in interpreting the bonding properties of $Au_{36}(SR)_{24}$ and suggest that FCC-like structure in gold thiolate nanoclusters should be treated differently from its bulk counterpart.

COLL 183

Local structure, electronic behavior, and surface reactivity of CO-reduced platinum-iron oxide nanoparticles

*Paul N Duchesne[1], Guangxu Chen[2], Nanfeng Zheng[2], **Peng Zhang**[1], peng.zhang@dal.ca.Â (1) Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H4R2, CanadaÂ (2) State Key Laboratory for Physical Chemistry of Solid Surfaces, and Department of Chemistry, Xiamen University, Xiamen, Fujian 361005, China*

A series of platinum-iron oxide nanoparticles (NPs) was synthesized using a “clean” CO-reduction method that employed different ratios of Pt:Fe precursor salts in oleylamine at elevated temperatures. High-resolution transmission electron microscopy (HRTEM) and energy-dispersive X-ray spectroscopy (EDS) studies revealed that nearly

monodisperse NPs with mean diameters of 3.5-4.4 nm and varied elemental compositions ($Pt_{54}Fe_{46}$, $Pt_{70}Fe_{30}$, and $Pt_{87}Fe_{13}$) were obtained. X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements at Pt L3- and Fe K-edge revealed that these NPs all consisted of a Pt core with amorphous iron oxide on the surface. Furthermore, it was observed that the local structure (e.g. Pt-Pt bond distance and coordination number) and electronic behavior of the NPs (e.g. Pt d-electron density and Fe valence state) are dependent on the Pt:Fe precursor ratios used in their synthesis. Quantum mechanical ab initio calculations were employed to interpret the results from X-ray spectroscopy and help elucidate the relationships between local structure and electronic properties in the NP samples. Finally, the surface reactivity of these NPs in the oxygen reduction reaction (ORR) was explored, demonstrating higher electrocatalytic activity for all the three platinum-iron oxide samples in comparison with a commercial Pt catalyst. The surface reactivity was also found to be sensitive to the Pt:Fe ratios of the NPs, and could be correlated with their local structure and electronic behavior.

COLL 184

Williamson ether-type reaction of hydroxyl-terminated GaP(111)B surfaces with alkyl and benzyl bromides characterized by X-ray photoelectron and infrared spectroscopy

Elizabeth S Brown, *esbrow@umich.edu, Sabrina L Peczonczyk, Stephen Maldonado.Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, United States*

Gallium phosphide (GaP) is an important optoelectronic material for light emitting diodes and solar powered generation of chemical fuels due to its good carrier mobilities and midsized bandgap (2.26 eV). The native oxide creates surface states that serve as trap sites which facilitate charge recombination. Functionalization of the surface with covalently bound organic molecules can slow oxide formation and reduce trap sites. Though functionalization strategies have been outlined previously on GaP(100) and GaP(111)A, no work has been done towards investigating functionalization routes of the phosphorus-rich GaP(111)B surface. Presented herein is a strategy of functionalization of a hydroxyl-terminated GaP(111)B with alkyl and benzyl bromides, following a Williamson ether-type reaction. The reaction was monitored by X-ray photoelectron and grazing-angle attenuated total reflectance spectroscopies. Non-nucleophilic bases promoted the reaction, providing surfaces with increased hydrophobicity and higher monolayer coverage. Quantum yield of modified electrodes was measured with sub-band gap wavelengths to semi-quantitatively evaluate the population of surface states. This versatile reaction strategy exhibits control over the electrochemical behavior of GaP electrodes by introducing well-ordered, covalently bound organic molecules to the surface that impart a reduction in deleterious surface states.

COLL 185

Interfacial electronic structure of CO absorbed on a platinum electrode in electrochemical environment probed by double resonance sum frequency generation spectroscopy

Shuo Yang[1,2], *yangshuo0723@163.com, Hidenori Noguchi*[1,2], *Kohei Uosaki*[1,2]*.Â (1) Graduate School of Chemical Science and Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, JapanÂ (2) Global Research Center for Environment and Energy based on Nanomaterials Science (GREEN), National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0044, Japan*

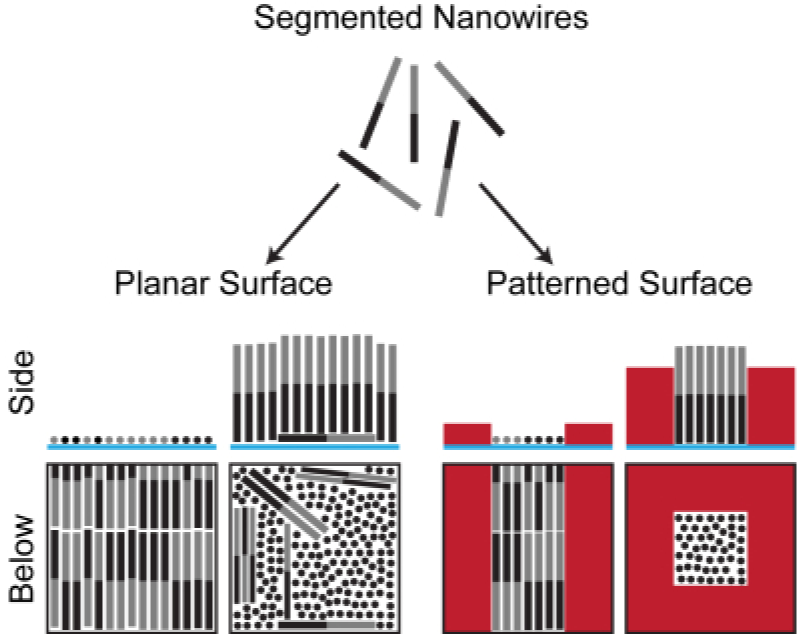
Absorbed CO on Pt surface has attracted much interest among scientists in surface science, catalysis, and electrochemistry. Information about oxidation mechanisms of CO on Pt, which depends on geometric and electronic structures of CO/Pt interface, is important to design and develop new catalysts for various reactions including H_2-O_2 and direct methanol fuel cells. Small amount of CO present in H_2 produced from fossil fuel readily adsorbs on Pt and inhibits H_2 oxidation. Adsorbed CO is also formed when Pt is in contact with methanol solution and inhibits the methanol oxidation reaction. Compared to extensive study on CO/Pt system under ultrahigh vacuum (UHV), interfacial electronic structure of CO/Pt interface in electrochemical environment is less understood due to the difficulty in determining it in solution. Accordingly, it is very important to investigate interfacial electronic structure of CO/Pt under electrochemical condition. Because of the presence of solution, it is not possible to use techniques with electron probes, which are most powerful in UHV. Double resonance sum frequency generation (DR-SFG) spectroscopy, which is a highly surface-sensitive nonlinear optical technique with the tunable frequencies of both incident fundamental lights, i.e., visible and IR, can provide information of surface molecular and electronic structures, which is not obtained by traditional surface vibrational technique. Here, we employed DR-SFG technique to probe potential-dependent electronic structure of CO/Pt interface in methanol solution. SFG signal due to C-O stretching was observed and was dependent on frequency of visible light as a result of the energetic coupling of electronic transition with the input visible photon and/or output SF photon, i.e., double resonance effect. Furthermore, resonant visible energy linearly depended on electrode potentials. Thus, the electronic resonance could be explained by the transition from Fermi energy, E_f, of Pt to the unoccupied $5\sigma_a$ anti-bonding state of CO.

COLL 186

Nanowire interactions and their effect on particle dense assemblies

David J Kirby[1], *djk291@psu.edu, Benjamin D Smith*[1], *Kristen A Fichthorn*[2,3], *Allison Wustrow*[1], *Christine D Keating*[1]*.Â (1) Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, United StatesÂ (2) Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802, United StatesÂ (3) Department of Physics, The Pennsylvania State University, University Park, PA 16802, United States*

Asymmetric nanomaterials (i.e. nanowires) have shown promise in energy collection, energy storage, and sensing platforms. Development of new assembly strategies will open up a wider range of materials and allow combination of multiple materials in a single architecture. Using nanoparticle interactions, such as van der Waals and electrostatics, researchers have created many fascinating new structures. Material and shape anisotropy complicate these interactions that are well understood for spherical nanoparticles. The work presented here addresses the assembly of particle dense arrays of single and multi-segment nanowires 4-8 µm in length and ~300 nm in diameter. Monte Carlo simulations are used in conjunction with experimental assemblies to explore the effect of van der Waals interactions on the alignment of material segments in striped nanowires. Multiple types of materials were examined in both horizontally and vertically oriented arrays. Planar and lithographically patterned assembly substrates were used to study the interparticle interactions in bulk particle assemblies and to isolate and orient small populations.



COLL 187

Stable supramolecular assemblies from facially amphiphilic oligomers

Krishna R Raghupathi, *kreddy.rp@gmail.com, William Rowley, Sankaran Thayumanavan.Department of Chemistry, University of Massachusetts Amherst, Amherst, Massachusetts 01003, United States*

Amphiphilic molecules which spontaneously self-assemble into stable supramolecular aggregates have garnered significant interest due to their applications in drug delivery, sensing and diagnostics. Amphiphiles with high molecular weights are usually preferred in most of these applications due to their low critical aggregation concentrations (CAC) and also due to the improved stability of the aggregates formed from these amphiphiles.

In this work we investigate a class of amphiphilic oligomers which form stable supramolecular assemblies at low concentrations, akin to high molecular weight polymeric systems. Since the molecular weights of the oligomers in study are significantly less than the polymeric systems, we hypothesized that the geometry of these oligomeric amphiphiles plays a crucial role in dictating the CAC, size and stability of the aggregates formed. Here we particularly study a system which utilizes intramolecular hydrogen bonding interactions to induce structure and rigidity into the amphiphile's backbone which therefore changes the geometry of the resultant amphiphile. We have observed that the assembly characteristics of this hydrogen bond stabilized amphiphiles vary drastically from their control amphiphiles (no hydrogen bond stabilization), indicating the important role of amphiphile's geometry in assembly formation. The structure of the amphiphiles is investigated using NMR spectroscopy, and the aggregates formed from these amphiphiles are characterized by light scattering and microscopic techniques.

COLL 188

Infrared and ultraviolet irradiation of gold and silver colloids

Rachel P. Marini*, rmarini@msudenver.edu, Michael B. Jacobs.Department of Chemistry, Metropolitan State University of Denver, Denver, CO 80217, United States*

Gold and silver colloid solutions were studied for their potential to absorb radiation. The gold and silver colloid solutions were synthesized via a citrate reduction. Absorbance maximums were collected using UV-Vis spectroscopy to estimate the properties of the colloid solutions. The red color of the gold colloid solution is indicative of a 10 – 20 nm particle size. This gives rise to an absorption signal at 525 nm. The grey-green colored silver colloid solution gives rise to an absorption signal at 418 nm. The colloid samples were irradiated directly using an Infrared bulb and UV (short and long-wave) lamp. Temperature vs. time was collected for both the gold and silver colloid samples. Both the gold and silver colloid samples increased linearly compared with the blank. The gold colloid solution gives rise to the steepest slope indicating a greater absorption of radiation compared to the silver colloid solution.

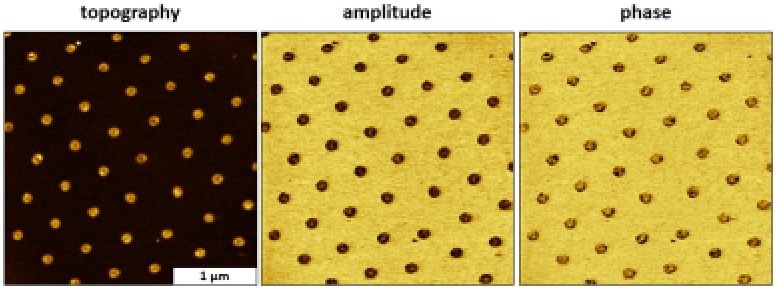
COLL 189

Sample stage designed for force modulation microscopy

Lu Lu[1]*, llu6@lsu.edu, Song Xu*[2]*, Chang-Uk Lee*[3]*, Donghui Zhang*[1]*, Garno Jayne*[1]*.Â (1) Chemistry, Louisiana State Univeristy, Baton Rouge, Louisiana 70803, United StatesÂ (2) Sonimoto Laboratory, Bloomfield, Michigan 48323, United StatesÂ (3) Center for Applied Energy Research, University of Kentucky, Lexington, Kentucky 40506, United States*

A prototype sample stage for force modulation microscopy (FMM) was designed and tested. Among the modes of atomic force microscopy (AFM), the FMM mode is

commonly used to acquire mechanical properties of samples along with topographical information. The FMM mode has been particularly useful for investigations with polymers and organic thin films. To configure a scanning probe microscope for FMM mode, the scanner is operated in contact-mode while the sample stage is driven to vibrate. Information of the topography, elastic response and surface adhesion can be acquired simultaneously. The sample stage design is adaptable for a tip-mounted scanner. A piezoactuator was embedded within the sample stage, to drive the sample vibration corresponding to the selected parameters of the alternating current. The FMM stage was constructed with machined polycarbonate using a coaxial cable connection to apply current to the actuator element. Several samples were tested using the designed sample stage, such as octadecyltrichlorosilane nanopatterns, periodic arrays of silane ring nanostructures prepared on silicon



, and a cyclic gel polymer of poly(N-methyl-glycine)$_{100}$-*b*-poly(N-decyl-glycine)$_{10}$containing fibrils. Successful characterizations were achieved for all three samples with exquisite nanoscale resolution. The FMM stage enables simple operation and was capable of obtaining high-resolution topography images at resonant frequencies. Future plans will be to modify the stage design to accommodate machined glass components, for accomplishing experiments in solvent media.

COLL 190

Area and capacitance characterization of nickel, cobalt, and nickel-cobalt electrodeposited thin films

Matthew J Gira[1,2]*, hampton@hope.edu, Jennifer R. Hampton*[1]*.Â (1) Department of Physics, Hope College, Holland, Michigan 49423, United StatesÂ (2) Department of Chemistry, Hope College, Holland, Michigan 49423, United States*

Many catalysts in energy production, specifically hydrogen and methanol fuel cells, use platinum as an effective catalyst. Platinum used in these fuel cells is uneconomical causing any energy production mechanisms that use platinum to be cost ineffective. There have been many studies with different combinations of platinum with different metals such as nickel, copper, iron, and cobalt to lessen the amount of platinum needed. However, these studies have relied on platinum being in the thin film electrodes. Through the use of electrodeposition, nickel, cobalt, and nickel-cobalt thin films were created with controlled potential electrolysis without the need of platinum.

Characterization of these thin film electrodes were done with cyclic voltammetry and atomic force microscopy. With these methods, the electrochemical area, capacitance, and roughness factor of each thin film electrode were able to be determined. Correlation of these data and the significance of these measurements help to determine the effectiveness that these thin film electrodes could have as catalysts or in other energy applications.

This material is based upon work supported by the National Science Foundation under NSF-RUI Grant No. DMR-1104725 and NSF-MRI Grant No. CHE-1126462.

COLL 191

Characterization of electrodeposited and dealloyed NiFeCu thin films

Willie F. Washington[1,2]*, hampton@hope.edu, Jennifer R. Hampton*[1]*.Â (1) Department of Physics, Hope College, Holland, Michigan 49423, United StatesÂ (2) Department of Chemistry, Park University, Parkville, MO 64152, United States*

Porous thin films have been of interest due to their increased catalytic activity. Previously porous films were developed by dealloying binary and ternary alloy systems using noble metals. This project looked at altering the ratio of Ni+Fe/Cu, a set of less noble metals, and characterizing the different ratios before and after the dealloying process. Scanning electron microscopy (SEM) was utilized to examine the surfaces and energy dispersive spectroscopy (EDS) was used to characterize chemical composition. Deposition was performed with controlled potential electrolysis, dealloying with linear sweep voltammetry, and capacitance measurements with cyclic voltammetry. Analysis of EDS data shows that a larger percentage of copper was removed from films with a high copper concentration. Data also showed that iron tended to remain within the film while a small amount of nickel was removed when the copper levels were increased.

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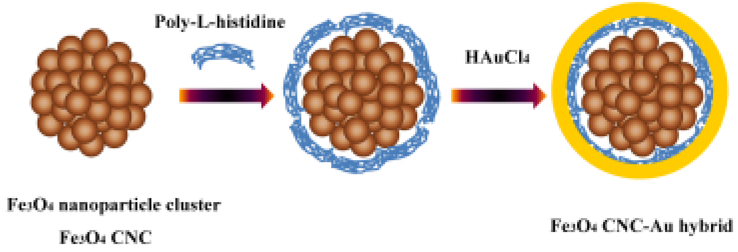
COLL 192

Multifunctional Fe_3O_4 nanoparicle cluster/gold core-shell nanoprobes for high-performance magnetic resonance and X-ray computed tomography imaging

Lina Wu[1,2]*, chemigirl@163.com, Kai Wang*[1,2]*, Kezheng Wang*[1,2]*, Xilin Sun*[1,2]*, Tao Huang*[1,2]*, Baozhong Shen*[1,2]*.Â (1) Department of Radiology, the 4th Affiliated Hospital of Harbin Medical University, Harbin, Heilongjiang 150001, ChinaÂ (2) Key Laboratory of Molecular Imaging in College of Heilongjiang Province, Harbin Medical University, Harbin, China*

Combinatorial nanoparticles are vigorously developed as promising probes because of their extensive application in multi-modality imaging which can combine the complementary strengths of different imaging modalities to enable comprehensive diagnostic function. Herein, multifunctional Fe_3O_4 nanoparicle cluster/gold core-shell nanoprobes with high performance on dual bioimaging of magnetic resonance and X-ray computed tomography imaging are fabricated by a facile layer-by-layer assembly. The superparamagnetic Fe_3O_4 nanoparicle clusters with a size of around 100 nm were firstly synthesized by a solvothermal approach. The Au shell was subsequently nucleation anchoring and growth on Fe_3O_4 nanoparicle clusters. The nanoprobes inherit the excellent physicochemical properties from their building blocks, exhibiting superparamagnetic property, high saturation magnetization, extensive X-ray attenuation and near-IR absorption. They show a high performance on the magnetic resonance imaging and computed tomography imaging simultaneously. The fabricated Fe_3O_4 nanoparicle cluster/gold core-shell nanoprobes have great potential as a new type of multifunctional contrast for diagnostic and therapeutic applications.



COLL 193

Novel water-based dispersant gels for the treatment of oil spills

Olasehinde G Owoseni[1], *oowoseni@tulane.edu, Jibao G He*[1], *Gary McPherson*[1], *Vijay John*[1], *Srinivasa R Raghavan*[2]*.Â (1) Department of Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana 70118, United StatesÂ (2) Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, Maryland 20742, United States*

Oil spill dispersants are a blend of surfactants in a solvent. While surfactants are the active ingredients, the solvent aids surfactant transport through the oil layer to the oil-water interface where it reduces the interfacial tension. Typical dispersants are formulated with organic solvents such as glycol and light petroleum distillates. However, there have been concerns over the toxicity of these organic solvents. Here, we seek to develop a novel dispersant gel formulation with a predominantly water-based solvent. We show that a gel-like surfactant mesophase is formed upon addition of water to a micellar solution consisting of an anionic surfactant, sodium bis (2-ethylhexyl) sulfosuccinate (AOT, DOSS) and zwitterionic surfactant, phosphatidylcholine (lecithin) in a small amount of paraffin such as isooctane to maintain solubility of the AOT. This crystalline mesophase consists of nanostructured aqueous and organic domains that transition from reverse hexagonal at low water content to multilamellar vesicular structures at high water content as shown by cryo electron microscopy and small angle neutron scattering. The introduction of nonionic surfactants such as Polysorbate 80 (Tween 80) and Sorbitan monooleate (Span 80) into the gel system serves to lower interfacial tensions to levels appropriate for dispersion of oil. The replacement of DOSS with a widely available phospholipid and the minimization of organic solvent use is the key to the development of such alternative dispsersant systems.

COLL 194

Surface modification and characterization of degradable 3D electrospun mesoporous silica nanofibers for tissue engineering

Khomson KeratiThamkul[1]*, keratith@augsburg.edu, Michael Stoick*[2]*, Mary Ann Yang*[2]*, Yui Whei Chen-Yang*[3]*,* ***Z. Vivian Feng***[1]*, feng@augsburg.edu.Â (1) Department of Chemistry, Augsburg College, Minneapolis, MN 55454, United StatesÂ (2) Department of Science, Concordia University-St Paul, St Paul, MN 55104, United StatesÂ (3) Department of Chemistry, Chung Yuan Christian University, Chung-Li, Taoyuang 32023, Taiwan Republic of China*

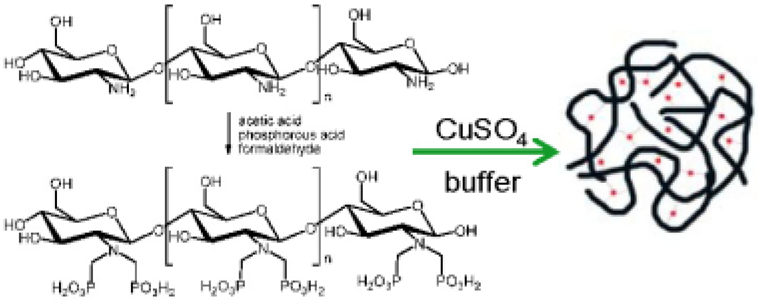
We examined the surface properties and the dissolution behavior of electrospun mesoporous silica nanofibers (MSNF) as potential degradable scaffolding material for primary hippocampal neuron cell growth and differentiation. Two different surface functionalization chemicals, poly-d-lysine (PDL) and 3-aminopropyltriethoxysilane (APTS), produced bioactive surfaces that promote cell adhesion. Surface amino group densities were assessed using fluorescence microscopy with fluorescein Isothiocyanate (FITC) as fluorescent probes. PDL-modified surfaces resulted in higher amino group densities than those modified with APTS. Silica dissolution of the various modified versus nonmodified MSNF were assess by both silicomolybdate blue method tests and ICP-OES. SEM image analysis during the dissolution process confirms there to be continuous dissolution during which fibers collapse, flatten, and eventually fully dissolve into solution. Interactions between MSNF and neurons were also examined using SEM and ICP-OES to better understand the effect of cell attachment and growth on MSFN dissolution.

COLL 195

Nanoparticles composed of chitosan crosslinked with transition metals as drug delivery in cancer targeting

Duong Nguyen[1]*, petros@unt.edu, Meghan Konda*[2]*, Lee Hughes*[2]*, Robby A Petros*[1]*.Â (1) Department of Chemistry, University of North Texas, Denton, TX 76203, United StatesÂ (2) Department of Biological Sciences, University of North Texas, Denton, TX 76203, United States*

Conventional anticancer agents exhibit various side effects resulting from non-selective targeting, drug resistance within cancer cells, and insufficient accumulation of therapeutic in the target tumor. It is critical to develop a drug delivery system capable of successfully encapsulating and releasing anticancer agents that can be triggered at the target site. Our strategy is to synthesize a controlled-release drug delivery system composed of the biopolymer chitosan that has been crosslinked with transition metals. Transition metals could potentially fulfill two roles, one as cross linking agent as well as therapeutic. We are investigating the formation of nanoparticles via the ionotropic gelation of phosphonate-modified chitosan in the presence of copper(2+) and covalent crosslinking of chitosan with cobalt(3+). Copper-chitosan (CuCs) nanoparticles appear to be 15-80 nm in diameter while Cobalt-chitosan (CoCs) nanoparticle has larger size of 100-137nm. In order to enhance the specificity of target binding, the nanoparticle surface will be decorated with peptides that bind to the transferrin receptor, which is over expressed in cancer cells. Phage display was employed to identify peptides with high affinity to transferrin.



COLL 196

Post-polymerization modification and adhesion behavior of a catechol functionalized polymer brush surface

Wei Guo, *wei.guo@eagles.usm.edu, William White, Derek L Patton.School of Polymers and High Performance Materials, University of Southern Mississippi, Hattiesburg, MS 39406, United States*

Ultrathin films of a polymer brush with pendent catechol groups were synthesized via surface-initiated polymerization (SIP) from silicon substrates followed by post-polymerization modification (PPM). The obtained surfaces of catechol bearing polymer brush were studied as a PPM platform to further introduce various functional groups via oxidation and thiol-Michael reactions. Surfaces with regional selective multi-functionalities were generated using microcontact stamp oxidation and modification. The adhesion behavior of the brush surfaces in both air and aqueous conditions were studied using the quantitative nanomechanical AFM technique.

COLL 197

Surface-active polyperoxide copolymer: Synthesis, characterization, application

Andriy Popadyuk[1], *andriy.popadyuk@my.ndsu.edu, Ihor Tarnavchyk*[1], *Nadiya Popadyuk*[1], *Ananiy Kohut*[2], *Volodymyr Samaryk*[2], *Stanislav Voronov*[2], *Andriy Voronov*[1]*.Â (1) Department of Coatings and Polymeric Materials, North Dakota State University, Fargo, North Dakota 58103, United StatesÂ (2) Department of Organic Chemistry, Lviv Polytechnic National University, Lviv, Ukraine*

Amongst the numerous techniques of surface modification, ranging from physical adsorption up to high-energy plasma treatment of substrate, usage of multifunctional polymers resides an important place. By introducing different functional groups in structure of polymeric surface modifier, it is possible to combine different mechanisms of modification in a single treatment step.

In this study, the goals were to synthesize and characterize surface-active polyperoxide copolymer, with two different, peroxide and anhydride, functional groups in its structure, and utilize the functionality for surface modification process. Peroxide groups bring ability to generate free radicals and anhydride groups – upon hydrolysis - surface activity and micelle formation.

Amphiphilic polyperoxide (tBPMAAm-co-MA) was synthesized via free-radical copolymerization of maleic anhydride and N-(t-butyl peroxymethyl)-acrylamide, peroxide-containing monomer that was designed and synthesized in our group.

In order to establish control over polyperoxide copolymer composition, series of kinetic studies were performed. Co-monomer reactivity ratios (r_1 and r_2) were determined as well as how the copolymer composition can be tuned in this process with feed and conversion control.

As an example of application of amphiphilic polyperoxide for surface modification, emulsion polymerization of styrene was conducted in the presence of tBPMAAm-co-MA as initiator and surfactant ('inisurf'), The process yields monodisperse latex particles, functionalized with peroxide and carboxyl groups.

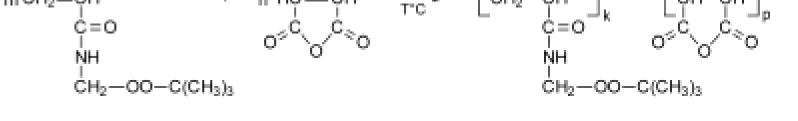


Figure 1. Scheme of tBPMAAm-co-MA copolymerization.

COLL 198

Azole functionalized nanoparticles for imaging and drug delivery

Ronaldo Cavazos, *petros@unt.edu, Robby A Petros.Department of Chemistry, University of North Texas, Denton, TX 76203, United States*

Nanoparticle (NP)-based drug delivery approaches have great potential enhancing treatment efficacy for chemotherapeutics. Furthermore, metal-loaded NPs can also provide a powerful theranostic tool in battling cancer. In this study, biodegradable *N*-azole-functionalized acrylate based nanoparticles were synthesized and then analyzed for their anticancer potential in vitro. Assembly of the NPs was conducted by free-radical polymerization of methyl methacrylate (MMA), polyethylene glycol-diacrylate (PEG-DA), and an azole-functionalized acrylate-based monomer. The azole-functionalized acrylate-based monomer was synthesized by reacting 1,1-carbonyldiimidazole (CDI) with 4-(hydroxymethyl)imidazole and 2-hydroxyethyl acrylate sequentially. Once formed, the nanoparticles were loaded with Ru to serve as the active therapeutic. Control nanoparticles were tested against both normal human cell and cancer cell lines to establish their toxicity profiles. Details of the synthesis and characterization of the Ru-loaded particles will be discussed along with their pharmacological properties.

COLL 199

Synthesis of coinage metal nanowires under ambient, seedless, surfactantless conditions

Crystal Lewis[1], *Krysle28@gmail.com, Lei Wang*[1], *Haiqing Liu*[1], *Stanislaus Wong*[1,2]*.Â (1) Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794-3400, United StatesÂ (2) Condensed Matter Physics and Materials Sciences Department, Brookhaven National Laboratory, Upton, New York 11973, United States*

In this report, crystalline elemental Cu and Ni nanowires have been successfully synthesized through a simplistic, malleable, solution-based protocol involving the utilization of a U-tube double diffusion apparatus under ambient conditions. The nanowires prepared within the 50 and 200 nm template membrane pore channels maintain diameters ranging from ~90-230 nm with lengths attaining the micrometer scale. To mitigate for the unwanted but very facile oxidation of these nanomaterials to their oxide analogues, our synthesis mechanism relies on a carefully calibrated reaction between the corresponding metal precursor solution and an aqueous reducing agent solution, resulting in the production of pure, monodisperse metallic nanostructures. These as-prepared nanowires were subsequently characterized from an applications' perspective so as to investigate their optical and photocatalytic properties.

COLL 200

Measurements of enthalpy of immersion for hydrophobic fumed silica nanospheres at elevated temperatures and pressures

Angkana Pongpilaipruet[1], *angkana_mot@hotmail.com, Rathanawan Magaraphan*[1], *Rolf Jentoft*[2], *Brian P. Grady*[3]*.Â (1) Polymer Processing and Polymer Nanomaterials Research Unit, The Petroleum and Petrochemical College, Chulalongkorn University, Pathumwan, Bangkok 10330, ThailandÂ (2) School of Chemical, Biological and Materials Engineering, University of Oklahoma, Norman, Oklahoma 73019-1004, United StatesÂ (3) School of Chemical, Biological and Materials Engineering, the Instisute for Applied Surfactant Research, University of Oklahoma, Norman, Oklahoma 73019-1004, United States*

The measurement of contact angle between a solid and a liquid presents difficulties when the solid is a powder. The Washburn method uses capillary flow to measure this contact angle of powders, but has some drawbacks. One drawback is the extreme difficulty in
adapting this method to pressures greater than atmospheric. Heat flow microcalorimetry offers an opportunity to measure the contact angle at elevated temperatures and pressures. In this poster, we describe heat flow microcalorimetry measurements of a hydrophobic silica with water containing three different surfactants types; non-ionic, cationic and anionic surfactants at three different temperatures, 40°C, 75°C and 125°C.

COLL 201

Facile synthesis methods for water soluble histamine copolymers and its attachment to quantum dots

Anand Viswanath, *anand.vithu@gmail.com, Shen Yi, Andrew B Greytak, Brian C Benicewicz.Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States*

Polymeric imidazole based ligands are highly useful in coordinating to quantum dot materials, mainly due to their resistance to degradation and robust attachment to quantum dots. Methods to synthesize such polymers mainly use imidazole moieties as the monomer, which requires extensive synthetic steps and purification methods. Outlined herein is a facile post modification strategy aided by the use of the N-methacryloxy succinimide (NMS) monomer. As the polymer needs to be water soluble to enable dispersion of quantum dots in water, a PEG based methacrylate is also used as a comonomer along with NMS. The NMS essentially behaves as an activated ester along the chain and facilitates the attachment of the imidazole to the polymer backbone. This approach is extremely versatile as it provides both water solubility and the addition of activated esters along the chain whereby any nucleophilic compound can be directly added on the polymer chain. Studies of attachment of the copolymers to quantum dots showed that better dispersion quality was observed with smaller MW copolymers, while maintaining high quantum yields. Overall, a simple and robust postmodification method for the effective functionalization of quantum dots with multidentate imidazole moieties is outlined.

COLL 202

Synthesis and characterization of hybrid graphene oxide for chemical toxin detection

Rajashekhar Kanchanapally*, raja_shekhar66@yahoo.com, Paresh Ray.Chemistry & Biochemistry, Jackson State University, Jackson, MS 39217, United States*

Here we will discuss our recent report on the synthesis & characterization of plasmonic nanoparticle attached hybrid graphene oxide for the detection of chemical toxin like Hg^{2+} and melamine. Our result shows that label free sensor can be developed using hybrid graphene oxide for the detection of chemical toxin in parts per quadrillion (PPQ) level. We will also discussed how our developed plasmonic graphene oxide base assay can be used for the detection of chemical toxin from food sample.

COLL 203

Adsorption isotherm of various anionic surfactants on natural rubber

Angkana Pongpilaipruet[1]*, angkana_mot@hotmail.com, Rathanawan Magaraphan*[1]*, Brian P. Grady*[2]*.Â (1) Polymer Processing and Polymer Nanomaterials Research Unit, The Petroleum and Petrochemical College, Chulalongkorn University, Pathumwan, Bangkok 10330, ThailandÂ (2) School of Chemical, Biological and Materials Engineering, The Institute for Applied Surfactant Research, University of Oklahoma, Norman, Oklahoma 73019-1004, United States*

Natural rubber (NR) latex was employed as a substrate for admicellar polymerization. Adsorption isotherms of the anionic surfactants, sodium octyl sulfate, sodium decyl sulfate, sodium dodecyl sulfate, sodium dodecylbenzenesulfonateand sodium monododecyl phosphate, were investigated using High-Performance Liquid Chromatography. The aim of this work was to determine the appropriate surfactant concentration to avoid emulsion polymerization, i.e. determine the concentration at which the adsorption reached a plateau, which is normally assigned as the critical micelle concentration (CMC). The CMC might shift vs. that measured with no NR because of the presence of water-soluble natural rubber components. We will compare the results with the CMCs measured without any rubber present.

COLL 204

Influence of acid base sites on the aldol condensation of acetaldehyde on TiO_2-SiO_2 surface

Dilip K Paul*, dpaul@pittstate.edu.Department of Chemistry, Pittsburg State University, Pittsburg, KS 66762, United States*

Chemisorption of pyridine was applied as a method for studying the acidic properties of titania-silica nanoparticles prepared by sol-gel method. The infrared spectra of adsorbed pyridine were used to evaluate the concentration and the relative strengths of different

acid sites. These studies showed that the amount pyridine bound to different acid sites follow the order Lpy>Hpy>Bpy, and the relative thermal stabilites for different sites was found to be LA>BA>H-bond. In order to determine the role of acid sites on these mixed oxide catalysts, a model compound, acetaldehyde adsorption was examined at different temperatures. It has been found that at 233 K, acetaldehyde adsorbed through hydrogen bonding to surface hydroxyl groups as well as through Lewis acid sites, and upon warming to room temperature, the formation of 2-butenal was observed as the product of aldol condensation reaction. However, the adsorption of acetaldehyde over pyridine-covered surface indicated that the extent of aldehyde adsorption is significantly reduced which in turn affected the aldol condensation reaction. This suggests that the acid sites play an important role in catalyzing the condensation reaction.

COLL 205

QCM-D and computational study of Al^{3+} effects on supported lipid bilayer structure

Hannah K Wayment-Steele[1], *hkws2011@pomona.edu, Lewis E Johnson*[1], *Angelika Kunze*[2], *Sofia Svedhem*[2], *Malkiat S Johal*[1]*.Â (1) Department of Chemistry, Pomona College, Claremont, CA 91711, United StatesÂ (2) Department of Applied Physics, Chalmers University of Technology, Gothenburg, Sweden*

Aluminum ions are a well-known neurotoxin. They derive toxicity from the structural changes they induces in lipid membranes upon binding. Al3+ is known to increase bilayer rigidity, facilitate vesicle fusion, and induce vesicle rupture. However, the mechanisms for these processes are not fully understood. We implement the Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D) technique to study the effects of aqueous Al3+ ions on 1:1 POPC-POPG Supported Lipid Bilayers (SLBs). The QCM-D provides real-time monitoring of changes in mass and viscoelasticity of thin films, allowing one to determine the kinetics of binding processes. We combine these findings with molecular dynamics simulations to better understand the mechanism of the system. Understanding Al3+-bilayer interactions is important for a better understanding of mechanism of toxicity of aluminum in biological systems.

COLL 206

Enhanced cellular uptake of amphiphilic gold nanoparticles bearing ester groups

Kenya Kobayashi[1], *kobayashi@poly.es.hokudai.ac.jp, Kenichi Niikura*[2], *Chie Takeuchi*[2], *Kyoji Hagiwara*[1], *Yoshihiro Ito*[1], *Yoshihito Osada*[1], *Kuniharu Ijiro*[2]*.Â (1) Nanomedical Engineering Laboratory, RIKEN, Wako, Saitama Prefecture 351-0198, JapanÂ (2) Research Institute of Electron Science, Hokkaido University, Sapporo, Hokkaido 001-0020, Japan*

Recently our group reported the PEG derivative ligands to give amphiphilicity to gold nanoparticles (AuNPs). Four PEG derivative ligands bearing ether or ester

functionalities at the terminal of the ligands were synthesized and attached to 10 nm AuNPs. Subsequently AuNPs coated with ester- or ether-PEGs were administrated to the HeLa cells and the cellular uptake levels were analysed by ICP. After 3 hours incubation, AuNPs possessing ester terminal were significantly internalized compared to AuNPs possessing ether terminal. Extension of incubation time to 24 hours resulted in larger amount of cellular uptake of AuNPs and ester-terminal ligand is still superior to the corresponding ether-terminal ligand. It is expected that hydrolysis of ester moiety to convert to carboxylate can be the driving force of enhanced cellular uptake. In conclusion, newly ester terminal PEG derivative ligands for the modification of the AuNPs surface were synthesized and the advantages of the ester ligands over ether derivative were disclosed.

COLL 207

Antimicrobial nanoparticles

***Shaunteri M Tomorrow-Perryman**, shaunteriperryman@gmail.com, Valerie Goss.Department of Chemistry and Physic, Chicago State University, Chicago, Il 60628, United States*

Metallic nanoparticles as antimicrobial agents are useful in preparing clean environments or surfaces as these particles are bactericidal. Nanoparticles made from silver nitrate $AgNO_3$, gold chloride $HAuCl_4$ and copper nitrate $Cu(NO_3)_2$ solutions provide a suitable bactericidal for HB101 strain of Escherichia coli (E.coli). We wanted to determine the millimolar concentrations of the metallic nanoparticles that would be effective as a bactericidal. Further, to understand their behavior, we studied silver, gold and copper nanoparticle up-take properties of E.coli. The E.coli lawn was cultivated with a LB agar recipe. After cultivation, each dish was impregnated with (small round shaped filter papers soaked separately) metal concentration ranging from 1 mM to 1 M. In all experiments, the negative controls were deionized H_2O and sodium citrate, and the positive control was a common disinfectant. We concluded that 4 mM of silver nanoparticle, 16 mM gold nanoparticle, and 24 mM of copper nanoparticle solutions were able to destabilize the bacterial growth. After one day of incubation at 37°C an inhibition zones were observed. This zone provides evidence for low concentration limits for bactericide activity. High-resolution SEM images show destructed morphological changes.

COLL 208

Characterization of site-specific groundwater colloids at various depths: Mobile-LIBD, PCS, ICP-MS, TEM investigation of the KURT groundwater colloids

***Tae-Jin Park**[1], etjpark@kaeri.re.kr, Tae-Yup Lee[2], Min-Hoon Baik[1], Jong-Tae Jeong[1], Kyungsu Kim[1].Â (1) Radioactive Waste Disposal Research Division, Korea Atomic Energy Research Institute, Daejeon, Republic of KoreaÂ (2) R&D Office, Korea Radioactive Waste Agency (KORAD), Republic of Korea*

The KAERI Underground Research Tunnel (KURT) serves as a generic underground research site in Korea and provides relevant domestic geological values including site-specific data related to groundwater at various geological depths (40 – 500 m). Not only chemical and physical properties of the KURT groundwater, but also the characteristics of the groundwater colloids is of fundamental importance in further understanding the transport and retardation of the radionuclides resulting from the colloidal nanoparticle migration. Here, we report the characteristics of the KURT groundwater colloids analyzed by the mobile Laser-Induced Breakdown Detection (M-LIBD) system along with complementary techniques including Inductively-Coupled Plasma Mass Spectrometry (ICP-MS), Transmission Electron Microscopy (TEM), and Photon Correlation Spectroscopy (PCS). Due to the low concentration of the natural groundwater colloids for measurements, the colloids were concentrated using tangential flow ultra-filtration method. The size of the KURT groundwater colloids at various geological depths measured from the LIBD system ranges from 70 to 125 nm, whereas that from PCS and TEM does from 240 to 260 nm and 50 to 200 nm, respectively. In the measurement of colloid concentrations at various depths, both LIBD and ICP-MS methods show colloid concentrations ranging from 20 and 40 ppb. The characteristics of the KURT groundwater at various depths were compared with those from other countries and analyzed for use in safety assessments.

COLL 209

Measuring electronic properties of self-assembled monolayers using conductive probe atomic force microscopy

Heather Malone, *hmalone@monmouthcollege.edu, Mitchell Heuermann, Lindsay Ditzler.Chemistry, Monmouth College, Monmouth, IL 61462, United States*

The measurement of electronic properties of single molecules and molecular assemblies is essential in developing molecular electronics to replace the bulky and expensive material used today. Conductive probe atomic force microscopy (CP-AFM) is used to measure electrical properties at the nanoscale. CP-AFM can simultaneously and independently measure the force, current, and bias at metal-molecule-metal (m-M-m) junctions. These junctions are formed between the AFM probe and self-assembled monolayers (SAMs) attached to an ultra-flat gold surface through a thiol linker. The contact geometry (i.e. the contact between the metal electrodes and the molecules) and intermolecular interactions at these m-M-m junctions play a significant role on conductivity in these systems. This study examines the electrical properties of SAMs composed of biphenyl molecules with single, double, and triple thiol linkers. The focus being the effect of contact geometry, intermolecular interactions, and molecular packing on the electrical conductivity of these assemblies.

COLL 210

Influence of ligands in photoluminescence properties of $CuInS_2$/ZnS core/shell structures

Armando Pena - Duarte[1], *armando.pena@upr.edu, Maharaj Tomar*[1], *Sandra Loydover*[2], *Luis Rivera*[2]*.Â (1) Physics Department, University of Puerto Rico, Mayaguez, PR 00681-9000, Puerto RicoÂ (2) Chemistry Department, University of Puerto Rico, Mayaguez, PR 00681-9000, Puerto Rico*

Strongly luminescent $CuInS_2$/ZnS core/shell nanoparticles are synthesized using two different methods. One method is the reaction of copper and indium acetate, dodecanethiol, octadecene, in inert atmosphere at 260°C during 1h. In second method, thiourea was employed as source of sulfur. After the formation of the core, temperature was lowered to 240° C and 20 ml of ZnS precursor was added drop by drop. The reaction was continued for additional 30 minutes and finally cooled to room temperature. Ethanol and acetone was added followed by centrifuging for precipitation. ZnS precursor was prepared mixing two aqueous solutions of zinc acetate and sodium diethyldithiocarbamate, and then product of this reaction was dissolved in oleylamine with vigorous stirring. Structural characterization by x-ray diffraction shows the characteristic peaks (112), (204), (220), (132) of $CuInS_2$ nanoparticles and the peaks (112), (110), (132) of $CuInS_2$/ZnS core-shell. Photoluminescence of the core/shell structure reveals emission observed in red and near-IR regions. We observe a decrease in the luminescence emission intensity when we use thiourea as precursor. High resolution transmission electron microscopy (HRTEM) images of $CuInS_2$/ZnS core/shell structures are significantly circular with diameters of approximately 5nm, and have homogeneous particle size distribution.

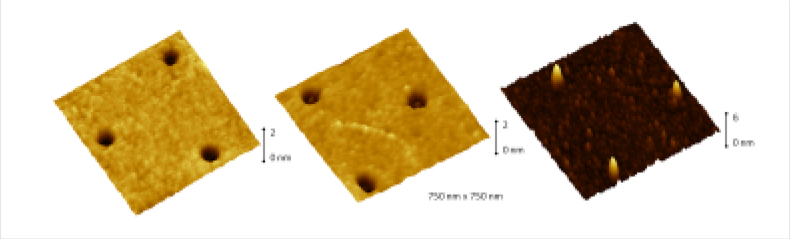
COLL 211

Nanoscale siloxane reaction vessels for surface-directed synthesis of rare earth oxide nanoparticles

Lauren E Englade-Franklin[1], *lengla5@lsu.edu, Gregory Morrison*[3], *Azzy Francis*[1], *Susan D Verberne-Sutton*[1], *Steve M Deese*[1], *Julia Y Chan*[2], *Jayne C Garno*[1]*.Â (1) Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, United StatesÂ (2) Department of Chemistry, The University of Texas at Dallas, Richardson, Texas 75080, United StatesÂ (3) Department of Chemistry, University of South Carolina, Columbia, South Carolina 29201, United States*

By combining particle lithography with organosilane chemistry, we have developed a method to prepare nanosized reaction vessels to provide containers for surface-directed synthesis of individual nanoparticles. This approach provides a means to control the size and arrangement of nanoparticles without the use of surfactants. The obvious problem with synthesis of materials containing rare earth elements is that very high temperatures (800-1200^{o}C) are required for preparing nanocrystals. Although larger macroscopic crystals can be prepared in ovens using inert environments, these cannot be easily formed or molded into desired small shapes and geometries. A methyl-terminated self-assembled monolayer (octadecyltrichlorosilane, OTS) was used as a patterned resist to deposit a solution of rare earth precursor salts. Nanoholes within OTS were used as nanoscopic vessels to confine the liquid precursor solution during

synthesis. The organosilane template was removed by heat treatment; however, the salt residues were converted to rare earth oxide nanoparticles. The fabrication process was characterized using atomic force microscopy to evaluate surface changes throughout the steps of the reaction. Images were acquired of the nanoscale reaction vessels, after addition of the precursor solution, and after heating the samples. Rare earth oxide nanomaterials have useful properties such as upconversion, catalysis, and magnetism. For applications as displays, optical filters, or for use in miniature electronics, the nanoparticles must be prepared with defined size and be strategically arranged as surface arrays.



COLL 212

Electrochemical investigation of quantum phenomena and density of states of hyperbolic metamaterials

***Olivia Penrose-Sadique**, cebonner@nsu.edu, Yuri A. Barnakov, Srujana Prayakarao, Carl E Bonner.Center for Materials Research, Norfolk State University, Norfolk, Virginia 23504, United States*

The motivation of the research is to understand the quantum phenomena of charge transfer characteristics of hyperbolic metamaterials, materials in which the dielectric constant is different in different directions and negative in one direction. The research will observe the rate enhancement of optical processes dependent on the density of states. An enhancement for electronic density of states such as for chemical reactions is expected. Electron transfer in which the rate of the density of states as described by the Marcus theory will be observed using Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) of electron transfer at the surface of the electrode in our electrochemical cell. Our system consisting of a reference electrode with $FeCl_3$ redox couple, a counter electrode of Pt, and a working electrode of SAM coated Au on In-doped SnO_2 will be used to observe distance dependence on electron transfer rate. The electron transfer rates of our redox couple on bare Au, Au layers coated with self-assembled monolayers (SAMs), and Au on top of metamaterial will be compared. Metamaterials composed of alternating layers of MgF_2 and Au will be deposited in several layers on top of the working electrode. The electron transfer rates on bare Au and SAM coated Au will be internally compared then compared to the rate of ET at the Au electrode on the metamaterial substrate. CV data will be examined to understand the mechanism of reduction of the redox couple and to extrapolate ET kinetic and diffusion coefficients. EIS measurements will help to understand the thermodynamic parameters in the reaction.

COLL 213

Fluorescent multiresponsive nanostructures consisting of magnetite core and conjugated block copolymers

***Sourav Chatterjee**[1], schatt1@tigers.lsu.edu, Cornelia Rosu[1], Evgueni E. Nesterov[2], Paul S. Russo[1].Â (1) Department of Chemistry and Macromolecular Studies Group, Louisiana State University, Baton Rouge, LA 70803, United StatesÂ (2) Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, United States*

Core-shell hybrid nanostructures have received an increased interest because of their many current and potential applications. Such nanostructures show combined properties of the core and shell which neither component can display alone. An increase in sensitivity of fluorescent chemo- and biodetection devices can be achieved as a response to external stimuli such as magnetic field. In this work, shells of fluorescent conjugated polymers and block copolymers (e.g. polythiophenes, poly-*p*-phenylenes) were prepared on magnetic (superparamagnetic) nanoparticles consisting of a magnetite core coated with a layer of silica by using surface-initiated living polymerization. The goal of this research was to investigate the change in fluorescent properties as a function of silica shell thickness, order of sublayers in the conjugated block copolymer shell, as well the effect of applied magnetic field, both in thin-film powder and in colloidal solution.

COLL 214

Controlled synthesis of luminescent Mn-doped zinc silicate colloidal microspheres by thermal hydrolysis of urea

***JUNG BO YOO**, yoojungbo@sogang.ac.kr, HAN SOL KIM, JA WOON LEE, NAM HWI HUR.department of chemistry, sogang university, seoul, mapo gu 121-742, Republic of Korea*

We report the synthesis, characterization, and photo-luminescent properties of Mn-doped zinc silicate ($SiO_2@Zn_2SiO_4:Mn^{2+}$) microspheres with a core/shell type structure. The $SiO_2@Zn_2SiO_4:Mn^{2+}$ samples were prepared using core/shell silica microspheres with average

diameter of 285 nm as templates. The synthesis was accomplished by controlled hydrolysis of urea at 353 K. The Mn-doped zinc silicate phase was grown solely within the silica shell. The α-phase ($SiO_2@\alpha\text{-}Zn_2SiO_4:Mn^{2+}$) was prepared at 950 K while the meta-stable β-phase ($SiO_2@\beta\text{-}Zn_2SiO_4:Mn^{2+}$) was obtained by annealing at 750 K and subsequent quenching to 298 K. The resultant α- and β-phase microspheres were fully characterized by various techniques such as X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, transmission electron microscopy, UV-visible spectroscopy, Brunauer-Emmett-Teller surface area, CIE's color coordinate, and photoluminescence (PL). Green luminescence

centering at 522 nm is detected in the α-phase, while the β-phase shows yellow

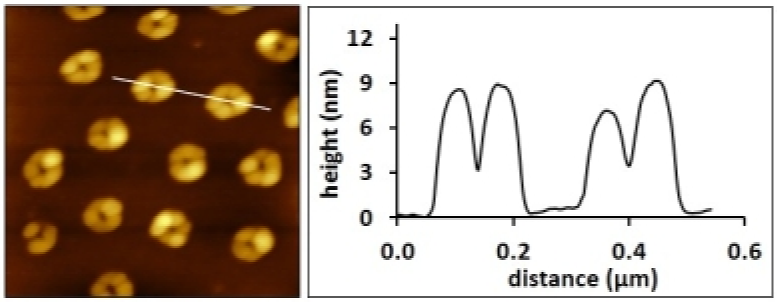
luminescence occurring at 572 nm. Especially, the α-phase exhibits excellent PL properties compared with that of commercial powder sample corresponding to the α-phase. The emission intensities of the α-phase also are about 1.7 times higher than those of commercial sample. The luminance value of the α-phase is 248 cd/m^2, which is about four times higher than that of commercial sample.

COLL 215

Ring nanopatterns of 2-[methoxy(polyethyleneoxy)propyl]trichlorosilane characterized with contact-mode, tapping-mode and force modulation modes of atomic force microscopy

***Rasheda Gros**, rgros6@tigers.lsu.edu, Lu Lu, Jayne Garno.Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, United States*

Ring nanopatterns of 2-[methoxy(polyethyleneoxy)$_{6\text{-}9}$propyl]trichlorosilane (PEG) were generated on Si(111) using particle lithography and heated vapor deposition. A suspension of monodisperse latex mesospheres was deposited on a Si(111) substrate and dried to form a surface mask. The crystalline arrangement of the surface mask provided a structural template to guide the deposition of PEG-functionalized organosilane. The meniscus rings at the base of the latex mesospheres provided nanoscopic sites of water residues for depositing organosilane nanostructures. The surface mask was removed by steps of solvent rinsing and sonication, however the organosilanes persist on the surface to form ring nanopatterns. The sample was studied using contact-mode and tapping-mode atomic force microscopy (AFM), an example topograph is shown in the figure. There are 16 nanorings viewed within a scan area of 1x1 micron. The periodicity measures 300 nm, which matches to the diameter of the latex mesospheres used as a surface mask. The centers of the rings pinpoint the locations where the mesospheres were touching the substrate. In this example, the nanorings measure ~9 nm in height, corresponding to a self-polymerized multilayer.



Force modulation microscopy was also used to characterize the sample to provide information of the elastic response for nanostructures of different thicknesses. A home-built sample stage constructed with polycarbonate material was used for force modulation measurements . Results will be compared for successive measurements of the same sample using multiple modes of AFM.

COLL 216

Polyaniline modified organic–inorganic hybridcation-exchange membranes for the separation of monovalent and multivalent ions

Zeid ALOthman[1], *zaothman@ksu.edu.sa, Moonis Khan*[1], *Masoom Siddiqui*[1], *Mahendra Kumar*[2]*.Â (1) Chemistry Department, King Saud University, Riyadh, Saudi ArabiaÂ (2) School of Biotechnology, Dublin City University, Dublin, Ireland*

Organic–inorganic hybrid cation-exchange membranes (CEMs) were chemically modified by in situ polymerization of aniline in acidic medium using $FeCl_3$ as an oxidizing agent. The presence of polyaniline (PANI) on the surface and inside membrane matrix was confirmed from PANI coating density and scanning electron microscopy.

Membranes were characterized in details by estimating water uptake, ion-exchange capacity, fixed ion concentration, counter-ion transport number and membrane conductivity. The values of N^{a+} transport number across the membranes were unchanged, whereas the values of Zn^{2+} and Al^{3+} transport number were decreased after modification with PANI. The dense nature of PANI modified membranes was evaluated through an electro-osmotic study. The selectivity of PANI modified membranes towards Na^+, Zn^{2+} and Al^{3+} ions was investigated by electrodialysis using single or binary mixture of electrolyte solutions (Na^+/Zn^{2+} and Na^+/Al^{3+}). The current and separation efficiencies of CEM and PANI modified membrane (CEM/PANI-120) for Na^+, Zn^{2+} and Al^{3+} were determined at varied applied current densities and electrolyte solution feed concentrations. The obtained values of current and separation efficiencies for CEM/PANI-120 membrane suggested the suitability of PANI modified membrane in electrodialysis selective separation of Na^+ from the binary mixture (Na^+/Zn^{2+} and Na^+/Al^{3+}) in aqueous solutions.

COLL 217

Cytotoxicity of nanoparticle organic surface coating agents

YING ZHANG, *ying.zhang.zoe@gmail.com, Brandon Newton, Eybriunna Lewis, Hongtao Yu.Department of Chemistry and Biochemistry, Jackson State Universtiy, Jackson, MS 39217, United States*

Abstract

Health impact of nanoparitcles has become a public concern with the great advances of nanoparticles for various applications. Coating agents are an integral part of nanoparticles, but little attention has been paid during toxicity studies of nanoparticles. As a result, there are inconsistent toxicity results for certain nanomaterials. In this study, we explore the cycotoxicity of 11 commonly used coating agents using two cell lines: human epidermal (HaCaT) and lung fibroblast (CRL-1490) cells, and at concentrations

of 3, 10, 30 and 100 µM, at two exposure time points: 2 h and 24 h, and with two different assays: MTT/MTS assay and Trypan Blue staining. It was found that 6 of the 11 studied coating agents are cytotoxic. Especially those with long aliphatic chains surfactants, both the cationic aliphatic amine/ammonium compounds, cetyltrimethylammonium bromide, olyelamine, tetraoctylammonium bromide, and hexadecylamine, and the anionic sodium dodecylsulfate, are the most toxic. In addition, exposure time, test methods, and use of different cell lines also affect the cytotoxicity results. Therefore, for nanoparticle toxicity tests, the complex factors for the test of a mixture, rather than for a pure compound, must be considered. The use of different test methods, cell lines, and exposure times must also be considered when comparing cytotoxicity results.

COLL 218

Janus gold nanoparticles: Control of the phase separation of two surface ligands

Ryo Iida[1], *iida@poly.es.hokudai.ac.jp, Kenichi Niikura*[2], *Shota Sekiguchi*[2], *Hideyuki Mitomo*[2], *Kuniharu Ijiro*[2]*.Â (1) Graduate School of Chemical Science and Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, JapanÂ (2) Research Institute of Electronic Science, Hokkaido University, Sapporo, Hokkaido 001-0020, Japan*

The property of nanoparticles is dependent on not only the core materials, but also the surface ligands. Design of the nanoparticle surface is important for promoting their self-assembly or also nanoparticle-cell interactions. The surface on nanoparticle is often modified with self-assembled monolayer (SAM) of surface ligands. Recently, the surface modifications of SAM using multiple kinds of ligands have been focused. Especially, the anisotropic particles with asymmetric geometry are called “Janus particles” and the simple and general method to fabricate the Janus nanoparticles is demanded due to their unique functions.

In this report, we used gold nanoparticles (AuNPs), and aimed to control the phase separation of two thiol ligands on the surface to create Janus AuNPs. AuNPs were covered with two thiol ligands with different alkyl chain length on various conditions, and the domain structure were analyzed by matrix-assisted laser desorption-ionization mass spectrometry (MALDI-TOF MS). The degree of phase separation in the mixed ligands were strongly dependent on the solvent, length of alkyl chain and mixing procedures of ligands. The Janus-type phase separation on AuNPs was observed using two ligands having the different length of alkyl chains (C11 and C3).

COLL 219

Photocatalytic degradation of non-biodegradable compounds: Roles of precious metals

Pramoch Rangsunvigit[1,2], *Pramoch.r@chula.ac.th, Sumaeth Chavadej*[1,2]*.Â (1) Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Bangkok*

10330, ThailandÂ (2) Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University, Bangkok, Bangkok 10330, Thailand

This work attempts on a comprehensive comparison of different precious metals on the photocatalytic degradation of a non-biodegradable compound, 4-chlorophenol (4-CP). Interestingly, 4-CP degradation does not depend on a catalyst used compared to photolysis. On the contrary, the presence of any of the catalyst significantly affects the intermediate, hydroquinone (HQ) and hydroxyhydroquinone (HHQ), degradation. The addition of a small amount of Pt into TiO_2 enhances the photocatalyst activity. The phase and adsorption capacity of the photocatalyst play important roles in the photocatalytic activity. Although the addition of Ag or Au into TiO_2 does not significantly improve the 4-CP degradation, it does on the degradation of the intermediate products.

COLL 220

Monodisperse gold nanobipyramids with yields approaching 100% and their plasmonic properties

***Qian Li**, liqian@phy.cuhk.edu.hk, Xiaolu Zhuo, Jianfang Wang.Department of Physics, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong Special Administrative Region of China*

The unique characteristics of localized plasmon resonances in metal nanocrystals include greatly enhanced optical cross-sections and concentration of electromagnetic energy near the metal surface. In particular, colloidal Au nanobipyramids (NBPs) are an intriguing type of metal nanocrystals owing to their attractive, excellent plasmonic properties. Compared with other colloidal Au nanocrystals, Au NBPs are nearly monodisperse and therefore their inhomogeneous spectral broadening is suppressed. In addition, the electric field enhancement exhibited by Au NBPs is much stronger than that of Au nanorods (NRs) with equivalent sizes owing to their much sharper tips. Such strong field enhancements make Au NBPs highly preferable as building units to design structures and devices for various high-performance plasmonic applications. However, it has been a great challenge to produce Au NBPs in high yields, which were typically limited below ~50%. This prevents the full utilization of Au NBPs in various plasmonic applications.

We have developed a method for the production of Au NBPs with yields up to 100% and longitudinal plasmon wavelengths tunable from ~650 nm to ~1350 nm by combining seed-mediated growth, Ag overgrowth into long nanorods, and depletion force-induced purification. The Ag segments on highly purified Au/Ag hetero-nanorods were etched away chemically to give Au NBPs having nearly the same shape and size as those obtained from the seed-mediated growth. We compared the extinction cross-sections of Au NBPs and NRs both experimentally and theoretically. Au NBPs were found to have larger extinction cross-sections than Au NRs. Single-particle dark-field scattering measurements indicated that Au NBPs possessed narrower FWHM values. We also compared the refractive index sensitivities and surface-enhanced Raman scattering

between Au NBPs and NRs. Our results showed unambiguously that Au NBPs exhibit much better plasmonic properties than Au NRs. Au NBPs are therefore expected to bring largely improved performances in various plasmon-based applications.

COLL 221

Fabrication of ZnO thin films and their application for inverted organic photovoltaic cells

***SOLEE KIM**, solee731@gmail.com, Jun-Hwan Park, Seong-Geun Oh.Department of Chemical Engineering, Hanyang University, Seongdong-gu, Seoul 133-791, Republic of Korea*

In this research, ZnO thin films were fabricated by using ZnO nanocrystals with controlled size and morphology. Firstly, nano-sized ZnO particles were synthesized by hydrolysis and condensation of zinc acetate dihydrate (Zn salt) and potassium hydroxide (KOH) in methanol. Also, water was added into the reaction medium in order to control the morphology of ZnO nanoparticles from spherical particles to rods. Secondly, the synthesized particles were dispersed in 1-butanol using methoxyethoxyacetic acid (MEA) as a ligand for obtaining transparent and stable dispersion. Finally, ZnO thin films were deposited onto the glass substrate by using the prepared ZnO dispersions through the spin coating process. The ZnO dispersions containing nanorods or spheres and the Zn salt solution were used for the fabrication of dense and smooth ZnO films. Also, the thermal treatment was performed to improve the connectivity and the crystallinity of ZnO particles by removing the organic fraction of the films. To investigate into the effects of ZnO layers having different morphology properties, the prepared ZnO film was used as an electron transport layer applied for inverted organic photovoltaic cells. The analyses were carried out by using FE-SEM, TEM, AFM, DLS, UV-Vis spectroscopy, and current density-voltage characteristics.

COLL 222

Microsized TiO_2 particles with nanoscale effect: Influence of hydroxyl concentration on their photocatalytic activities

***Jang Inseok**, insukz@hanyang.ac.kr, Seong-Geun Oh.Department of Chemical Engineering, Hanyang University, Seongdong-gu, Seoul 133-791, Republic of Korea*

3-dimensional hierarchical TiO_2 micro-sized particles were prepared by using modified sol-gel process with polyethylene glycol (PEG) as a surface-directing agent. After calcination at 450 °C, the crystal structure was anatase phase. The size and specific surface area of particles were 1.0-1.8 μm and 96.85 m^2/g, respectively. The specific surface area of the TiO_2 particles corresponded to that of the spherical nanoparticles with average size of 15.9 nm. Although the size of synthesized TiO_2 was micro-scale, they had the specific surface area similar to that of nano-scale particles due to their effect of morphological property. Subsequently, to modify the surface of TiO_2 with

hydroxyl groups, the hydroxylation treatment was carried out and the amount of surface hydroxyl groups was controlled by the changing concentration of aqueous NH_4OH solution. As the higher concentration of NH_4OH solution was used, the more hydroxyl groups were introduced on the TiO_2 surface. As an application of prepared TiO_2 for water treatment, their catalytic performances for the degradation of methylene blue were examined by using UV-Vis spectrophotometer with the assistance of UV lamp. After hydroxylation treatment, the TiO_2 macro-sized particles showed the higher performance of MB degradation than that of nano-sized P25 particles because of their large specific surface area and hydroxyl-rich surface.

COLL 223

Electrochemical glucose sensors based on an ionic liquid of Au_{25} nanocluster

***Kyuju Kwak**[1], kkj818@yonsei.ac.kr, S. Senthil Kumar[2], Kyunglim Pyo[1], Dongil Lee[1].Â (1) Department of Chemistry, Yonsei University, Seoul, Republic of KoreaÂ (2) Environmental & Analytical Chemistry Division, School of Advanced Sciences, VIT University, Vellore, India*

Ionic liquids have found many applications in electrochemical sensors due to their intrinsic ionic conductivity and electrochemical stability over wide potential window. In particular, ionic liquids were found to maintain the bioactivity of enzymes, which makes them ideally suited for the development of biosensors. In this talk, we present that a stable molten salt of a quantum-sized gold nanocluster can be prepared by ion-pairing of a Au_{25} nanocluster protected with (3-mercaptopropyl)sulfonate with imidazolium cation, 1-decyl-3-methylimidazolium, and its application for the detection of glucose based on its unique electrochemical and biocompatible properties. To prepare electrochemical sensor, the glucose oxidase (GOx) was immobilized in the molten salt, which was subsequently cast on a glassy carbon electrode to form modified electrodes. Cyclic voltammograms of the modified electrode exhibited well-defined and reversible redox peaks corresponding to $Au_{25}^{0/1-}$ and $Au_{25}^{+1/0}$. The electrochemical sensor showed dramatic enhancements in both anodic and cathodic peak currents upon the addition of glucose, indicating the electrocatalytic activity of Au_{25} nanocluster. In addition, GOx immobilized in the molten salt exhibited higher biological activity, demonstrating that the Au_{25} ionic liquid acts as an excellent support for the enzymatic reaction of GOx.

COLL 224

Synthesis and characterization of quantum sized silver nanoclusters protected with 3-mercapto-1-propylsulfonate

***Kyunglim Pyo**, mylifetohoi@naver.com, Eunyeong Seo, Dongil Lee.Department of Chemistry, Yonsei University, Seoul, Republic of Korea*

For the past few years, silver nanoclusters (AgNCs) became one of the most vigorously studied fields for their abundance of the materials, low cost and interesting optical properties, compared to gold nanoclusters. However, the low stability of the AgNCs has always been a big challenge. In this poster, we present the synthesis and characterization of a very stable, highly pure, and water soluble AgNCs protected by 3-mercapto-1-propylsulfonate ligands (MPS). The synthesis was carried out at 0 °C by reducing $AgNO_3$ with sodium borohydride in the presence of MPS ligands. Thus prepared cluster mixture was further purified by poly-acrylamide gel electrophoresis (PAGE), which isolated two major clusters. These two AgNCs were found to be $Ag_{44}(MPS)_{30}$ and $Ag_{32}(MPS)_{19}$, identified by electro spray ionization mass spectrometry (ESI-MS). These clusters were water-soluble and found to be stable at room temperature for more than a month. The presence of sulfonate terminal groups at the end of the ligands enabled facile modification of the anionic clusters by ion-pairing with functional cations. Anionic liquid of Ag cluster could be prepared by ion-pairing with 1,3-dimethylimidazolium cation.

COLL 225

Effects of solvent, silver salt, and PVP on the reduction of silver ions in the polyol process

***Yunji Lee**, six976@hanmail.net, Jun-Hwan Park, Seong-Geun Oh.Department of Chemical Engineering, Hanyang University, Seongdong-gu, Seoul 133-791, Republic of Korea*

In this study, silver nanoparticles were prepared through polyol process. To increase the concentration of silver nanoparticle, effects of solvent, silver salt, and polyvinylpyrrolidone (PVP) on the reduction were investigated. The solvent effect was verified by using different solvents (ethanol, ethylene glycol, and glycerol). As the hydroxyl group in the solvent increased, the reduction ability also increased. Silver nitrate ($AgNO_3$), silver tetrafluoroborate ($AgBF_4$), silver fluoride (AgF), and silver perchlorate ($AgClO_4$) were employed as a precursor. According to the kind of silver salt, color of colloid was different. It is expected that the pH depending on the silver salt solution affected its reduction. Also, the effects of molecular weight and amount of PVP as a stabilizer and reducing agent were studied. The degree of reduction was measured by using UV-vis spectrophotometer and silver ion selective electrode (ISE). The particle size was analyzed with dynamic light scattering (DLS) and transmission electron microscopy (TEM).

COLL 226

Tungsten and silver tip etching dynamics and effects on STM atomic resolution

***Blake Birmingham**, blake_birmingham@baylor.edu, Indra-Mani Ghimire, Kenneth Park, Zhenrong Zhang.Department of Physics, Baylor University, Waco, Texas 76706, United States*

Tip Enhanced Raman Spectroscopy (TERS) utilizes a Raman Spectroscopy system and a Scanning Tunneling Microscope (STM) to produce images of a sample surface with correlated compositional data. The sharpness and geometry of the metal tip are critical to TERS signal. In this study, the electrochemical tip-etching process was studied systematically by varying the voltage, current, etching time, and amount of etching solution for both silver and tungsten. The etched tips were examined via Scanning Electron Microscope (SEM) to determine the relationship of the geometry and the sharpness to the varied etching parameters. The sharpest tips were further tested in a Scanning Tunneling Microscope (STM) by imaging standard HOPG samples at atmospheric pressure and in vacuum. Atomic resolution STM images confirm tip etching parameters have been established for reliably producing suitable tips of both tungsten and silver.

COLL 227

Morphology and optical properties of organic/inorganic hybrid thin films

Saleem G Rao[1]*, saleemg@kfupm.edu.sa, Muhammad A Gondal*[1]*, Muhammad A Dastageer*[1]*, Zain H Yammani*[2]*.Â (1) King Fahd University of Petroleum and Minerals, Dhahran, --- Please Select --- 31261, Saudi ArabiaÂ (2) Center of Excellence in Nanotechnology, King Fahd University of Petroleum and Minerals, Dhahran, --- Please Select --- 31261, Saudi Arabia*

Interaction of first few deposited atomic layers with substrate play very important role in growth and morphology of very thin films. For many good quality thin films buffer layer is essential to overcome the low interaction issues. Self assembled monolayers (SAMs) of organic molecules are good alternate to control the surface properties of metallic and semiconducting surfaces in addition to their wide range applications from molecular electronics to immobilization of bio-molecules. In addition, single/multilayer hybrid thin films with SAM and other nanostructures in between have been reported to develop hybrids with more interesting physical properties. Morphology of inorganic thin film strongly depends upon organic functional group (OFG) of SAM and NS underneath. Depending upon the OFG of SAM a chemical reaction may take place at the interface between first atomic layer and OFG of SAM. Interaction between SAM and NS in addition to morphology can affect other physical properties of the deposited thin films. Morphology and optical properties of such ZnO and TiO_2 hybrid thin films of different thicknesses will be presented.

COLL 228

Kinetic study of the formation of Au/MgO core/shell nanoparticles for drug testing

Arely A Muniz Dominicci*, ejferrer@ponce.inter.edu, Joseph Gonzalez Gonzalez, Nicole Colon Ithier, Pedro Rivera Pomales, Eulalia Medina Perez, Edmy Ferrer Torres.Department of Science and Technology, Interamerican University of Puerto Rico, Ponce, Puerto Rico 00715, Puerto Rico*

We report a synthesis of Au/MgO core/shell nanoparticles using the sonochemical and titration methods. The purpose of our work is to address the development of a biosensor for drug testing. The synthesis consisted of a two step method: the formation of the gold nanoparticles and the reduction of the MgO precursors. In addition, we analyze the formation of the core shell nanoparticles varying the heating time, the titration rate and the ultrasonic time. The nanoparticles were characterized using UV-VIS, IR and scanning electron microscopy (SEM). The optical spectroscopy studies indicate the Localized Surface Plasmon Resonance (LSPR) band absorption at 526 nm. The Au/MgO core/shell absorption shows three important peaks centered in 280 nm, 530 nm and 700 nm. The formation of these new peaks suggested the achievement of the Au/MgO nanoparticles. We are working in the functionalization of the core shells for detection of pseudoephedrine. The optical studies show new band formations suggesting the interaction of the nanoparticles with the drug.

COLL 229

Rationally designed SERS based gold nanopopcorn pathogens and monitoring of antibiotic susceptibility

***Thomas J. Ondera**, jumathomasondera@hotmail.com, Ashton T. Hamme II.Department of Chemistry & Biochemistry, Jackson State University, Jackson, MS 39217, United States*

We report a facile strategy to fabricate a highly sensitive surface-enhanced Raman scattering (SERS)-based sensors with excellent reproducibility and stability based on uniform and well-controlled Gold nanopopcorn (AuNPs) attached functionalized-single-walled carbon nanotube (AuNPs attached to functionalized-SWCNTs) substrates. In this strategy, sharp tip and edge, size, and inter-particle distance controlled AuNPs are evenly attached on long SWCNTs previously doubly ester modified by esterification and [2 + 3] Huisgen cycloaddition reaction under MW irradiation through a multistep approach, yielding stable SERS-based substrates. The AuNPs attached functionalized-SWCNT nanohybrid exhibits good reproducibility and good stability in an aqueous environment. Furthermore, biosensors constructed with AuNPs attached functionalized-SWCNT substrates have diverse applications that are demonstrated with monoclonal anti-*E.coli* antibody-conjugated AuNPs attached functionalized- SWCNTs for selective, label-free, rapid detection of low concentration of *E. coli* in drinking water and monitoring antibiotic susceptibility for diagnostic purposes. The synergy-type enhancement effect arising from the respective components of the nanohybrid due to their intrinsic noble properties indicates that our facile SERS-based sensor fabrication strategy has the potential for further application in multiplex detection and in raw samples.

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COLL 230

Aggregation characteristics of rhamnolipid biosurfactants and several synthetic variants

Ryan J Eismin[1], *pembertn@email.arizona.edu, Clifford S Coss*[1], *Raina M Maier*[2], *Robin Polt*[1], *Jeanne E Pemberton*[1]*.Â (1) Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ 85721, United StatesÂ (2) Department of Soil, Water and Environmental Science, University of Arizona, Tucson, AZ 85721, United States*

Rhamnolipids are of current interest as greener alternatives to common synthetic surfactants. However, little is known about the fundamental aggregation properties of these surfactants. To better understand these aggregation properties, surface tensiometry, dynamic light scattering, and static and time-resolved fluorescence spectroscopy were applied to aggregates formed from the native monorhamnolipid mixture produced by *Pseudomonas aeruginosa* ATCC 9027 and to aggregates formed from all possible stereoisomers (R,R; R,S; S,R; and S,S) of the most common naturally-occurring monorhamnolipid congener, Rha-C10-C10. For concentrations above the critical micelle concentration (CMC) of ~180 μM at pH 8, globular micelles of ~2-3 nm predominate along with two other minor aggregates, likely bilayers and vesicles, with dimensions of ~12 and ~140 nm, respectively. Monorhamnolipid micelles were further probed in fluorescence quenching studies with pyrene as the probe and benzophenone to determine average aggregation number (N_{agg}) of these aggregates. Micelles from these monorhamnolipids have N-$_{agg}$- valuesof ~30-35 molecules.

COLL 231

Structure-function relationships of bio-inspired rhamnolipid surfactants

Ricardo Palos-Pacheco, *pembertn@email.arizona.edu, Clifford S Coss, Hui Wang, Robin Polt, Jeanne E Pemberton.Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ 85721, United States*

Rhamnolipids are amphiphilic glycolipids with outstanding surfactant properties that are found in nature and are potential candidates for biodegradable and non-toxic replacements of current synthetic surfactants. Novel synthetic variants of monorhamnolipids and their bio-inspired analogues were produced and studied to address questions about surfactant function related to specific structural features including: 1) the role of the outer lipid tail, 2) lipid tail stereochemistry, 3) the role of the carboxylic acid group, 4) lipid tail length in single and double chain monorhamnolipids, and 5) lipid tail symmetry. Access to pure materials at the gram scale with specific structural features bio-inspired but not found in nature, impossible to harvest and isolate from microbial colonies, or that are impractical to produce by means of the synthetic methodologies previously reported, required development of an original method to obtain them in diastereomerically pure form and with the desired lipid tails. Studies using surface tension, pulse gradient spin echo nuclear magnetic resonance and light

scattering were performed to determine water/air interface affinity, critical micelle concentration, cross sectional area, minimum surface tension, and aggregate size. The effect of structural differences on these properties reveals the ability to tailor monorhamnolipid and related analogue surfactant function.

COLL 232

Fabrication of porous molybdenum sulfide monolith

Salama Almarzooqi, *salmarzooqi@pi.ac.ae, Marios Katsiotis, Saeed M. Alhassan.Department of Chemical Engineering, The Petroleum Institute, Abu Dhabi, United Arab Emirates*

Molybdenum sulfide is two-dimensional layered material; it has been known historically as a catalyst for hydro-desulfurization and as a lubricant. Recent interest in the layered material has stemmed from the isolation of single layer graphene and subsequent isolation and evaluation of a long list of other two-dimensional materials. Unlike graphene, Molybdenum sulfide is a semi-conductor and has been demonstrated in transistors applications. In addition, a single layer has a tunable and large photothermoelectric effect. It has been shown that MoS_2 with various secondary architectures (beyond layered geometry) has been synthesized. In this work we will present our work on fabrication of porous MoS_2 monoliths, which can be used in several applications including separation, hydrodesulfurization and catalyst support. The monolith has been characterized using various characterization techniques including scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy and BET analysis.

COLL 233

Orientation and reaction chemistry of phosphonic acid-modified indium-zinc oxide surfaces in organic photovoltaic devices

Lingzi Sang[1], *pembertn@email.arizona.edu, Dallas L Matz*[1], *Jeanne E Pemberton*[1], *Matthew Gliboff*[2], *Kristina M Knesting*[2], *David S Ginger*[2], *Ajaya K Sigdel*[3], *Joseph J Berry*[3], *Anthony J Giordano*[4], *Seth R Marder*[4], *Hong Li*[4], *Jean-Luc Bredas*[4]*.Â (1) Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ 85721, United StatesÂ (2) Department of Chemistry, University of Washington, Seattle, WA 98195-1700, United StatesÂ (3) National Renewable Energy Laboratory, Golden, CO 80401, United StatesÂ (4) Department of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332-0400, United States*

Phosphonic acids (PAs) are useful as surface modifiers to tailor work function and increase surface wettability of transparent conductive oxide electrodes in organic photovoltaic devices. When ordered PA monolayers are formed on oxide substrates, the interface dipole and electronic structure are affected by the functional group properties, binding mode and orientation of the PA modifiers. Using octylphosphonic acid (OPA),

F_{13}-octylphosphonic acid (F_{13}OPA), perfluorinated phenyl phosphonic acid (F_5PPA), benzyl phosphonic acid (BnPA), and perfluorinated benzyl phosphonic acid (F_5BnPA) as a group of representative model PA surface modifiers, polarization modulation-infrared reflection adsorption spectroscopy (PM-IRRAS) was used to determine binding mode and molecular orientation on indium-zinc oxide (IZO) substrates. In addition to binding of the PA monolayer, the surface modification process induces the formation of defects on these IZO substrates as indicated by changes in the IR responses of these interfaces. The presence of such defects is important, as they likely change surface electronic properties that affect electron transfer and charge recombination processes at these interfaces in devices.

COLL 234

FRET analysis of mass transport behavior through thin polymer films under laminar flow

***Huan Wang**, pembertn@email.arizona.edu, Jeanne E Pemberton.Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ 85721, United States*

Tethered polymer layers at solid fluid interfaces are used widely in a variety of surface science applications. Although many of these applications require exposure to dynamic flow conditions, most commonly laminar flow, mass transport through these polymer films is a fundamental process that is still poorly, defined despite its critical role. In this work, Förster resonance energy transfer (FRET) is employed to image the mass transport process through thin polymer layers (dry thickness ~120 nm) in real time using total internal reflectance fluorescence (TIRF) microscopy. Poly(N-isopropylacrylamide) films were used as model polymers and were tethered to glass coverslips to which fluorescent donor molecules (fluorescein isothiocynate) had been previously attached. These modified glass coverslips were subsequently used in a pressure-driven laminar flow environment for TIRF imaging. These layers were exposed to solutions of fluorescent acceptor molecules (rhodamine B) in good and theta solvents at varying flow rates and the decay of the donor fluorescence by FRET monitored with time. With the polymer layer in a good solvent, the fluorescence intensity decay rate increases with applied flow rate. The decay curves were fit to a general power law with high correlation factors consistent with percolation of the acceptor through the thin polymer film. These results have important implications for the use of polymeric materials in solvents in devices used in dynamic flow environments.

COLL 235

SWCNT hybrid popcorn shaped magnetic core-plasmonic shell multifunctional nanoparticle for targeted magnetic separation and enrichment: Label-free SERS imaging and photothermal destruction of multi drug resistant Salmonella

***Yunfeng Lin**, linyunfeng123@gmail.com, Ashton T. Hamme II.Department of Chemistry & Biochemistry, Jackson State University, Jackson, MS 39217, United States*

Multidrug-resistant (MDR) *Salmonella enterica serover Typhimurium definitive type 104* (DT104) presents one of the greatest challenges in public health care in today's society. Due to the resistance to drugs, current technology cannot effectively kill the presence of MDR *Salmonella* inside of the human body. As a result, the development of physiologically benign and highly sensitive methods for the detection and/or killing of the aforementioned bacteria is in high demand. Driven by the negative heath impacts of these bacteria, we developed a single walled carbon nanotube (SWCNT) hybrid multifunctional popcorn shaped iron core-gold plasmonic shell approach to target and magnetically separate MDR *Salmonella* DT104. After functionalization of the SWCNT through a 1,3-dipolar cycloaddition with methyl nitro acetate and subsequent SWCNT attachment of the gold shell-iron core nanoparticles and MDR *Salmonella* targeted antibodies, bacterial detection was achieved by the use of label free surface enhanced Raman spectroscopy (SERS), and via selective photothermal methods, destruction of the targeted bacteria was also accomplished. In order to confirm the successful synthesis of the nanoparticles and nanohybrids, a combination of FTIR, SERS, UV Spectroscopy, and TEM, were used. Experimental data show that our SWCNT hybrid antibody-conjugated popcorn shaped magnetic core-plasmonic shell nanoparticles can be used for targeted separation & SERS imaging of MDR *Salmonella*. A targeted photothermal experiment, using 670-nm light at 1.5 W/cm^2 for 15 minutes, resulted in selective irreparable damage to most of the MDR *Salmonella*.

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COLL 236

Application of silver nanowires on gold mirrors to surface-enhanced fluorescence

***Randy Sronce**[1], tshtoyko@uttyler.edu, Tanya Shtoyko[1], Ryan Rich[3], Sangram Raut[3], Ignacy Gryczynski[2], Karol Gryczynski[3].Â (1) Department of Chemistry and Biochemistry, The University of Texas at Tyler, Tyler, TX 75799, United StatesÂ (2) Department of Cell Biology & Anatomy, University of North Texas, Fort Worth, TX 76107, United StatesÂ (3) Department of Molecular Biology & Immunology, University of North Texas, Fort Worth, TX 76107, United States*

Silver nanowires were prepared on gold mirrors covering glass slides. The silver nanowires were made by self-assembly of silver nanoprisms. Characterization of the slides with silver nanowires was done using AFM, SEM, and confocal microscopy. The silver nanowires on gold mirrors were used for surface-enhanced fluorescence studies.

COLL 237

Characterization of non-detonable,non-hazardous explosives training aids for military explosives

***Rajasekar Pitchimani**[1], raj@xplosafe.com, Evgueni Kadossov[1], Shadi Alizadeh[2], Nicholas F Materer[2], Allen Apblett[2].Â (1) Xplosafe LLC, Stillwater, OK 74074, United StatesÂ (2) Department of Chemistry, Oklahoma State University, Stillwater, OK 74078, United States*

Commercially available training aids for canines are either pure explosive powders or explosives mixed with materials like silica. These training aids are not easy to handle or to dispose of after use. They also represent a hazard for both the canines and their handlers. XploSafe manufactures a set of materials that produce vapors of military explosives, such as TNT, RDX and PETN. These materials or training aids are produced in pellet form, making them extremely easy to handle. Direct injection mass spectrometry was used to analyze these training aids for both purity and intensity of the generated vapors. The vapors were compared to samples of actual explosives. They were also subject to open flame, impact and friction testing to confirm the non-explosive nature.

COLL 238

Rebar graphene for flexible all-carbon transparent electrodes

*Zheng Yan[1], **Zhiwei Peng**[1], zhiwei.peng@rice.edu, Gilberto Casillas[4], Jian Lin[2,3], Changsheng Xiang[1], Haiqing Zhou[1], Yang Yang[1], Gedeng Ruan[1], Abdul-Rahman O. Raji[1], Errol L. G. Samuel[1], Robert H. Hauge[1,2,5], Miguel Jose-Yacaman[4], James Tour[1,2,3].Â (1) Department of Chemistry, Rice University, Houston, TX 77005, United StatesÂ (2) Richard E. Smalley Institute for Nanoscale Science and Technology, Houston, TX 77005, United StatesÂ (3) Department of Mechanical Engineering and Materials Science, Rice University, Houston, TX 77005, United StatesÂ (4) Department Physics and Astronomy, University of Texas at San Antonio, San Antonio, TX 78249, United StatesÂ (5) King Abdulaziz University, Jeddah, Saudi Arabia*

1D carbon nanotubes (CNTs) and 2D graphene (G) are among the most studied carbon allotropes in the last decade due to their excellent electronic, mechanical and optical properties. Here we demonstrate the formation of planar G/CNT hybrid sheets by annealing functionalized CNTs on Cu foils. The CNTs act as reinforcing bars (rebar), toughening the graphene through both π-π stacking domains and covalent bonding where the CNTs partially unzip and form a seamless 2D hybrid as revealed by aberration-corrected scanning transmission electron microscopy (STEM) analysis. The as-made sp^2-carbon based heterostructures can be transferred onto target substrates without the need for a polymer-coating as a result of the structural reinforcement of the CNTs. In addition, we demonstrate the use of these new G/CNT hybrids as flexible all-carbon transparent electrodes. Other 1D or 2D nanomaterials, such as carbon onions and boron nitride nanotubes, can also function the similar roles as CNTs.

COLL 239

Selective detection and photothermal therapy of breast cancer cells using iron core gold shell nanoparticle-SWCNT hybrid nanostructures

***Bhanu Priya Viraka Nellore**, bhanupriyareddy.v@gmail.com, Zhen Fan, Paresh C. Ray, Ashton T. Hamme II.Chemistry & Biochemistry, Jackson State University, Jackson, MS 39217, United States*

Due to the fact that gold nanoparticles possess unique optical properties and are considered to have low toxicity toward humans, the use of gold nanoparticle based biological detection devices and therapeutic agents are very attractive. Multifunctional nanomaterials can potentially be even more superior because more than one physical property can be exploited to target or separate a particular biological agent. Single walled carbon nanotubes (SWCNTs) arrayed with iron core gold shell nanoparticles have the potential to be used for medical diagnosis via magnetic resonance imaging (MRI) because of the magnetic properties of the iron core, and the plasmonic gold shell can be useful for photothermal therapy through irradiation at a specific wavelength or cancer detection through surface enhanced Raman spectroscopy. After synthesizing the desired iron oxide nanoparticle, a specific synthetic protocol was used to encase the iron nanoparticle with gold thereby creating a gold nanoshell. These iron core gold shell nanoparticles were then anchored onto a functionalized SWCNT through the formation of a sulfur carbon bond. Through the incorporation of a SKBR-3 aptamer, the nano-hybrid selectively bound to the SKBR-3 cells which, upon exposing to irradiation with a laser, were killed due to heat generated by the nanoparticles.

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COLL 240

Effect of functionalization on the surface reactivity of the alumina nanopores

***Evgueni B Kadossov**[1,2], evgueni@xplosafe.com, Allen W Apblett[1], Nicholas F Materer[1].Â (1) Department of Chemistry, Oklahoma State University, Stillwater, OK 74078, United StatesÂ (2) XploSafe, LLC, Stillwater, OK 74074, United States*

The surface reactivity of pure and functionalized anodized aluminum oxide nanopores (AAO) has been studied by the hybrid quantum mechanics/molecular mechanics approach. Adsoprtion of small organic probe molecules (including explosives RDX, PETN, TNT and TATP) on the pore surface was computed using the B3LYP/6-31G* for the adsorbate and its immediate vicinity and a universal force field for the rest of the system. The obtained adsorption energies correspond to physisorption consistent with the absence of the chemical bonding between the probe molecules and the pores. Functionalization of AAO with various groups allows for fine-tuning the surface reactivity towards the adsorbed species. The adsorption energy of the probe molecules depends

on the pore size, adsorbate geometry, and the polarity and the chain length of the functional groups.

COLL 241

Functionalization of mesoporous silica powders and pellets

***Shadi Alizadeh**[1], shadia@okstate.edu, Rajasekar Pitchimani[2], Allen W Apblett[1], Nicholas F Materer[1].Â (1) Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, United StatesÂ (2) XploSafe, Stillwater, Oklahoma 74074, United States*

Functionalization of the silica surface with organic/inorganic moieties has a lot of potential applications in various fields, like catalysis, sensors, etc. Powder and pellet forms of mesoporous silica were reacted first with triethylamine, and then functionalized with alkylmethoxy and alkylethoxysilanes. Solid-state ^{29}Si and ^{13}C CP/MASNMR spectroscopy, total internal reflection FTIR, and thermogravimetric analysis was used to characterize the functionalized samples. Results show samples functionalized with hexyl trimethoxysilane have highest loading as determined by solid state NMR. Direct injection mass spectroscopy was used to look at the stability of these materials. Significant hydrolysis due to absorbed water was observed for many of the samples. The hexyl trimethoxysilane functionalized material has a substantially lower hydrolysis rate when compared to the methyl functionalized samples.

COLL 242

Frictional properties of graphene on hydrophilic and hydrophobic silica surfaces with nanoscale roughness

***Jessica Spear**[1], jessica.spear@mail.chem.tamu.edu, James Custer[2], James Batteas[1].Â (1) Department of Chemistry, Texas A&M University, College Station, Tx 77843, United StatesÂ (2) Department of Chemistry, Muhlenberg College, Allentown, PA 18104, United States*

Microelectromechanical system devices (MEMS) suffer from severe wear and short lifetimes from high pressure asperity-asperity contacts due to the nature of their rough surfaces. Recently nanoscale carbon lubricants, such as graphene, are of interest as protective surface coatings for MEMS. Here, AFM has been used to investigate the frictional properties of graphene on hydrophilic and hydrophobic nanoparticle films, which model the nanoscaled asperities found on realistic surfaces. These AFM studies revealed that graphene partially conforms to the rough surfaces and as the number of layers increase, conformity decreases due to stiffening of the thicker layers, but increases under mechanical loading. Friction nominally decreases as a function of layer thickness, but was also found to depend on contact area of the tip and interfacial shear strain of the graphene associated with its adhesion to the substrate.

COLL 243

Segregation of dye molecules on TiO_2 surfaces through the use of covalent organic framework monolayers

***Robert W Cotta**, RCotta047@g.rwu.edu, Venkata Neti, Luis Echegoyen.Department of Chemistry, University of Texas at El Paso, El Paso, TX 79968, United States*

Dye-sensitized solar cells (DSSCs) are promising for collecting solar energy. However, one of the difficulties is that dyes tend to aggregate on the surface of the titanium dioxide (TiO_2) leading to lower efficiencies. To improve this, a novel concept was investigated where covalent-organic framework (COF) monolayers were formed on the surface of the titania electrodes and then coated with dye molecules. COF monolayers on surfaces are very useful due to the variable pore size of the frameworks that can be tuned to specific dyes and lead to increased efficiencies and decreased aggregation. The COF monolayers used were previously reported on Au, Ag and HOPG surfaces. Surface characterization techniques such as scanning tunneling microscopy (STM), contact angle, and UV-Vis absorption spectra were used to characterize the successive layers. AM 1.5 solar simulation and external quantum efficiency measurements were used to determine the impact of the nanostructures on the overall photovoltaic performances.

COLL 244

Dissociation of chlorobenzene on a double dimer cluster model of Si(100) surface

***Eric D. Butson**[1], butson@okstate.edu, Qing Zhu[2], Nicholas F. Materer[1].Â (1) Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, United StatesÂ (2) Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261, United States*

The adsorption and dissociation of chlorobenzene on Si(100) surface was modeled using density functional theory. A double dimer cluster was used to represent the (100) face of silicon. Initial adsorption occurs by breaking one double bond on the phenyl ring and forming two new carbon-silicon bonds with the dimer cluster. For further dissociation to occur, the system must undergo a spin crossing process from the singlet electronic configuration to a higher energy triplet state. After this spin crossing event, the carbon-chorine bond is broken and a new silicon-chlorine bond is formed. This cleavage is followed by an additional cleavage of the bond between one of the two carbons attaching the ring to the silicon dimer. This restores the aromaticity of the phenyl ring, and results in a lower energy product. The final product is a dissociation product with chlorine and a phenyl ring attached directly to the (100) surface of silicon.

COLL 245

Capping agent removal and improved biosensing with gold nanostars

***Carlos Matti**, cm17@albion.edu, Debrina Jana, Jie He, Laura Sagle.University of Cincinnati, Cincinnati, Ohio 45220, United States*

Complex nanoparticle stuctures, such as nanostars[1] and spiky nanoshells[2] and nanorods[3], have been shown to have increased field intensities and increased sensitivity to changes in index of refraction. However, their utilization in Localized Surface Plasmon Resonance (LSPR) biosensing has been severely limited by the presence of capping agents, which coat the surface of the metal structures and prevent protein binding. In this presentation, a method for removing the capping agent polyvinylpyrrolidone (PVP) from gold nanostars is described. The capping agent free nanostars are then utilized towards biosensing by measuring shifts in LSPR frequency upon addition of a biotin linker followed by Streptavidin protein. The measurements reveal large blue shifts in more than one LSPR peak frequency (~40 nm) with PVP removal. Upon biotin functionalization and protein binding, red shifts of similar magnitude are observed in the same peaks. Moreover, the measured SERS intensities of benzenethiol absorbed on both PVP coated and uncoated nanostars show that uncoated nanostars have significantly higher SERS enhancement factors, revealing the uncapped gold nanostars as one of the best SERS substrates known.

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COLL 246

Nanoscale patterning of proteins on spatially-selective templates of organosilanes prepared by particle lithography

***Zachary L. Highland**, zhighl1@tigers.lsu.edu, Lauren E. Englade-Franklin, ChaMarra K. Saner, Cody N. Leegwater, Rene A. Girard, Jayne C. Garno.Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, United States*

We are developing approaches for surface patterning of proteins using particle lithography to prepare spatially selective nanopatterns of organosilanes. Our goals are to apply measurements with scanning probe microscopy (SPM) for studies of biochemical reactions at the molecular level. High resolution SPM imaging can be achieved with well-defined surface arrangements of proteins that can persist despite the perturbation of a scanning probe. The headgroups of silane self-assembled monolayers (SAMs) provide robust sites for linking proteins to glass, mica or silicon substrates. Our strategy was to prepare chemically patterned surfaces of organosilane SAMs to direct the binding of proteins within spatially confined surface sites. Spatially selective surfaces were fabricated using particle lithography with selected diameters of monodisperse mesospheres of latex or silica. Protocols based on particle lithography offer advantages of high throughput, reproducibility and ease of preparation. By changing the diameter of the mesosphere masks, the periodicity and surface density of reactive sites (nanoholes) can be reproducibly controlled to simultaneously generate millions of organosilane nanostructures. For example, the number of protein binding sites can be adjusted to range from three to 80 nanopatterns per square micron. Images acquired with SPM disclose that proteins (fibronectin, fibrinogen) attached primarily to the surface areas presenting reactive head groups, which were surrounded by methyl or PEG-functionalized silanes. Analysis of the surface changes after each reaction step was visualized using SPM. The activity for binding antibodies was evaluated to confirm that after immobilization the surface-bound protein retained capacity for binding IgG. Studies with SPM provide advantages of achieving nanoscale resolution for detecting surface changes without requiring chemical modification of proteins or fluorescent labels. Surface platforms of organosilane nanopatterns are suitable for studies of protein binding, such as for screening the selectivity of fluorescent markers and for investigating the binding of small molecules to proteins.

COLL 247

Single-stranded RNA selective permeation through nanopores in a virus capsule surface

Naotoshi Sugimura[1]*, sugimura@poly.es.hokudai.ac.jp, Kenichi Niikura*[2]*, Kyoji Hagiwara*[3]*, Chie Takeuchi*[2]*, Hideyuki Mitomo*[2]*, Kuniharu Ijiro*[2]*.Â (1) Graduate School of Chemical Science and Engineering, Hokkaido University, Sapporo, Hokkaido 060-0808, JapanÂ (2) Research Institute of Electronic Science (RIES), Hokkaido University, Sapporo, Hokkaido 001-0020, JapanÂ (3) RIKEN, Wako, Saitama 351-0198, Japan*

Virus-like particles (VLPs), which are the genome-free component of native viruses, have been studied as therapeutic or diagnostic tools because of their inner space that can hold drug molecules and good dispersion in serum. There are many 2.0 nm apertures, “nanopores”, in a VLP surface which small molecules can permeate but larger molecules cannot. Here, we report that single-stranded RNAs (ssRNAs) can pass through nanopores in a surface of VLPs from JC polyomavirus, but double stranded RNAs can not.
Capsid viral protein 1 (VP1) derived from JCV contains six cysteine residues, however only cysteines located on the internal surface of the virus particle, are exposed to the solvent. VLPs were incubated with single or double stranded FITC-labeled RNAs which contain the thiol reactive group: N-succinimidyl 3-(2-pyridyldithio)propionate (SPDP) at room temperature for 1 h. The number of encapsulated RNAs through cysteines in a single VLP was estimated after purification by size exclusion chromatography (SEC) by fluorescent measurement. The number of encapsulated ssRNAs was larger than that of dsRNAs, indicating that ssRNA can pass through nanopores in a surface of VLPs. Our results suggest that virus capsules could be useful device for trapping or sensing of target ssRNAs.

COLL 248

Optical properties of bi-icosahedral Au_{25} and Au_{24}clusters: Influence of central gold atom

Viraj D Thanthirige[1], *virajdhanushka.thanthirige@wmich.edu, Ekkehard Sinn*[1], *Rongchao Jin*[2], *Guda Ramakrishna*[1]*.Â (1) Department of Chemistry, Western Michigan University, kalamazoo, MI 49008-5413, United StatesÂ (2) Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, United States*

Temperature-dependent absorption and ultrafast luminescence measurements of $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2\ ]^+$ (bi-Au24) were studied and compared with $[Au_{25}(PPh_3)_{10}(C_6S)_5Cl_2\ ]^{2+}$ (bi-Au$_{-25}$). The investigations are carried out on these two clusters as they are structurally similar except for the absence of central Au atom for bi-Au$_{24}$.

Figure 1. Crystal structures of bi-Au$_{25}$ and bi-Au$_{24}$ clusters . Both crystal structures are identical except for the central core Au atom.

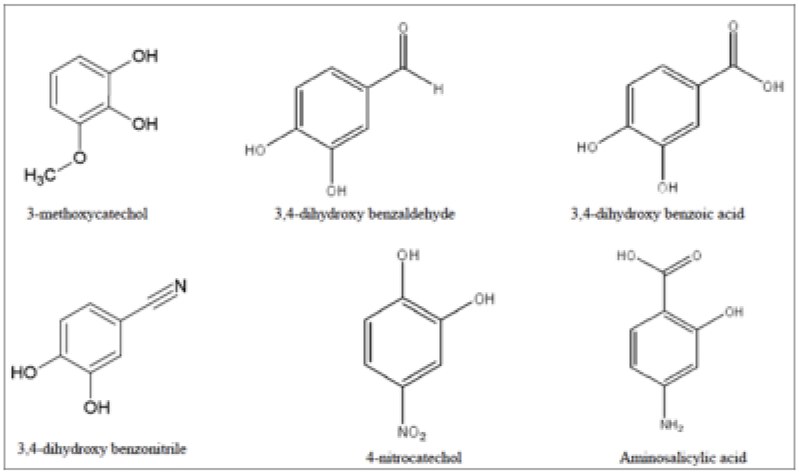
The objective of the work is to probe the influence of the central gold atom on the optical transitions and electron-phonon interactions in bi-icosahedral nanoclusters. The investigations are focused both on the electron-phonon as well as hydrogen bonding interactions of axial Cl atoms with hydrogen bonding solvents and their influence on the vibronic transitions. It was theoretically shown that the absorption at 670 nm arises due to coupling of two icosahedrons which Au $_{25}$ does have and Au$_{24}$ does not. While for Au$_{24}$, broad band at ~560 nm was observed which was due to the interactions of the two units (two Au$_{12}$ units) and 415 nm shoulder Peak and 383 nm band is due to the electronic transitions related to the localized electronic structures of the individual 12 units. All these peaks becoming sharper and blue shifted when it goes to lower temperatures and it increases the Oscillator strength and also it showed a new peak around 480 nm in lower temperatures. The electron-phonon interactions were obtained from fitting the band gap data as a function of temperature. Solvent dependent absorption measurements and Ultrafast luminescence measurements shows the hydrogen bonding formation of clusters with the solvents.

COLL 249

Ultrafast charge-transfer luminescence dynamics in catechol derivatives sensitized TiO_2 nanoparticles

Jameel A. Hasan, *jameelahhasan@gmail.com.Department of Chemistry, Western Michigan University, Kalamazoo, Michigan 49008, United States*

Small molecules with ene-diol anchoring groups such as catechol form localized molecule-semiconductor charge-transfer complex with TiO_2 nanoparticles. We have shown in an earlier investigation that ultrafast luminescence dynamics and corresponding anisotropy can be used to probe the localized/delocalized nature of the transitions and the charge-transfer dynamics. In this work, efforts were focused to understand the donor and acceptor strength of small molecule on the localized/delocalized nature of the charge-transfer transitions and correlate them to charge separation dynamics. The investigated molecules, as seen in figure1, include 4-nitrocatechol, 3-methoxy catechol and 3,4-dihydroxy benzoic acid, 3,4-dihydroxy benzonitrile and 3,4-dihydroxy benzaldehyde, and aminosalicyclic acid. The femtosecond fluorescence upconversion and transient absorption measurements are utilized to probe the charge-transfer dynamics in these catechol derivatives sensitized TiO2 nanoparticles. Interesting charge-transfer dynamics is observed. The ultrafast luminescence dynamics and anisotropy measurements have shown that increasing the donor strength of the catechol led to relatively more delocalized charge-transfer transitions than the catechol derivatives with an acceptor. The transient absorption dynamics have shown that the charge recombination is slowed down with increasing donor strength of catechol suggesting that the hole is localized away from the surface of the nanoparticle and thus increasing the charge separation. In addition, the charge recombination dynamics for catechols in solution and thin films are found to be entirely different. Though the solution phase measurements have shown ultrafast charge recombination for catechol sensitized TiO_2 nanoparticles, the thin film investigations have shown long-lived charge separation suggesting that the chromophores with catechol can be used in solar cell and photocatalytic applications.



COLL 250

Catalytic pyrolysis of cellulose over bimetallic (Ni-Co) oxide nanoparticles

Hongyi Wu, *hongyi_wu@subr.edu*, ***Edwin Walker***, *hywu2002@gmail.com.Southern University, Baton Rouge, LA 70813, United States*

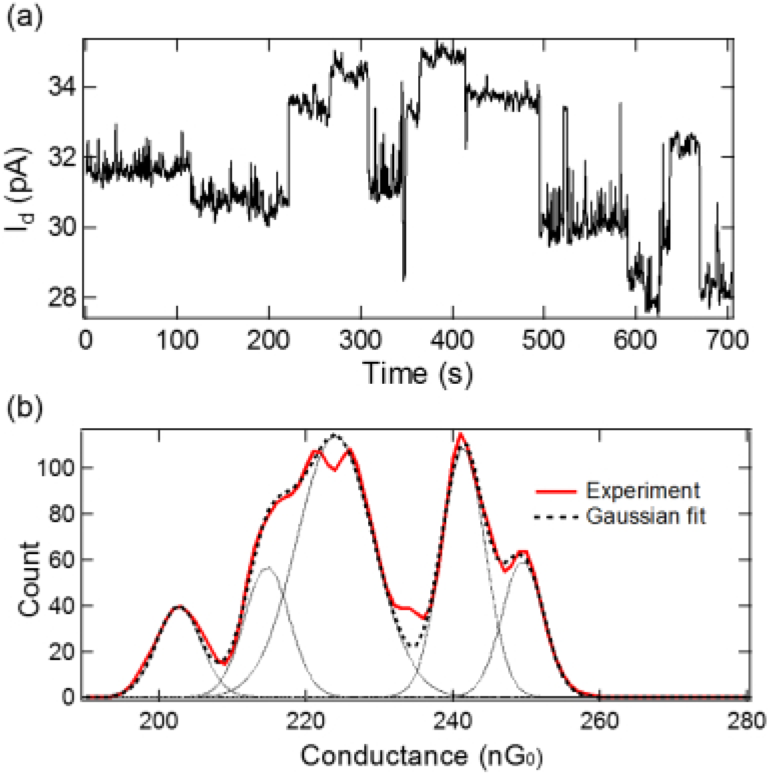
Bimetallic (Ni-Co, 1:1) oxide nanoparticles (BNPs) supported on Al_2O_3 was prepared by using the G1 PAMAM dendrimer as template which immobilized metal ion on substrate. Thermally removal of dendrimer backbone resulted formation of Al_2O_3 supported Ni-Co oxide NPs with a mean size of ~4.3 nm, as indicated by (X-ray Diffraction) XRD, and transmission electronic microscope (TEM). BET and drift FTIR techniques were also used for the surface characterization. To evaluate the catalytic activity of the synthetic Ni-Co BNPs with comparison to the mono NiO nanoclusters prepared by same dendrimer technique and micro-size NiO particles prepared by traditional impregnation, all the catalysts were premixed with cellulose fine crystal in a 10wt% ratio for pyrolysis test (N_2 atmosphere). The weight loss of cellulose was monitored by TGA from 100 to 800 ºC and the final yield of char was weighed immediately after cool down. Under the same experimental condition, the initial temperature of cellulose decomposition (weight loss) and the mass of char yield were examined in all three catalysts case, using pure cellulose pyrolysis as reference.

COLL 251

Multistate switching of redox active unimolecular device based on electroless plated gold nanogap electrodes

Yoshiki Kobayashi[1,3]*, ykobayashi@nanoele.msl.titech.ac.jp, Aoyama Eiki*[1,3]*, Makoto Kawamoto*[1,3]*, Yoshiaki Shoji*[2]*, Takanori Fukushima*[2]*, Yutaka Majima*[1,3,4]*.Â (1) Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Kanagawa 226-8503, JapanÂ (2) Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama, Kanagawa 226-8503, JapanÂ (3) CREST-JST, Yokohama, Kanagawa 226-8503, JapanÂ (4) Department of Printed Electronics Engineering, Sunchon National University, Sunchon 540-742, Japan*

As a function of molecule is peculiar to applicable, the π conjugated structure molecular devices attract much attention as nanoscale devices in recent years. In order to realize a molecule device, it is necessary to establish the fabrication processes of solid state molecular devices. In this study, a filler molecule (1) which has multi-electronic oxidation-reduction activity was introduced into the gold nanogap electrode from its solution. The filler molecule (1) was introduced between Gold nanogap electrodes with a 1~3 nm gap separation were prepared by EB lithography and a surface catalyzed electroless gold plating method. The current-voltage characteristic was measured performed at 9 K and room temperature under a vacuum. Tunneling current showed several constant states under a constant bias voltage at 9 K (fig.1a). Conductance states shows five values, by the Gaussian fitting of the histogram, and they are 203 nG_0, 215 nG_0, 224 nG_0, 241 nG_0, and 250 nG_0, respectively (fig.1b). Here, G_0 is 77 μS. These multi-stage switching effect are attributes to multi states of one filler molecule (1) oxidation-reduction. Therefore, this filler molecule (1) is a candidate of a component of multi-stage memory.



COLL 252

XAFS and DFT study on Ni_2P catalyst for hydrodeoxygenation of bio-oil

***Ji-Sue Moon**, harry2030@naver.com, Yong-Kul Lee.Department of Chemical Engineering, Dankook University, Yongin, Gyunggi 448701, Republic of Korea*

A Ni_2P/SiO_2 catalyst was prepared and applied for the hydrodeoxygenation of guaiacol. The physical properties of the catalyst samples were characterized by BET, CO uptake chemisorption, and TPR. X-ray diffraction (XRD) and extended X-ray absorption fine structure (XAFS) spectroscopy were used to obtain structural properties for the supported Ni_2P catalysts. Hydrodeoxygenation (HDO) tests were performed in a continuous flow fixed-bed reactor at 523-573 K, and 1 or 8 atm, and an LHSV of 2.0 h^{-1}. The Ni_2P/ SiO_2gave an HDO conversion over 90% with two different reaction pathways being identified; at 1 atm direct deoxygenation was dominant to produce benzene, and at 8 atm prehydrogenation followed by deoxygenation was preferred to produce cyclohexane. A combined X-ray absorption fine structure spectroscopy and density functional theory analysis revealed that the active site of Ni_2P catalysts is composed of three-fold hollow Ni and P sites which lead to adsorption of H or OH groups. These results suggest that direct deoxygenation is favored over OH surface, and prehydrogenation was favored over the more reduced surface of Ni_2P catalyst.

COLL 253

Synthesis and characterization of environmentally benign nanoparticles

Alexander P Richter[1]*, aprichte@ncsu.edu, Vesselin N. Paunov*[2]*, Simeon D. Stoyanov*[3]*, Orlin D. Velev*[1]*.Â (1) Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27606, United StatesÂ (2) Department of Chemistry, University of Hull, Hull, United KingdomÂ (3) Laboratory of Physical Chemistry and Colloid Science, University of Wageningen, Wageningen, United States*

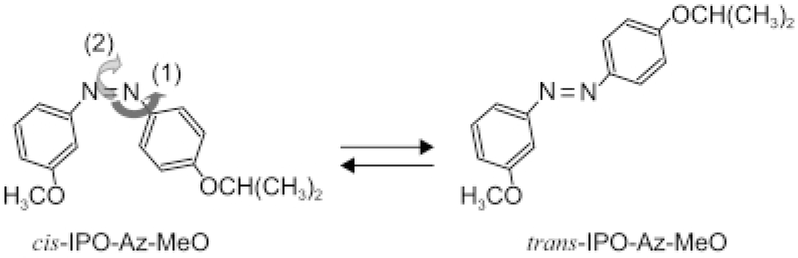
There has been a growing interest in replacing current non-biodegradable and toxic nanosystems with environmentally benign biopolymer based ones to minimize post-utilization hazards due to uncontrolled accumulation of nanoparticles in the environment. Lignin based nanoparticles (NPs) are biodegradable, environmentally benign, and may be potentially employed as foam and emulsion stabilizers, as drug delivery system, and as matrices for environmental remediation systems. We will report means of synthesizing such Environmentally benign Nanoparticles (EbNPs) in a simple, inexpensive, and non-toxic way. Dynamic Light Scattering is employed to measure EbNP size distributions as a function of the operating parameters such as pH drop magnitude, initial modified lignin loading in stock solution, and choice of solvent. Particle morphologies and shapes are determined by Transmission Electron Microscopy. We used two modified lignin, Indulin AT (IAT) and High Purity Lignin (HP-L), and applied environmentally friendly acid precipitation technology and solvent exchange precipitation method for EbNP synthesis. For IAT EbNP formation, the water-water based pH drop method results in nanoparticles with only limited pH stability ranging from pH 1.80 to pH 3.0. By utilizing the ethylene glycol (EG)-water based pH drop method we were able to obtain IAT EbNPs with increased pH stability ranging from pH 4.0 to 9.0. IAT is dissolved in EG, in which IAT EbNPs formation is triggered upon acid addition. We hypothesize that the pH stability of these EbNPs is due to a favorable molecular stacking facilitated by EG prior to precipitation. For HP-L EbNP synthesis we employed a solvent antisolvent precipitation process resulting in EbNPs with pH stability ranging from pH 4.0 to 9.0. All native IAT and HP-L EbNPs bear negative surface charges and are electrostatically stabilized. Post treatment options for surface charge modification to positive via adsorption of positively charged polyelectrolytes have been explored and formulated.

COLL 254

STM study of isomerization mechanism for a single azobenzene derivative

Emiko Kazuma[1]*, emiko.kazuma@riken.jp, Mina R Han*[2]*, Junepyo Oh*[1]*, Yousoo Kim*[1]*.Â (1) Surface & Interface Science Laboratory, RIKEN, Wako, Saitama 351-0198, JapanÂ (2) Department of Molecular Design & Engineering, Research Center for Materials Backcasting Technology, Nagoya University, Nagoya, Aichi 464-8603, Japan*

The *cis-trans* isomerization mechanism of azobenzene has still been a controversial issue. The proposed reaction pathways are (1) the CNN bending (inversion) and (2) the CNNC torsion (rotation). We visualized the isomerization reaction of a single 4-isopropoxy-3'-methoxyazobenzene (IPO-Az-MeO) molecule on a Ag(111) surface by scanning tunneling microscopy (STM). The IPO-Az-MeO molecules deposited on Ag have two stable *cis*-structures (*cis*-A, B) and the reversible conformational changes between *cis* and *trans* were achieved by injection of tunneling electrons. We found that the conformational changes from *cis*-A were based on the inversion pathway, but on the other hand, the changes from *cis*-B were based on the inversion or rotation pathway, which suggests that the isomerization mechanism is different depending on the initial structure of the molecules.

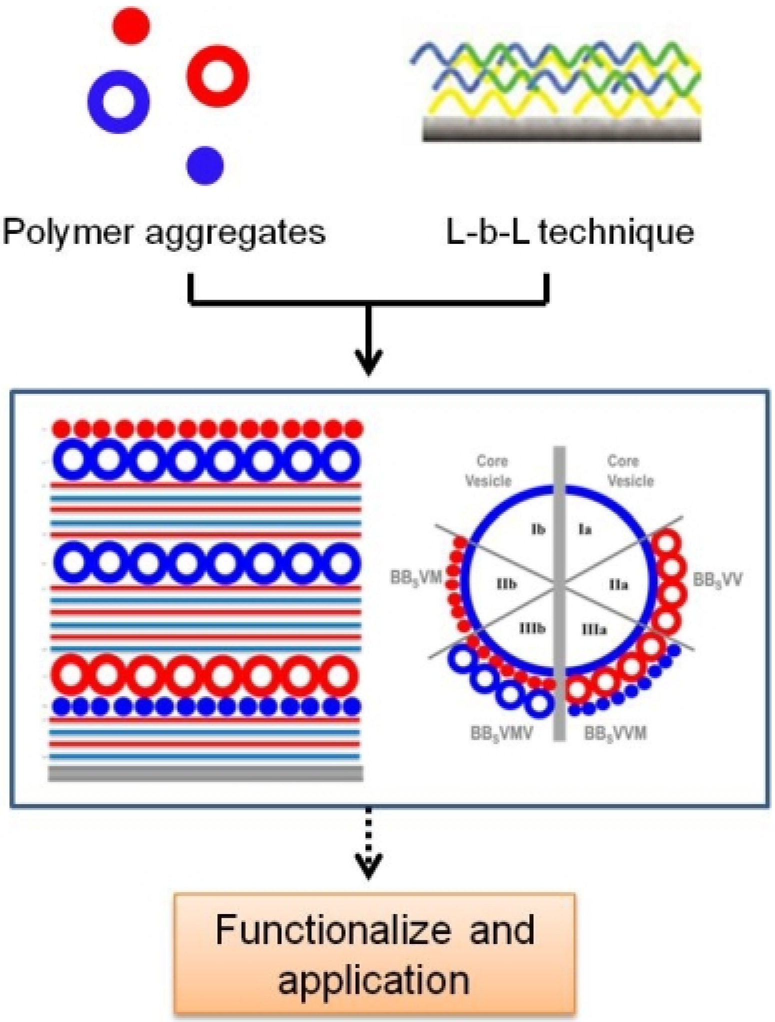


COLL 255

Layer-by-layer assembly of amphiphilic diblock copolymer aggregates

Lin Xiao[1,2]*, xiao_forest@yahoo.com, Renata Vyhnalkova*[2]*, Guang Yang*[1]*, Adi Eisenberg*[2]*.Â (1) College of Life Science and Technology, Huazhong University of Science and Technology, Wuhan, Hubei 430074, ChinaÂ (2) Department of Chemistry, McGill University, Montreal, Quebec H3A 2K6, Canada*

Planar and spherical layer-by-layer (LbL) multilayer structures composed of various combinations of sequentially deposited self-assembled layers of individual block copolymer aggregates (vesicles, micelles) with negatively or positively charged corona chains were prepared and characterized. The multilayers consist of the combinations of layers of various charged species: vesicles or micelles of poly(styrene)-b-poly(vinyl pyridine) (PS-b-P4VP) or of poly(styrene)-b-poly(acrylic acid) (PS-b-PAA). The strong interaction between the successive layers is achieved by electrostatic interactions between the oppositely charged aggregate layers. The overall thickness/size of such planar and spherical multilayers can vary depending on the complexity of the structure. Moreover, rather dense layers of aggregates with their original morphologies were achieved compared with the previous studies, and the reason for which was disclosed preliminarily. These novel multilayer structures including the first examples of block copolymer vesicles aggregating onto block copolymer vesicles could potentially be used as carriers for multiple functional components.



COLL 256

Structure-property relationships of polymer surfactants for enhanced oil recovery

Jason A. Mann[1], *jam12@rice.edu, Alexander Rodríguez-Hernández*[1], *Gedeng Ruan*[1], *James M. Tour*[1,2,3]*.Â (1) Department of Chemistry, Rice University, Houston, Texas 77005, United StatesÂ (2) Department of Mechanical Engineering and Materials Science, Rice University, Houston, Texas 77005, United StatesÂ (3) Smalley Institute for Nanoscale Science and Technology, Rice University, Houston, Texas 77005, United States*

Primary extraction of crude oil obtains less than half of a reservoir's total oil. Increasing worldwide energy demand has driven increased interest in enhanced oil recovery (EOR), which will provide access to two to three times more oil from each well. However, the efficiency and economic viability of current EOR technologies have prevented their industry wide implementation. Surfactant polymer flooding uses a

complex mixture of small molecule surfactants and macromolecular viscosifiers to mobilize trapped oil and enhance fluid control. However, these methods often require additives to achieve the ultra-low oil-water interfacial tensions required to mobilize trapped oil, and thus require substantial formulation. To overcome this limitation we have leveraged controlled radical polymerization to develop a modular synthesis of polymer surfactants, allowing us to study the structure-property relationships associated with ultra-low interfacial tension.

COLL 257

Understanding bacterial adhesion: For design of materials to control biofouling

Sumedha Sharma, *sumedha.sharma1@gmail.com, Jacinta C Conrad.Department of Chemical and Biomolecular Engineering, University of Houston, Houston, Texas 77204, United States*

Rational design of anti-fouling surfaces for applications in oil recovery and transport, water treatment and healthcare requires preventing bacterial adhesion as a critical first step towards reducing biofilm formation. Conversely, applications in bioenergy such as biological fuel cells may require promoting attachment of cells to surfaces. Controlling bacterial attachment for all such applications requires fundamental understanding of bacteria-surface interactions and adhesion mechanisms. We investigate the attachment behavior of *Escherichia coli* on silanized glass surfaces during flow through a linear channel at flow rates of 0.1—1 mL/min using confocal microscopy. We deposit self-assembled monolayers of organosilanes on glass and track the position and orientation of bacteria deposited on these surfaces during flow using high-throughput image processing algorithms. We find significant difference in deposition and mode of attachment of cells as a function of surface chemistry and surface energy. We find that the deposition rate is higher and cells move less on cationic surfaces than on a neutral surface of comparable surface energy. Deposition on a neutral surface is comparable to that on an unmodified glass surface. The localized angular displacement on unmodified glass and non-cationic surfaces indicates that the cells are tethered via bacterial appendages. Our results suggest that for cationic surfaces, electrostatic interaction is a dominant mechanism of attachment while for non-cationic surfaces, appendage driven mechanism emerges as the dominant one.

COLL 258

Computational study of surface assembly of anisotropic nanoparticle dimers

Blake A Wilson, *blake.wilson@utdallas.edu, Irving C Tsou, Steven O Nielsen.Chemistry, University of Texas at Dallas, Richardson, Texas 75080, United States*

Formation and controlled growth of ordered phases on a surface is of great interest in electronics research and development. Although the self assembly of many different nanoparticle systems have been extensively studied, advances in nanoparticle synthesis techniques over the past decade have allowed for the creation of ever more complex multi-meric nanoparticle units, such as dimers, trimers, and tetramers. The surface self assembly of these relatively new types of structures have yet to be well characterized. Our work focuses on charged nanoparticle dimers using molecular simulation techniques. We anticipate that a unique combination of size and charge anisotropy within nanoparticle dimers will lead to interesting ordered phases on a surface. Computational study and characterization of these systems will lead to a better understanding of the interactions which could drive surface assembly within multi-meric nanoparticle systems.

COLL 259

Site-directed nanochelators for reversing metal-induced protein aggregation

***Marilyn R. Mackiewicz**, mackiewi@pdx.edu, Molly Clifton.Department of Chemistry, Portland State University, Portland, OR 97201, United States*

The cognitive decline in Alzheimer's disease (AD) resulting from neuronal cell death has no cure, identified cause, or early diagnoses. With patient care estimated at >$604 billion/year globally, there is strong motivation to develop early diagnostics and therapeutics. According to the “metal hypothesis of AD”, metals such as Fe^{II}, Cu^{II}, Zn^{II}, and Al^{III} bind to beta amyloid (Aβ) peptides to form oligomers and aggregates that deposit in the form of senile plaques. These metallated-Aβ species disrupt membranes or undergo redox cycling aerobically in the presence of $Cu^{I/II}$ or $Fe^{III/II}$ and a reducing agent to generate reactive oxygen species (ROS). The resulting oxidative stress leads to weakened synaptic cell signaling and neuronal cell death. However, depending on the experimental conditions and type of beta amyloid aggregate; inhibitory effects have been observed. For example, Cu^{II} ions are known to inhibit aggregation and fibrillation by Zn^{II} ions. Consequently, a better understanding of how metals induce aggregation is crucial. Despite these contradictory studies, the most convincing evidence that suggest there is a link between metal ions and Aβ comes from chelation studies showing clinical improvement of patients with AD. These studies demonstrate that metal chelation is a sound disease modifying strategy. While chelators are effective *in vitro,* there are associated toxicities *in vivo*, >98% fail to cross the blood brain barrier (BBB), and very few target metallated-Aβ. Site-directed metal specific chelators that cross the BBB is of significant interest. Therefore, we will present a new class of chelators with a modified architecture to target metallated-Aβ. These chelators templated on gold nanoparticles that can be used as a vehicular platform to improve delivery across the BBB and metal capture. Fluorescence anisotropy, dynamic light scattering, and the localized surface plasmon resonance band of gold nanoparticles will demonstrate the utility of these nanochelators to reverse metal-induced aggregation.

COLL 260

Nanochelators for sensing and targeting iron in cancer cells

***Tan Nguyen**, tan7@pdx.edu, Marilyn R Mackiewicz.Department of Chemistry, Portland State University, Portland, OR 97201, United States*

Despite rapid advances in early diagnostics and treatments, cancer remains one of the most deadly diseases killing over 1500 Americans each day. These are the driving forces for new cancer therapies and diagnostics. Cancer begins with accumulation of mutations in DNA causing a normal cell to transform into a proliferating tumor cell. The resulting unregulated cell growth is governed by disruption in reactive oxygen species (ROS) and iron (Fe) homeostasis that are carefully managed in normal cells. Iron catalyzes Fenton reactions to produce ROS that damage DNA and other biomolecules leading to carcinogenesis. While high levels of ROS are detrimental to the cell, it also stimulate oncogene c-Myc allowing tumor cells to adapt to high levels of ROS enhancing cell proliferation. While the mechanisms of Fe homeostasis and the effects of ROS species are not well understood, these species are excellent molecular targets. The most convincing evidence supporting iron depletion as a disease modifying strategy comes from studies showing that chelators have significant antiproliferative properties reducing tumor growth through Fe chelation. Unfortunately, chelators also bind to Fe in normal cells presenting a similar challenge to traditional chemotherapy where the administered drug affects the whole body leading to toxicity. To minimize the effects on healthy cells site-directed iron chelators are needed. In addition, iron-chelates that produce ROS to kill cancer cells are also of significant interest. Therefore, we will discuss the design of a new class of site-directed iron chelators using a gold nanoparticle platform. We will demonstrate that these chelators have high iron uptake using dynamic light scattering, and the localized surface plasmon resonance of gold nanoparticles. In addition, using a fluorophore-label we will show that nanochelators can detect metal ions at low concentrations. These nanochelators will serve as a platform for developing optical chelating agents and metal sensors.

COLL 261

Paper-based colorimetric sensor for sensitive and selective detection of 2,4,6-trinitrotoluene

***Shantelle I Hughes**, shanihu2@gmail.com, Samuel S. R. Dasary, Hongtao Yu.Chemistry and Biochemistry, Jackson State University, Jackson, MS 39217, United States*

Colorimetric sensors on patterned paper or plastic have been developed as the least expensive, user-friendly alternative to conventional analytical instrumentations. Despite the rapid progress, significant advancements are still necessary to achieve highly sensitive detection of a broad range of chemical targets. In this approach, a charge tranbsfer complex strategy for the recognition of 2,4,6-trinitrotoluene (TNT) is adopted using 3-aminopropyltriethoxy silane (APTES). TNT selectively forms an intense red complex when mixed with aminosilanes and the color intensity is directly proportional to TNT concentration. The UV-Vis spectrum of the complex shows a strong peak around 530 nm. The amine terminated silane slides/glass fiber filter paper form an active site

for TNT binding, resulting in a sharp color change from white to intense red color. Due to the absence of the charge transfer complex in the other nitroaromatics, this test is highly selective. Selectivity tests against other nitroaromatics, such as picric acid, 2,4-dinitrotoluene, and 4-nitrophenol, showed no interference with TNT. The color intensity of the paper sensor increased with increasing TNT concentration and was later quantified using simple color intensity quantification software. Since TNT and its degradation products enter environmental water and soil, liquid phase samples were tested. TNT concentration as low as 1 µM in spiked samples and 5 µM in environmental samples could be repeatedly tested without any difficulty. The paper sensor is rapid and it took less than 5 minutes for the color development and color scanning. The coating and preparation of the filter papers as sensor platforms was carried out in toluene medium and inert atmosphere.

COLL 262

Studies of MgO and ZnO clusters and nanoparticles: Nucleation and growth by sonochemical method synthesis

***Anthony Lopez Collazo**, ejferrer@ponce.inter.edu, Carolina Pellicier, Angel G. Colon Santiago, Joseph Gonzalez Gonzalez, Eulalia Medina Perez, Edmy J Ferrer Torres.Department of Science and Technology, Interamerican University of Puerto Rico, Ponce, Puerto Rico 00715, Puerto Rico*

Synthesis of ZnO and MgO nanoparticles was done using sonochemical method. Colloidal and powder nanoparticles were obtained using zinc sulfate hydrate and magnesium chloride as zinc and magnesium sources respectively. Tetramethyl ammonium was employed as a surfactant. Polyvinyl Alcohol (PVA) and Polyethileneglycol (PEG) were used as stabilizers. Characterization, following synthesis, was done using optical spectroscopy (Ultraviolet Spectroscopy), Infrared Spectroscopy (FT-IR), X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). Kinetics studies were done to further information on nucleation and growth. These studies include changes in: reactants concentrations, sonication time and titration rate and heating time. Optical studies show the formation of the clusters and the nanostructures. The absorption bands for the nanostructures formation were centered in 358 nm for ZnO nanoparticles and 335 nm for MgO nanoparticles.

COLL 263

Interaction of phenol with ZnO(1010) and (0001) surfaces

***Mark F DiTusa**[1], mditus1@gmail.com, Chad A Thibodeaux[2], Matthew C Patterson[1], Orhan Kilzilkaya[3], Richard L Kurtz[1], Phillip T Sprunger[1], Erwin D Poliakoff[2].Â (1) Department of Physics and Astronomy, Louisiana State University, Baton Rouge, LA 70803, United StatesÂ (2) Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, United StatesÂ (3) Center for Advanced Microstructures and Devices, Baton Rouge, LA 70808, United States*

The electronic and structural properties of phenol adsorbed on ZnO(10$\underline{1}$0) and (0001) surfaces has been studied both experimentally and computationally. The motivation of this study is to understand how environmentally persistent free radicals (EPFRs) are formed in nature. Metal oxides particles such as ZnO and TiO_2 are known to create EPFRs when exposed to chemicals such as phenol and catechol. The research attempts to better understand the underlying mechanism of EPFR formation on metal oxides, and corresponding electron transfer/reduction, by probing the atomic and electronic properties of chemisorbed species as a function of dose and annealing temperature. Based on prior EPR measurements, it is known that phenol forms free radicals when exposed on ZnO power at elevated temperatures (> 400 K). In the current study, phenol was dosed onto single-crystal ZnO(10$\underline{1}$0) (non-polar surface) and ZnO(0001) (solely zinc terminated) surfaces under UHV conditions at differing temperatures. The samples were examined with low energy electron spectroscopy (LEED) and electron energy loss spectroscopy (EELS) both before and after dosage with phenol. LEED shows that the phenol created a c(2x2) superstructure on the surface of the ZnO(10$\underline{1}$0) at 300 K. Electronic EELS confirms phenol's presence. When physisorbed (100 L) at 96 K, EELS reveals the $\pi \rightarrow \pi^*$ at 6.5 eV is nearly unperturbed from the phenol gas phase value (6.68 eV). However, at temperatures between 300 and 500 K, the $\pi \rightarrow \pi^*$ transition of phenol shifted down by 0.5 eV due to a collapsed HOMO-LUMO gap. This reflects a perturbation of the electronic properties associated with chemisorption that varies slightly depending upon crystallographic surface. Ongoing calculations (Gaussian/TD-DFT) will also be presented along with vibrational properties. These tests help to better elucidate the propensity of radical formation and stabilization on these metal-oxide surfaces.

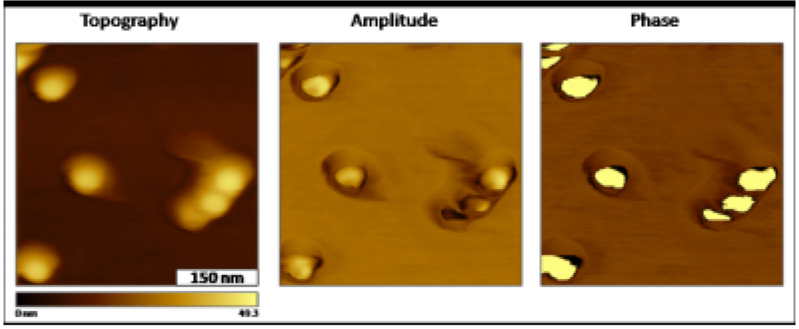
COLL 264

Subsurface imaging of the metal cores of polymer coated cobalt nanoparticles with force modulation microscopy

Steve M Deese[1]*, sdeese1@lsu.edu, Lauren E Englade-Franklin*[1]*, Lawrence J Hill*[2]*, Jeff Pyun*[2]*, Julia Y Chan*[3]*, Jayne C Garno*[1]*.Â (1) Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, United StatesÂ (2) Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ 85721, United StatesÂ (3) Department of Chemistry, University of Texas at Dallas, Richardson, TX 75080, United States*

The force modulation microscopy (FMM) mode of scanning probe microscopy is often used to characterize hard and soft regions of heterogeneous polymer films. The FMM mode can acquire information of the mechanical properties of samples along with information of topography. Phase and amplitude images are acquired simultaneously with topography frames that sensitively disclose fine details of the surface morphology. For FMM, the scanner is operated in contact-mode while the sample stage is driven to vibrate. For our investigations, a home-built FMM sample stage was constructed with a piezoactuator located underneath the sample to drive the sample vibration. The magnitude and frequency of vibration can be controlled according to selected parameters of the driving AC signal. As the tip is scanned in contact with the vibrating

surface, the force applied by the probe is modulated according to the hardness or softness of sample domains. When characterizing core-shell nanoparticles of cobalt encapsulated within a film of polystyrene, we found that the hard core of the metal nanoparticles could be sensitively imaged using FMM at resonant frequencies. Essentially, FMM enabled discrimination of subsurface features of polymer-coated cobalt nanoparticles. Particle lithography was applied for preparing samples to organize the arrangement of nanoparticles into circular rings on surfaces of Si(111). Successful FMM characterizations were achieved reproducibly for nanoparticle samples with exquisite resolution at the level of individual nanoparticles measuring 30 nm in diameter.



COLL 265

Antimicrobial activity of enhanced antibiotics mixed with MgO, and CuO nanoparticles

Raul Aleno Torres, *ejferrer@ponce.inter.edu, Mariel del Rosario Baez Miranda, Anthony Lopez Collazo, Jamie Ann Velez Castro, Marangelie Feliciano, Eulalia Medina Perez, Lourdes Diaz Figueroa, Edmy J Ferrer Torres.Science and Technology, Interamerican University of Puerto Rico, Ponce Campus, Ponce, Puerto Rico 00715, Puerto Rico*

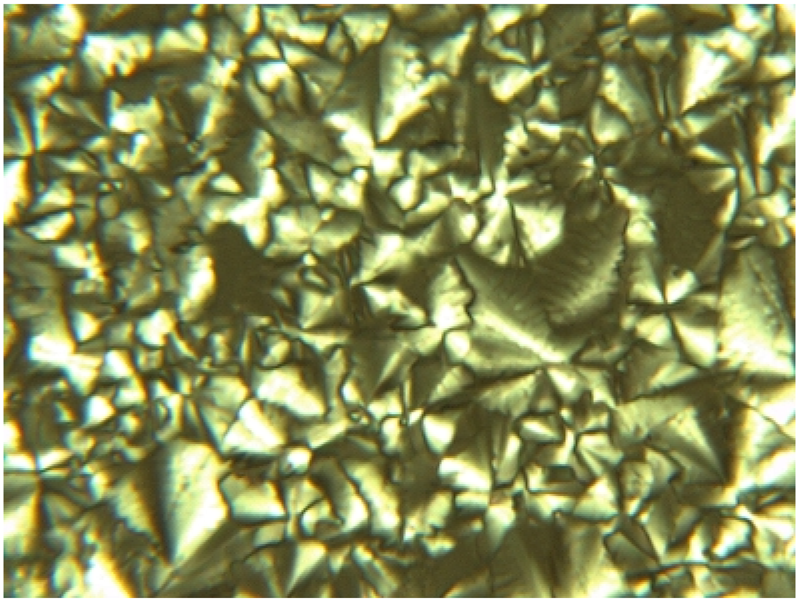
Resistance of bacteria to antimicrobial agents leads to the increase of strongest bacteria strains capable of causing dangerous infections. Scientists are challenged creating new antibiotics for bacteria that continuously increase their resistance. Nanotechnology provides innovative alternatives for treatments. This study shows the antimicrobial effects of enhanced antibiotics with MgO and CuO nanoparticles. Our goal is to develop more effective treatments against resistant bacteria, and nosocomial infections, developing new enhanced antimicrobial agents using nanoparticles. Three antibiotics, Gentamicin, Ciprofloxacin, and Cephalexin, at two different concentrations were used against *Escherichia coli* (ATCC # 10536), *Staphylococcus aureus* (ATCC # BAA-1026), and *Pseudomonas aeruginosa*. (ATCC # 10145). Our results revealed the impact of specific concentrations of antibiotics comparing to concentrations of antibiotics mixed with nanoparticles.

COLL 266

Synthesis and characterization of the theromotropic properties of polymerizable catanionic surfactants

***Kanika Marwaha**, joser@uhd.edu, Robin Jose, Bonnie Flowers, Cynthia A Quiñones, Troy A Cather.Natural Sciences, Universty of Houston Downtown, Houston, TX 77002, United States*

Two novel polymerizable catanionic surfactants were prepared from (12-Acryloyloxydodecyl)trimethylammonium bromide with sodium bis(2-ethylhexyl)sulfosuccinate (AOT) and sodium dodecylbenzenesulfonate (SDBS), respectively. Their structures and purities were established using a combination of techniques involving Fourier Transform Nuclear Magnetic Resonance (FTNMR) and elemental analyses. Characterization of their thermotropic properties using Thermo Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) show that these molecules have high thermal stabilities and are ionic liquids. Presence of acrylate group reduces their isotropization temperature compared to the non polymerizable counterpart. Furthermore, Polarized Light Microscopy (PLM) done on these molecules shows them existing as liquid crystals at room temperature. Polymerized samples show different mesomorphism than the monomeric surfactants and did not show liquid crystallinity at room temperature.

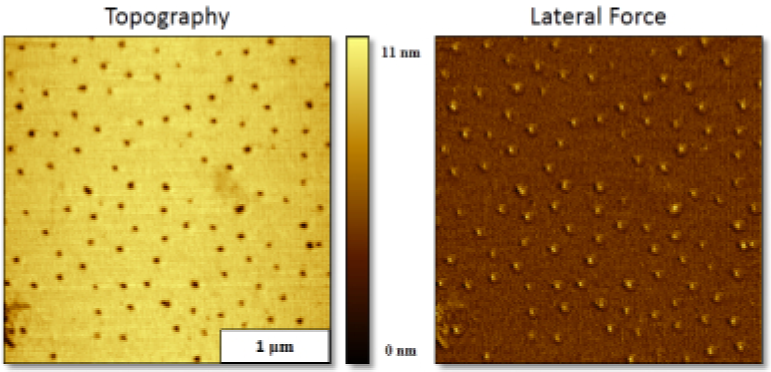


COLL 267

Nanostructures of organosilanes prepared on Si(111) using particle lithography: Characterizations with atomic force microscopy

***Cody N Leegwater**, cleegw1@tigers.lsu.edu, Zachary L Highland, ChaMarra K Saner, Phillip C Chambers, Jayne C Garno.Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, United States*

There are not many tools available for making patterns at the nanoscale, however particle lithography requires only a few basic chemistry steps with a centrifuge, lab oven and inexpensive glassware. Expensive equipment such as lasers, electron or ion beams and cleanrooms were not needed for making exquisitely small patterns. Approaches with particle lithography were used to prepare nanopatterns of organosilanes with designed packing densities. Different strategies were used with octadecyltrichlorosilane (OTS) and 2-[methoxy(polyethyleneoxy)propyl] trichlorosilane (PEG-silane). To accomplish particle lithography the substrates were coated with size-sorted latex or silica mesospheres. The mesospheres provide a surface mask for protocols using vapor-phase deposition or an immersion procedure. The surface mask of mesoparticles was removed by steps of rinsing and sonication. Organosilane molecules self-assemble in areas of the substrate that were not protected by the mesospheres to form nanopatterns. Samples were characterized with atomic force microscopy (AFM) to evaluate parameters of surface coverage, height, and periodicity. Precise local measurements of the heights of nanostructures were obtained with AFM cursor profiles. Exposed areas of Si(111) that were protected by the mesospheres provided millions of regularly-arranged nanoscopic sites that can be used for further chemical reactions. Organosilane nanostructures of OTS and PEG-silane provide a hydrophobic resist for further patterning steps with nanoparticles, polymers or proteins. Example AFM images of nanostructures will be presented to illustrate the versatility and reproducibility of particle lithography procedures.

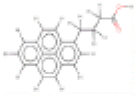


COLL 268

Molecular dynamics study of the interface between polyaromatic hydrocarbons (PAH's) and graphene: Insights into the aqueous dispersion mechanism of graphene

***Elias Gebremedhn Azene**[1], EliasGebremedhn.AZENE@umons.ac.be, Liping Chen[1], Andrea Minoia[1], Andrea Schlierf[2], Vincenzo Palermo[2], David Beljonne[1].Â (1) Department of Chemistry, University of Mons, Mons, Hainaut 7000, BelgiumÂ (2) Department of FUNCTIONAL ORGANIC MATERIALS for Hi-Tech applications, ISOF – National Research Council, Bologna, Italy*

Amphiphilic compounds such as polyaromatic hydrocarbons (PAH's) with hydrophilic side chains are widely used, as surfactants, in liquid-phase graphene exfoliation method.[1,2]Whereas, understanding the PAH-graphene interface and the mechanism of the exfoliation process is very helpful for designing surfactants with enhanced effects, little is known in this regard. In this work, the interface between graphene and pyrene compounds with systematic pattern of functionalization was studied, theoretically, using force field methods. We have compared the relative conformation, in ethanol and vacuo, of pyrene compounds with long-chain polar side-groups on graphene surface. We show that in vacuo, the functional side groups interact with the surface to form a mixture of conformations, while in ethanol they are fully desorbed from the surface and hang in the solvent medium. We have also studied the adsorption mechanism of pyrene-based pH-indicator dyes (pyrene sulfonates), on the surface of graphene, in aqueous medium. When the pyrene core is highly functionalized with sulfonate, local minima were observed on the adsorption free energy profiles, which correspond to a metastable conformation in which the molecules are in an edge-on interaction with the surface. In addition, the more the number of functional groups, the more the pyrene core is engulfed and becomes less accessible. This reduces the attractive dispersive interaction of the core with the surface and the hydrophobicity of the molecule, resulting in lower adsorption free energy. But this situation is also dependent on the pattern of functionalization; in the case when two corners of the core bear sulfonates, higher dipole moment and adsorption free energy were found than for the case only one corner is functionalized. Our results demonstrate the role of polar groups vs. aromatic cores in suspension stabilization and how the extent and pattern of functionalization affects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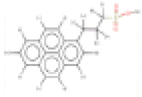
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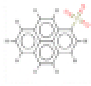
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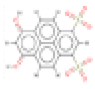
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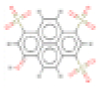
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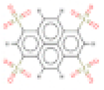
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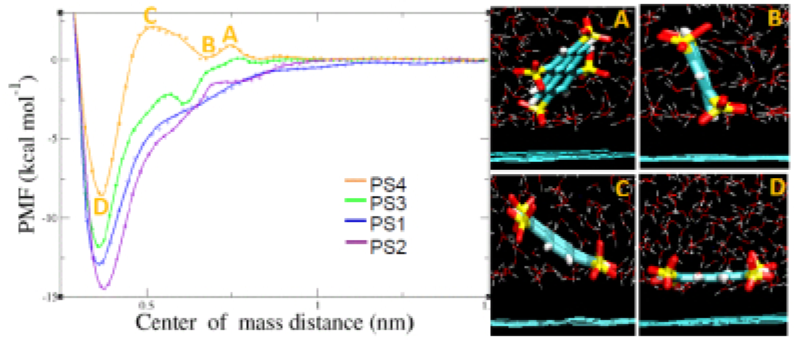

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COLL 269

Multiplex detection of DNA using silicon photonic microring resonators via electrostatic functionalization

Stephanie N. Lankford[1,2]*, slankford@monmouthcollege.edu, Richard M. Graybill*[1]*, Ryan C. Bailey*[1]*.Â (1) Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United StatesÂ (2) Department of Chemistry, Monmouth College, Monmouth, IL 61462, United States*

Silicon photonic microring resonators are a newly established platform for sensitive, multiplexed (128 sensors/chip), label-free, and real time detection of biomolecular binding. Recently, our group has shown the ability of silicon photonic microring resonators to quantitatively detect DNA, miRNA, mRNA, and proteins . These biosensors are capable of having a significant impact on science and medicine, especially in a clinical setting, due to the inherent efficiency, cost (<$1/assay), and scalability of each trial.

Here we present a novel microring chip functionalization protocol which will decrease analysis time and complexity by replacing covalent linkage between the capture strand and sensor surface with electrostatic interactions. Ultimately, this will be applied to detect asymmetric PCR products to quantitate the expression levels of multiple mRNA (30+) relevant to glioblastoma multiforme, a lethal brain tumor.

COLL 270

Assembly of 2D highly-ordered arrays of nanoparticle dimers directly on a substrate

Maria T. Perez Cardenas, *materesa@umd.edu, Melissa Meyerson, Zhihong Nie.Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, United States*

Two dimensional array (2D) of metal nanoparticles (MNPs) are of great interest in the field of energy, optoelectronics, and biosensing because of their intrinsic optical properties such as localized surface plasmon resonance. Top-down techniques such as electron beam lithography and vapor deposition are commonly used to fabricate highly ordered 2D array of MNPs. Though these techniques offer superior flexibility and precision in arranging MNPs directly on a substrate, they are complex and expensive. In order to incorporate nanostructures into functional devices, it is imperative to create an effective, reproducible, and economic method to manipulate the systematic arrangement of nanostructures patterning, alignment, and orientation on a substrate. We developed a method to fabricate highly ordered 2D arrays of dimers of MNPs with different compositions, sizes, and shapes directly on a substrate in a controlled manner. This method involves i) the assembly of MNPs into 2D array with hexagonal packing directly on a substrate via solvent evaporation process, ii) the selective removal of thiol ligands from the top surface of MNPs by selective etching process without deteriorating the 2D array, and iii) the subsequent assembly of other MNPs on top of the 2D array through functional linkers or electrostatic interactions. MNPs with different sizes can be readily integrated into the arrays to produce dimers with controlled symmetry. The distance between dimer islands can be precisely controlled by tuning the ligands on the MNP surface. This is a simple, and low-cost, general method for generating high-quality arrays without the need of sophisticated and expensive instruments. Scanning electron microscopy and atomic force microscopy were used to study the morphology of the nanostructures as well as the topology of the 2D array of MNP dimers. This highly ordered array of dimers may find applications in *surface-enhanced Raman scattering* signal detection, photovoltaic devices, and photonic crystals.

COLL 271

Preparation and characterization of $Sn_{1-x}Fe_xO_{2-\delta}$ fibers, powders, and films

Juan M Rodriguez[1], Amanda J Watson[1], Ildeman Abrego[1], Jose Ardinsson[2], Carlos Samudio[3], ***Eleicer A Ching[1]****, eleicer.ching@utp.ac.pa.Â (1) Department of Natural Science, Technological University of Panama, Panama, Panama, PanamaÂ (2) Development Center of Nuclear Technology, Federal University of Minas Gerais, Minas Gerais, Bello Horizonte, BrazilÂ (3) University of Passo Fundo, Passo Fundo, Porto Alegre, Brazil*

Transparent and conducting tin oxide is of great interest due to their potential technological applications, such as: gas sensors, energy conversion, catalysts and others. Appropriate doping can further enhance the conductivity of the SnO_2 material with little loss of transparency. Isolated tin iron oxide ($Sn_{1-x}Fe_xO_{2-d}$) fibers with x(%)= 0, 2, 4, 6, 8 and 10 were prepared by electrospinning technique. Anhydrous $SnCl_4$, $FeCl_3$, different alcohols, chloroform and PEO polymer were used as precursor materials.

Appropriate mixture of these reagents defines the deposition solution. The samples were deposited on glass substrate and annealed at 500^o C. The fibers are characterized by scanning electron microscopy (SEM), impedance spectroscopy and temperature dependence current-voltage measurements. The results are presented and discussed, including a transport phenomenal model simulation.

The homogeneous fibers with diameter between 2 to 10 mm were used with sensor purpose. Thus, water vapor sensor responses were also measured and the experimental results are tested using the Freundlich isotherms model.

Also, powder and films deposited on glass substrate were prepared with the same fiber deposition solution and annealed at 500^o C. The samples were structurally characterized by Raman spectroscopy, Mossbauer spectroscopy, and X-ray diffraction (XRD). The results indicate the formation of SnO_2 rutile structure with iron ions occupying two different sites, where one of them is related to oxygen vacancy nearest neighbor.

COLL 272

TCO-SnO_2 thin films prepared by spray pyrolysis technique

Héctor Miranda[1], ***Amanda J Watson***[1]*, amanda.watson@utp.ac.pa, Ildeman Abrego*[1]*, Carlos Samudio*[2]*, Jose Ardinsson*[3]*, Eleicer Ching-Prado*[1]*.Â (1) Department of Natural Science, Technological University of Panama, Panama, Panama, PanamaÂ (2) University of Passo Fundo, Brazil, Porto Alegre, BrazilÂ (3) Development Center of Nuclear Technology (CDTN), Federal University of Minas Gerais, Bello Horizonte, Brazil*

Spray pyrolysis technique was used to deposit thin films of Tin oxide (SnO_2) on glass substrates using as precursor $SnCl_2.2H_2O$ solution. The samples were prepared for different thickness at annealing temperature of 500°C for 2 hours. The film thickness was controlled with the different numbers of sprayed.

The surface of the films was characterized morphologically by Scanning Electron Microscopy (SEM). The characterization by X-Ray Diffraction showed well defined bands that indicate a SnO_2rutile phase.

Propriety optical studies were made by comparing UV-Visible transmittance spectra of the different films and Van der Pauw of four-point technique was used for the electrical measurements. The optical and electrical parameters permitted to calculate: the band gap, refractive index, film resistance and figure of merit, in order to evaluated Transparent Conductive Oxide (TCO) properties. Film thicknesses were obtained from fringes features in the transmittance spectra.

COLL 273

Giving molecules the squeeze: Self-assembled monolayers as model boundary lubricants in nanoasperity contacts

***Bradley W Ewers**, bewers@tamu.edu, James D. Batteas.Department of Chemistry, Texas A&M University, College Station, Texas 77842, United States*

Self-assembled monolayers (SAMs) have been considered as lubricants in a variety of systems, including bound and vapor phase lubricants in Microelectromechanical Systems devices (MEMS) and as boundary lubricant additives in traditional oil based lubricants. Their friction response however is not well understood, showing unique load dependence depending on surface morphology, environment, and load regime. Understanding the nature of SAM friction response has widespread implications, not only are they often used as boundary lubricants, they provide insight into the natural friction response of sliding interfaces, where adsorbed species and tribofilms formed during sliding act as boundary lubricants, similarly altering their friction and wear characteristics. Molecular Dynamics Simulations of SAMs of octadecyltrichlorosilane on silica nanoasperities were employed to study the redistribution of pressure in contacts as the SAMs are introduced, examining the load bearing of the film and the redistribution of pressure in the contact plane. Methods were developed to map the contact pressures into the 2-dimensional contact plane, to which continuum contact models could be fit for determination of commonly considered parameters like contact area and peak contact pressures. Dependence on surface packing density of the film and morphology of the contact were studied, providing insight into the evolution of contact characteristics from dry to boundary lubricated conditions. As the packing density of silane SAMs are known to vary with surface morphology and film formation conditions, this also provides perspective on the various friction responses observed. Furthermore, through isolation of the mechanical characteristics of SAMs in asperity contacts, it is possible to evaluate the vast body of knowledge of the frictional characteristics of SAMs in terms of both contact area and load dependent parameters, and to understand the relationship and interplay between these parameters that determines the overall friction response.

COLL 274

Poly (DL-lactide Co-glycolide) acid and PLGA/chitosan nanoparticles with entrapped lutein: Stability and antioxidant activity

***Toni T Borel**[1], tborel1@tigers.lsu.edu, Meocha Whaley[1], Cristina M Sabliov[1], Zhimin Xu[2], Yixiao Shen[2].Â (1) Department of Biological and Agricultural Engineering, Louisiana State University, Baton Rouge, LA 70803, United StatesÂ (2) Department of Food Science, Louisiana State University, Baton Rouge, LA 70803, United States*

Polymeric nanocarriers improve stability, solubility, and functionality of entrapped nutraceuticals. The hypothesis of this study is entrapping lutein, a hydrophobic antioxidant, in different polymeric nanoparticles (NPs) will improve its stability and antioxidant activity. The following objectives are proposed: 1. Synthesize and

characterize polymeric nanoparticles of poly lactic co-glycolic acid (PLGA) and PLGA NPs covered with a layer of chitosan (PLGA/Chi) from a physicochemical perspective, and 2. Assess functionality of the entrapped lutein as a function of type of polymer in which entrapped. Nanoparticles were synthesized by emulsion evaporation method. Characterization included size, zeta potential, and morphology measurement, followed by testing physical and chemical stability, and antioxidant activity of entrapped lutein. PLGA NPs loaded with lutein were in the size range of 119.2 nm ± 0.98 nm with a PDI of 0.17± .02 and a zeta potential of – 29 mV ± 1.1 mV in nanopure water. PLGA/Chi NPs loaded with lutein were in the size range of 145.9 ± .3 nm with a PDI of 0.25 ± .009 and a zeta potential of 21.2 mV ± 2.3 mV in nanopure water. PLGA NPs loaded with lutein were stable in the gastric environment for four hours as indicated by a constant size over time; in the intestinal environment particles were stable for 24 hours. PLGA and PLGA/Chi NPs protected the chemical stability of lutein in water for 72 hours. Lutein entrapped in PLGA and PLGA/ Chi NPs inhibited cholesterol oxidation to 7-ketocholesterol up to 86% after 24 hours and 65% after 72 hours while unentrapped lutein inhibited cholesterol oxidation by only 45% after 24 hours and 19% after 72 hours. These results support the hypothesis that PLGA NPs are enhancing stability and antioxidant activity of entrapped lutein and may find beneficial applications in biomedical and food science fields for delivery of lutein.

COLL 275

Synthesis and characterization of gold – copper bimetallic nanoalloys

Asantha C Dharmaratne, *acdharma@go.olemiss.edu, Amala Dass.Department Chemistry and Biochemistry, University of Mississippi, University, Mississippi 38677, United States*

The manipulation of elemental composition of nanoalloys or nanomaterials has led to invaluable discoveries with potential future applications. The properties of molecular gold nanoparticles can be modified upon successful copper doping. Such thiolate protected gold-copper nanoalloys would have drastic changes in properties such as electronic and catalytic in contrast to monometallic gold nanocluster itself[1]. Here we report a one phase synthesis to form gold-copper nanoclusters and propose probable sites for incorporation of copper atoms into the thiolate protected gold nanocluster. Mass spectrometric studies illustrate the foreign atom incorporation by the mass to charge ratio difference between two neighboring peaks. By adopting various separation techniques such as solvent fractionation, gold-copper nanoclusters can be isolated and characterized. $Au_{144-x}Cu_x(SR)_{60}$ alloy nanomolecules were synthesized and characterized by using ESI-MS and optical spectroscopy.

COLL 276

Synthesis of PbS quantum dots using thioacetamide as a sulfur source

***Alexander L. Morris**, greg.vanpatten@mtsu.edu, Amanda D. Evans, Morgan Brewer, Hannah Alsup, P. Gregory Van Patten.Department of Chemistry, Middle Tennessee State University, Murfreesboro, TN 37132, United States*

Thioacetamide (TA) has previously been reported by other authors as a sulfur source in the preparation of PbS quantum dots (QDs). Thioacetamide is stable, non-volatile, easy to handle safely, and inexpensive. However, in spite of these advantages, thioacetamide has been much less widely used than other precursors like hexamethyldisilathiane (HMDS) and sulfur/oleylamine (S/OA) mixtures. We examine here the utility of thioacetamide as a sulfide precursor for the preparation of high quality PbS QDs, and report a general procedure that yields highly luminescent QDs whose size and band gap energy can be tuned over a relatively wide range in the near infrared. These particles are easy to isolate, have moderately narrow size distributions, are highly soluble in non-polar organic solvents, and show strong band edge photoluminescence. We have characterized these PbS QDs using optical spectroscopy, TEM, and x-ray diffraction. Size tunability, size distributions, and PL quantum yields will be reported. In addition, the relative advantages and drawbacks of the PbS QD products obtained from the various sulfur sources (TA, HMDS, and S/OA) will be described.

COLL 277

Detailed study of Pb(II)/Cd(II) cation exchange reactions in PbS quantum dots

***Amanda D. Evans**, greg.vanpatten@mtsu.edu, Alexander L. Morris, Hannah Alsup, Morgan Brewer, P. Gregory Van Patten.Department of Chemistry, Middle Tennessee State University, Murfreesboro, TN 37132, United States*

Cation exchange reactions are a powerful tool for post-synthetic modification of semicondutor quantum dots (QDs). Partial and complete cation exchange reactions have previously been documented in multiple II-VI and IV-VI QD systems. Partial cation exchange is one approach to encapsulating QDs with a protective, inorganic shell material, while both partial and complete exchange can yield materials that are difficult or impossible to synthesize directly from molecular precursors. In this contribution, we study in detail the exchange of Pb(II) ions by Cd(II) ions under various reaction conditions. Factors such as reaction temperature, identity of the counter ion, QD size, and exclusion of air have been examined, and their effects are reported here. The effect of these factors on the composition, atomic distribution (core/shell vs. alloyed), and electronic structure of the resulting QDs will be reported. The data suggests that the particle size and reaction conditions can allow us to tune the core/shell system continuously between a type I and type II electronic structure.

COLL 278

Photochemistry of adsorbed nitrate formed from nitric acid adsorption on α-Fe_2O_3 particle surfaces: The role of adsorbed water in the formation of reduced nitrogen surface species

Charith E Nanayakkara[1], *charitheranga-nanayakkara@uiowa.edu, Pradeep M Jayaweera*[2], *Gayan Rubasinghege*[1], *Jonas Baltrusaitis*[3], *Vicki H Grassian*[1]*.Â (1) Department of Chemistry, University of Iowa, Iowa City, Iowa 52246, United StatesÂ (2) Department of Chemistry, University of Sri Jayewardenepura, Nugegoda, Sri LankaÂ (3) Faculty of Science and Engineering, University of Twente, Enschede, The Netherlands*

The surface photochemistry of nitric acid (HNO_3) adsorbed on hematite (α-Fe_2O_3) particle surfaces under different environmental conditions has been studied. Surface product formation and photochemistry of adsorbed nitrate is investigated using X-ray photoelectron spectroscopy (XPS). Adsorbed nitrate, formed from gas phase nitric acid adsorption, shows N1s peak at 407.4 eV. Upon irradiation with light (λ > 300 nm), the coverage of nitrate decreases, as indicated by the decrease in the peak at 407.4 eV, and there is the appearance of two lower binding energy peaks in the N1s region at 401.7 eV and 400.3 eV when the photolysis is done under low to moderate relative humidity conditions. The formation as well as the stability of these reduced nitrogen species, identified as NO^- and N^-, is further investigated as a function of water vapor pressure. Additionally, irradiation of adsorbed nitrate on α-Fe_2O_3 generates three nitrogen containing gas-phase products including NO_2, NO and N_2O as evident by FTIR spectroscopy. As shown here, different environmental conditions of water vapor pressure and the presence of molecular oxygen greatly influence the relative product distribution of gas-phase and surface-bound species. The atmospheric implications of these results are discussed.

COLL 279

Mixtures of a novel sulfoxide-based surfactant with various anionic surfactants

Khanh Ho, *khanh.t.ho@ou.edu, Guangzhe Yu, Brian Grady.Department of Chemical, Biological and Materials Engineering/Institute of Applied Surfactant Research, University of Oklahoma, Norman, OK 73019, United States*

The synergistic interaction parameter (β) according to Rubingh's one parameter model for nonideal mixtures was quantitatively determined for a novel sulfoxide-based nonionic surfactant and different anionic surfactants including sodium dodecyl benzene sulfonate, sodium dodecyl sulfate, andSteol CS-460. The critical micelle concentration was determined using surface tension measurements for each surfactant as well as their mixtures at different molar ratios. All mixtures exhibited synergism in mixed micelle formation with β parameter values in the range from -2 to -5, which is the range commonly found for anionic-nonionic mixtures.

COLL 280

Electrochemical behavior of micelle-solubilized ferrocene: A simple procedure to calculate the aggregation numbers of micellized cationic surface-active ionic liquids

***Omar A El Sreoud**, elseoud@usp.br, Paula D Galgano, Drochss P Valencia, Mauro Bertotti.Institute of Chemistry, University of SÃ£o Paulo, SÃ£o Paulo, SÃ£o Paulo, Brazil*

The micellar diffusion coefficient, $D_{\mathbf{mic}}$, is a fundamental property of surfactant aggregates in water. Its value sheds light on the changes in micellar structure as a function of experimental variables. From $D_{\mathbf{mic}}$, the micellar hydrodynamic radius, $R_{\mathbf{H}}$, hence aggregation number, $N_{\mathbf{agg}}$, can be calculated. We employed voltammetry with platinum disc microelectrodes (Autolab PGSTAT 30 potentiostat; 25 °C) to determine $D_{\mathbf{mic}}$ in water for a series of surface-active ionic liquids, SAILs, 1-R-3-methylimidazolium chloride; R = $C_{\mathbf{12}}$, $C_{\mathbf{14}}$, and $C_{\mathbf{16}}$. We employed ferrocene as electroactive probe, due to its very low solubility in water (9.8×10^{-6} mol/L), and high affinity for the micelle (association constant with CTABr = 1738). Consequently the contribution of the free, i.e., unbound probe can be neglected. We have calculated $N_{\mathbf{agg}}$ as a function of the length of (R) by the following sequence: (i) The limiting currents for the reversible electron transfer to the micelle-bound probe were calculated at different [SAIL] and extrapolated to the critical micelle concentration (determined by conductivity) to give $D_{\mathbf{mic}}$; (ii) $R_{\mathbf{H}}$ was calculated from $D_{\mathbf{mic}}$ by using the Stokes-Einstein equation; (iii) $N_{\mathbf{agg}}$ was calculated from $R_{\mathbf{H}}$, based on the monomer volume and spherical micellar geometry. We calculated the following $N_{\mathbf{agg}}$: 48, 79, 105 for R = $C_{\mathbf{12}}$, $C_{\mathbf{14}}$, and $C_{\mathbf{16}}$, respectively; these agree with the values calculated from light-scattering, 50, 76, 96, respectively (Galgano, El Seoud, J. Colloid Interface Sci. 2011, 361, 186). This application of microelectrodes has the merit of simplicity and low cost; no additional electrolyte is needed, e.g., as in light scattering

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COLL 281

Preconcentration and removal of chromium species using lysine functionalized magnetic iron nanoparticles

***Michael O Eaves**, eaves@email.uscupstate.edu, Anselm I Omoike.Department of Chemistry, Natural Sciences and Engineering Division, University of South Carolina Upstate, Spartanburg, South Carolina 29303, United States*

Magnetic iron nanoparticles (Fe_3O_4) were synthesized using co-precipitation method with aqueous Fe^{+2} and Fe^{+3} under alkaline conditions. Lysine was immobilized onto the surface of the magnetic iron nanoparticles and the nanoparticles were characterized using Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA). The removal of chromium species from water using lysine functionalized

magnetic iron nanoparticles (MNP) was investigated at Cr(VI) concentrations ranging from 0-80 ppm, and varying pH values (3.0, 4.0, and 7.0). The MNPs removed 77%-100% of Cr(VI) in the pH range studied. The potential application of the lysine functionalized magnetic iron nanoparticles for selective solid phase speciation and preconcentration of Cr (III) and Cr (VI) species in real matrices will be presented.

COLL 282

Coal derived antioxidant carbon nanoparticles

Alexander Rodríguez-Hernández[1], *ar58@rice.edu, Ruquan Ye*[1], *Jason A. Mann*[1], *Errol L.G. Samuel*[1], *Thomas A. Kent*[4,5,6], *James M. Tour*[1,2,3]*.Â (1) Department of Chemistry, Rice University, Houston, Texas 77005, United StatesÂ (2) Department of Mechanical Engineering and Materials Science, Rice University, Houston, Texas 77005, United StatesÂ (3) Smalley Institute for Nanoscale Science and Technology, Rice University, Houston, Texas 77005, United StatesÂ (4) Department of Neurology, Baylor College of Medicine, Houston, Texas 77030, United StatesÂ (5) Department of Neurosurgery, Baylor College ofMedicine, Houston, Texas 77030, United StatesÂ (6) Michael E. DeBakey VA Medical Center, Houston, Texas 77030, United States*

High levels of reactive oxygen species (ROS) are associated with a number of diseases including stroke, traumatic brain injury, heart disease, and chemotherapy-induced hearing loss. Numerous small-molecule and biologically derived antioxidants have been developed including vitamin E, poly(ethylene glycol) functionalized superoxide dismutase, and fullerene derivatives. However, these antioxidants are limited in both their rate and capacity to consume ROS. Here we present the synthesis and characterization of antioxidant carbon nanoparticles derived from coal. Oxidation of coal using nitric acid produces non-toxic, water soluble nanoparticles whose size is readily varied by altering the coal source as well as the synthetic conditions. These heavily oxidized graphitic nanoparticles show size-dependant fluorescence and exhibit excellent antioxidant activity *in vitro* in brain endothelial cells.

COLL 283

Ligand exchange reactions on $Au_{38}(SR)_{24}$ gold nanomolecules

Arun Jakkam, *jakkam.arun@gmail.com, Praneeth Reddy Nimmala, Amala Dass Antonysamy.Chemistry and Biochemistry, University of Mississippi, Oxford, MS 38655, United States*

Gold nanomolecules have wide range of applications in the field of catalysis, sensing, drug delivery. Gold nanomolecules contain precise number of gold atoms and ligands. These materials show size dependent optical and electrochemical properties. Gold nanomolecules comprise of metallic core and ligands. The core is responsible for the optical and electrochemical properties. Properties like solubility, functionality and reactivity are governed by the ligands in the monolayer. Using ligand exchange

experiments, the composition of the monolayer can be modified, there by altering the properties of the nanomolecule, which is very essential for developing potential applications like drug delivery, diagnosis and sensors. In the present work, ligand exchange of $Au_{38}SR_{24}$ with 7-mercapto-4-methyl coumarin was performed and monitored by mass spectrometry. UV-Vis spectroscopy was used to determine the effect on optical properties after ligand exchange. The resulting mixed monolayer nanomolecules comprising of 7-mercapto-4-methyl coumarin will be further analyzed by fluorescence spectroscopy.

COLL 284

Low-temperature approach to highly-emissive copper indium sulfide colloidal nanocrystals and their bio-imaging applications

***Jianying Ouyang**, Jianying.Ouyang@nrc-cnrc.gc.ca.Emerging Technology, National Research Council Canada, Ottawa, Ontario K1A 0R6, Canada*

We report our newly-developed low-temperature synthesis of colloidal photoluminescent (PL) $CuInS_2$ nanocrystals (NCs) and their *in vitro* and *in vivo* imaging applications. With diphenylphosphine sulphide (SDPP) as a S precursor made from elemental S and diphenylphosphine, this is a noninjection based approach in 1-dodecanethiol (DDT) with excellent synthetic reproducibility and large-scale capability. For a typical synthesis with copper iodide (CuI) as a Cu source and indium acetate ($In(OAc)_3$) as an In source, the growth temperature was as low as 160 °C and the feed molar ratios were 1Cu-to-1In-to-4S. Amazingly, the resulting $CuInS_2$ NCs in toluene exhibit quantum yield (QY) of ~23% with photoemission peaking at ~760 nm and full width at half maximum (FWHM) of ~140 nm. With a mean size of ~3.4 nm (measured from the vertices to the bases of the pyramids), they are pyramidal in shape with a crystal structure of tetragonal chalcopyrite. *In situ* ^{31}P NMR (monitored from 30 °C to 100 °C) and *in situ* absorption at 80 °C suggested that the Cu precursor should be less reactive toward SDPP than the In precursor. For our in vitro and in vivo imaging applications, $CuInS_2/ZnS$ core-shell QDs were synthesized; afterwards, dihydrolipoic acid (DHLA) or 11-mercaptoundecanoic acid (MUA) were used for ligand exchange and then bio-conjugation was performed. Two single-domain antibodies (sdAbs) were used. One was 2A3 for *in vitro* imaging of BxPC3 pancreatic cancer cells. The other was EG2 for *in vivo* imaging of a Glioblastoma U87MG brain tumour model. The bio-imaging data illustrate that the $CuInS_2$ NCs from our SDPP-based low-temperature noninjection approach are of good quality.

COLL 285

Functionalization of vicinal silicon surfaces: Insight into Si nanoparticle reactivity

***Willliam DeBenedetti**[2], william.debenedetti@utdallas.edu, Mat D Halls[2], Yves J. Chabal[1].Â (1) Materials Science, The University of Texas at Dallas, Richardson, Texas*

75080, United StatesÂ (2) Department of Materials Science and Engineering, Schrodinger Inc., CA, United States

Semiconductor nanoparticle (NP) surface chemistry has long been recognized as central to the development and optimization of opto-electronic devices (based on NPs photoluminescence properties). Much attention has been directed to group II-VI quantum dots (QDs) for a variety of targeted applications, although their toxicity renders them incompatible with biological systems. Consequently, there is a renewed interest in nanostructured silicon that is more compatible with existing technology and biologically friendly. Silicon NPs are capable of exhibiting high quantum yield emission and are considered environmentally adventitious compared to current Cd or Pb alternatives, but the origin of Si NP photoluminescence remains elusive. A significant advantage of using Si NPs is the ability to covalently modify their surface rather than employing datively bound ligands that can over time lead to aggregation, i.e. loss of opto-electronic properties. Though covalent surface modification of Si NPs has been realized, the mechanism of hydrosilylation at defect sites (steps) remains unknown, suggesting that work on model step surfaces could bring much needed insight. Herein we report the functionalization of vicinal silicon (111) surfaces with both monohydride and dihydride step edges using a 9^{o} off orientation in the (-1-12 &11-2) directions, respectively. Two reactions are studied as a function of immersion time on both model surfaces: i) thermal hydrosilylation with a terminal alkene (known to be concerted on flat surfaces) and ii) nucleophilic addition using small molecule (methanol). It is found that the nucleophilic system reacts preferentially at the step edge forming a bridge complex between the bridge and lower terrace hydrogen atoms, while the alkene reacts with all terrace and step (mono- and di-hydride) sites. Such selectivity opens the door for nanopatterning and provides important insight into the behavior of Si NPs.

COLL 286

Enhanced killing of multidrug resistant bacteria using silver nanoparticles combined with antibiotics

***Danielle A McShan**, dmcshan1981@yahoo.com, Hongtao Yu.Department of Chemistry and Biochemistry, Jackson State University, Jackson, MS 39217, United States*

Antibiotics resistant infections are becoming an increasing threat around the world. Each year in the United States alone, at least 2 million people acquire serious infections caused by bacteria that are resistant to one or more of the antibiotics designed to treat those infections. Silver nanoparticles (AgNP) have been shown to have effective antibacterial activity against a wide range of disease-causing bacteria. However, it is not practical to use AgNP as the main antibiotic agent. We therefore present data on the antibacterial effect of combined AgNP with one of the selected known antibiotics, tetracycline, enoxacin, neomycin, penicillin and kanamycin, at their minimum inhibitory concentration. Multidrug resistance bacteria strain DT104 was exposed to 0.5 to 12 µM of an antibiotics combined with 50 µM AgNP (10-50 nm) for 30 min or 2 hr. Results indicate a dose and time dependent killing enhancement of tetracycline and enoxacin

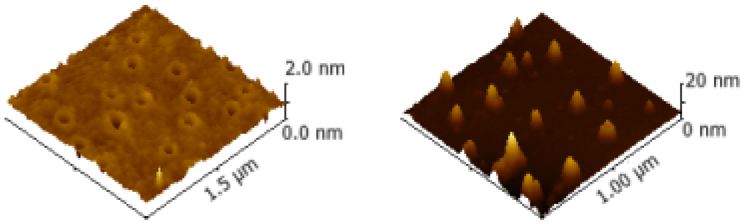
combined AgNP at doses as low as 0.5 µM for 2 hr. Kanamycin and neomycin/ AgNP combination only enhanced at 4 µM at 2 hr. Penicillin/AgNP showed no enhancement effect at both 30 min and 2 hr exposure time points. Our results suggest that combination of commonly used unresponsive antibiotics with AgNP increase their antimicrobial effectiveness over extended exposure times, implying that this combined treatment is a potential way to kill drug resistant pathogens.

COLL 287

Self-polymerization of 4-(chloromethyl)phenyltrichlorosilane within spatially-confined sites of Si(111) investigated in selected solvents

Phillip C Chambers[1]*, pchamb3@tigers.lsu.edu, Zorabel M Lejeune*[2]*, Lu Lu*[1]*, Jayne C Garno*[1]*.Â (1) Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70806, United StatesÂ (2) Department of Chemistry, Our Lady of the Lake College, Baton Rouge, Louisiana 70808, United States*

The surface assembly of 4-chloromethylphenyltrichlorosilane (CMPS) within exposed sites of nanopores was investigated in selected solvents to gain insight of the mechanism of self-polymerization. Our strategy was to prepare a test platform of nanoholes to confine the surface assembly of CMPS to discrete sites of Si(111) for the reaction to proceed. Areas surrounding the nanoholes were passivated with a methyl-terminated film, to prevent non-specific attachment of CMPS throughout the surface. Platforms of nanoholes were fabricated within a film of octadecyltrichlorosilane (OTS) using immersion particle lithography. After OTS nanopores were successfully prepared and characterized using atomic force microscopy (AFM) the samples were immersed in solutions of CMPS prepared with selected solvents (toluene, dichloromethane, bicyclohexane). The substrates were then removed at certain intervals to compare the growth of CMPS nanostructuctures over time according to the nature of the solvent. Analysis of AFM images provided quantitative information of the surface self-assembly reaction. Pillar nanostructures of CMPS with different heights and diameters were produced exclusively within the exposed nanopore areas of the Si(111) substrates. Throughout the reaction, the surrounding matrix of OTS did not show evidence of CMPS growth; the surface assembly of CMPS was strictly confined within the nanopores. The heights of CMPS nanostructures indicate that multilayers were formed, with taller columns generated after longer immersion times. These experiments demonstrate new directions for using particle lithography to study surface reactions at the molecular-level.



COLL 288

Atomic structure of thiolate-protected gold alloy molecules

Chanaka K Kumara, *ckkumara@go.olemiss.edu, Amala Dass.Department of Chemistry and Biochemistry, University of Mississippi, University, Mississippi 38677, United States*

Thiol protected gold molecules inherit interesting optical, electrochemical properties and catalytic activity along with their high stability. Metal heteroatom incorporation in to these gold nanomolecules leads to the modulation of electronic structure and enhanced catalytic activity. However, it is interesting to know, where these heteroatoms are incorporated into the gold molecules. It may lead to intermix or core-shell type alloy molecules. While some predictions based on theoretical/ computational calculations exist, there is a lack of experimental evidence for the location of the dopant atoms. In the current work, we present the experimental evidence for possible location of these heteroatoms using atomic structural analysis based on X-ray diffraction. $Au_{25-x}Ag_x(SR)_{18}$ and $Au_{38-x}Ag_x(SR)_{24}$ alloys were synthesized and atomic structures were analyzed using X- ray diffraction. Unlike the 25 and 38 metal atom count alloy molecules, $Au_{144-x}Ag_x$ show interesting optical properties upon alloying. Maximum silver atom incorporations was found to be 60 experimentally, which implies silver incorporations into the 60 atom shell of the predicted three shell $Au_{144}(SR)_{60}$ structure.

COLL 289

Controlled self-assembly of molecular and nanoparticle amphiphiles into patterned hybrid vesicles

Yijing Liu[1], *yliu1214@umd.edu, Yanchun Li*[2], *Jie He*[1], *Kaleb Duelge*[1], *Zhongyuan Lu*[2], *Zhihong Nie*[1]*.Â (1) Department of Chemistry& Biochemistry, University of Maryland College Park, College Park, MD 20742, United StatesÂ (2) State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun, Jilin 130023, China*

Polymer/inorganic nanoparticle (NP) hybrid materials have attracted tremendous attention, because of their properties arising from both inorganic materials (i.e., inherent optical, electrical, and magnetic properties) and from polymers (i.e., biocompatibility and processability). One way to create such hybrid structures is to incorporate inorganic NPs into the polymeric vesicular membranes. In order to meet the rising demand of new materials, it is critical to generate assembled structures with increasing complexity and fundamentally understand the assembly process. Particularly, assemblies with controllable surface patterns increase the complexity of the structures, while introducing new functionalities. However, to date, it still remains a grand challenge in synthesizing hybrid vesicles with controllable surface patterns.

Here we report a simple strategy to the assembly of hybrid vesicles with surface patterns by controlling entropy-driven lateral phase separation of molecular and nanoparticle amphiphiles (NPAs) within vesicular membranes. The binary assembly produced hybrid vesicles with various morphologies including spherical and non-spherical Janus-like vesicles, patchy vesicles, and heterogeneous vesicles. The different morphologies arise from the delicate interplay between the mismatch of the chain lengths of the two amphiphiles, the entanglement of polymer chains, and the diffusion rate of NPAs. Particularly, the entropic attraction between NPAs plays a dominant role in controlling the phase-separation and arrangement of two amphiphiles in the membranes. Remarkably, this strategy allows the preparation of hybrid Janus vesicles with intriguing non-spherical shapes. The use of NPAs in concurrent assembly not only significantly enlarges the library of tunable parameters (i.e., bending modulus, rigidity, and dimension) that are unattainable by molecular building blocks, but also enables us to effectively modulate the optical, electronic, and magnetic properties of the assembled structures. We envision that the controlled assembly of binary building blocks offers a powerful tool to develop novel hybrid nanostructures with new functionalities and applications.

COLL 290

Water soluble ultra small glutathione stabilized gold nanomolecules

Kothalawalage N Kothalawala, *knkothal@go.olemiss.edu, James L West, Amala Dass.Department of Chemistry and Biochemistry, University of Mississippi, University, MS 38677, United States*

Polydisperse mixtures of organo-thiolate capped gold nanomolecules with distinct number of gold atoms like $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$, $Au_{68}(SR)_{34}$, $Au_{102}(SR)_{44}$ and $Au_{144}(SR)_{60}$ have been well characterized and resolved. But there is no clear evidence

that the current synthetic approaches with water soluble ligands will give the same polydisperse, magic numbered nanomolecules in the same size regime as organo thiolates. In this study we show that, it is possible to synthesize a series of magic numbered polydisperse gold nanomolecules protected by a water soluble ligand, glutathione (SG). The nanomolecules are separated by using polyacrylamide gel electrophoresis (PAGE) and size exclusion chromatography (SEC). The separated nanomolecules are characterized by using mass spectrometry, UV-vis spectrometry and transmission electron microscopy. Unique properties such as water solubility, non-toxicity and bio-compatibility of these nanomolecules will lead to potential applications in biomedicine.

COLL 291

Activity and structure of Ni_2P catalysts in hydroconversion of polyaromatic hydrocarbons

***Yong-Su Kim**, yolee@dankook.ac.kr, Ki-Duk Kim, Yong-Kul Lee.Department of Chemical Engineering, Dankook University, Yongin, Gyunggi 448701, Republic of Korea*

Novel Ni_2P catalysts supported on zeolite were prepared and applied for tar-oil hydrocracking to maximize the BTX yield. Since the tar-oil derived from coal contains heterocyclic compounds like nitrogen, oxygen, sulfur compounds must be pre-treated to remove the heterocyclic compounds that can act as a catalytic poison. Pre-hydrotreating followed by hydro-cracking was thus adopted to convert tar-oil into BTX. As for the pre-hydrotreatment at different LHSV's with time on stream over the Ni_2P/SiO_2 catalysts, tetralin fraction increased from 31% to 40 % according to the increase of LHSV's. In contrast, decalin fraction decreased from 10% to 1%. The following hydrocracking of pre-hydrotreated tar-oil was conducted at 3.0MPa, 623K and 648K with varying LHSV's 1.0–3.0hr^{-1} in a fixed bed reactor over Ni_2P/zeolite catalysts, resulting in high selectivity of BTX by 61% at 648K. These results thus demonstrate that Ni_2P/zeolite catalysts significantly promote the hydrocracking of tar-oil.

COLL 292

Chlorogenic acid-reduced silver nanoparticles: Green synthesis, characterization, and excellent antibacterial activities against Pseudomonas aeruginosa

***Youmie Park**[1,2], youmiep@inje.ac.kr, Sang Hui Jun[1], Hyun-Seok Kim[2], Seonho Cho[2].Â (1) College of Pharmacy, Inje University, Gimhae, Gyeongnam 621-749, Republic of KoreaÂ (2) National Creative Research Initiatives (NCRI) Center for Isogeometric Optimal Design, Seoul National University, Seoul, Republic of Korea*

Chlorogenic acid (CGA, a caffeic acid ester of quinic acid) is a secondary phenolic metabolite in plants and is one of the well-known polyphenol compounds. There is approximately 70-350 mg of CGA in one cup of coffee. The beneficial effects of CGA itself, extracts containing CGA and coffee on human health include anti-oxidant, anti-inflammatory, anti-arthritic, anti-thrombotic, cholesterol-lowering, neuroprotective, anti-hypertensive, and chemopreventive activities. In the present report, CGA is employed as a reducing agent for the green synthesis of silver nanoparticles (AgNPs). The successful synthesis of CGA-AgNPs is confirmed by the characteristic surface plasmon resonance band at 415 nm in UV-Visible spectra. The reaction yield is 95.43% measured by inductively coupled plasma mass spectrometry. The average diameter is estimated to be 19.29 ± 8.23 nm. Mostly spherical- and irregular-shaped NPs are observed from the images of high resolution transmission electron microscopy and atomic force microscopy. From Fourier transform infrared spectra, the -C=O functional group of GCA are possibly involved in the coordination or complexation into AgNPs. CGA-AgNPs exert a superior antibacterial activity against two strains of *Pseudomonas aeruginosa* (minimum inhibitory concentration of 0.66 µg/mL) which is comparable to a standard antibiotic. The current green approach is easy to process and does not require any noxious chemicals as a reducing agent. The results suggest that biologically-active compounds from plant origin are capable of being a powerful reducing agent for the green synthesis of AgNPs.

COLL 293

Oriented assembled TiO_2 hierarchical nanowire arrays with a fast electrontransport property

***Xinjian Feng**, xjfeng2011@sinano.ac.cn.Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou, China*

Fast charge transport in the TiO_2 network is essential for effective charge collection, particularly in solid state cells where recombination is very fast. In order to increase the electron mobility, substantial efforts have been focused on developing one dimensional (1-D) TiO_2 (polycrystalline nanotube and single-crystalline nanowire) electrode materials for solar cells application. However, their surface area is much smaller than that of NP films, which will negatively impact the devices' overall performance. We report a facial seedless approach to fabricate orientated assembled 3D branched nanowire arrays on transparent fluorine doped tin oxide (FTO) glass substrate. The nano-branches grow epitaxially from specific crystal planes of the primary NW arrays. The as-prepared 3D B-NW arrays architecture offers high surface area, rapid charge transport property (comparable to 1D single crystal NW), and significantly improved photovoltaic device performance. orientation, to significantly improve the electrical transport properties of other oxide materials that currently have limited utility in solar cell and related applications because of their low carrier mobility.

COLL 294

Formation and hydrogenation of atomic N on Pt(111)

Zhu Liang[1]*, zliang4@uic.edu, Hyun Jin Yang*[2]*, Junepyo Oh*[2]*, Yousoo Kim*[2]*, Michael Trenary*[1]*.Â (1) Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60607, United StatesÂ (2) Surface and Interface Science Laboratory, RIKEN, Wako-shi, Saitama 351-0198, Japan*

The surface morphology and the reaction properties of chemisorbed N on a Pt(111) surface has been studied at the atomic level with low temperature scanning tunneling microscopy (LT-STM). At high coverages, two phases, p(2×2)-N and (√3×√3)R30°-N, are found to coexist at temperatures between 360 and 400 K. For both phases nitrogen occupies fcc-hollow sites. At temperatures of 400 K and slightly above, only the p(2×2)-N phase is present on the surface. At temperatures above 420 K, nitrogen starts to desorb. The p(2×2)-N phase shows a honey-comb structure in STM images with three nitrogen and three platinum atoms forming a six-member ring. At low coverages, incomplete (2×2) patches of N, but no (√3×√3)R30° structure, are observed on the surface. When N and O are coadsorbed on the surface, they form a mixed (2×2) overlayer of N+O at high coverages. N and O can be clearly distinguished from each other by their appearance in the STM images.

After exposing the N-covered surface to hydrogen gas, NH molecules were found to occupy fcc-hollow sites, while H atoms occupy atop sites. Manipulated by the STM tip, dissociation of NH bond and lateral transition of H are observed, and in both cases the response of the motion against applied bias voltage were measured. The threshold voltages of NH dissociation and H lateral transition were found to be around 440 mV and 270 mV, correspond to the excitation energy of N-H stretching and the Pt-H stretching modes, respectively. Substitution of H by D results in an isotope shift of -30 mV and -23 mV of the threshold voltages for ND dissociation and D lateral transition, respectively. Based on the above findings, we conclude that both processes are vibrationally induced.

COLL 295

Enhanced fluorescence of nano-colloid and its application on a targeted immunofluorescence labeling

***Hyong-Jun Kim**, hkim@kongju.ac.kr.Department of Chemical Engineering, Kongju National University, Cheonan, Republic of Korea*

Fluorescent materials are used in various fields to investigate a biological mechanism of a cell. The fluorescence labeling, as one of the analytical techniques, is commonly used to probe the structure of living cells. The fluorescence materials currently used in these fields are generally either organic molecules or inorganic semiconductors. Organic materials possess a serious drawback of the fluorescence quenching and inorganic materials have critical cyto-toxicity problem when used in a bio cell. Thus, many need new fluorescent material to overcome these problems. We developed a new fluorescent material to overcome these problems by introducing a heterocyclic structure of excited-state intramolecular proton transfer since the molecular structure showed remarkable

photophysical property and anticipate it is applied in the fluorescence labeling. Quinoline/THF solution is injected to the diacetylene vesicles of diameter of few 100 nm. As expected, synthesized quinoline nano assembly has the fascinating optical property.

COLL 296

Enhancing enzyme stability by construction of polymer-enzyme conjugate micelles for decontamination of organophosphate agents

Nisaraporn Suthiwangcharoen, *nisaraporn.suthiwangcharoen.ctr@mail.mil, Ramanathan Nagarajan.Molecular Sciences and Engineering Team, Natick Soldier Research, Development and Engineering Center, Natick, MA 01760, United States*

Enhancing the stability of enzymes under different working environments is essential if the potential of enzyme-based applications is to be realized for nanomedicine, sensing and molecular diagnostics, and chemical and biological decontamination. In this study, we focus on the enzyme, organophosphorus hydrolase (OPH) which has shown great promise for the non-toxic and non-corrosive decontamination of organophosphate agents (OPs). We describea facile approach to stabilize OPH using covalent conjugation with the amphiphilic block copolymer, Pluronic F127, leading to the formation of F127-OPH conjugate micelles, with the OPH on the micelle corona. SDS-PAGE and MALDI-TOF confirmed the successful conjugation, and transmission electron microscopy (TEM) and dynamic light scattering (DLS) revealed ~100 nm size micelles. The conjugate micelles showed significantly enhanced stability and higher activity compared to the free OPH when tested (i) in aqueous solutions at room temperature, (ii) in aqueous solutions at higher temperatures, (iii) after multiple freeze/thaw treatments, (iv) after lyophilization, and (v) in the presence of organic solvents. The F127-OPH conjugate micelles also decontaminated paraoxon (introduced as a chemical agent simulant) on a polystyrene film surface and on a CARC (Chemical Agent Resistant Coating) test panel more rapidly and to a larger extent compared to free OPH. We speculate that because the F127-OPH conjugate micelles allow higher local concentration and confinement of the OPH, they reduce the potential for enzyme denaturation and provide robustness to OPH at different working environments.

COLL 297

Interaction of gold nanoparticles with supported lipid bilayers

Terri A Camesano, *terric@wpi.edu, Elaheh Kamaloo, Christina Bailey, Kellie Waterman.Department of Chemical Engineering, Worcester Polytechnic Institute, Worcester, MA 01609, United States*

The rapid growth and development of engineered nanomaterials coupled with an extensive material base has led to increasing incorporation into consumer products, such as sunscreens and cosmetics, as well as drug delivery agents. In both of these types of applications, nanoparticles come into contact with the membranes of human

cells. Our research is geared towards understanding the properties of nanoparticles that influence their interaction with a cell membrane. The focus of this study is to determine the nano-specific (physical) properties, including size and functionalization of a gold nanoparticle, and to determine how these properties affect the interaction of gold nanoparticles with a supported lipid bilayer (SLB) composed of L-α-phosphatidylcholine (egg PC), which was used as a model cell membrane. For the size experiments, we examined gold nanoparticles that were 2, 5, 10 and 40 nm gold nanoparticles. Analysis of nanoparticle-cell membrane interactions was done using a quartz crystal microbalance with dissipation, which measures the frequency (***f***)and dissipation (**D**) changes directly associated with mass and conformation changes of the SLB. Different overtones for *f* and D allow for theoretical interpretation of changes correlated to different layers of the membrane. Gold nanoparticles on the size order of ≤5 nm promoted a more rigid membrane whereas gold nanoparticles ≥10 nm gave a more flexible membrane. None of the sizes and concentrations tested completely disrupted the cell membrane. In another portion of the study, we examined the role of chemically-functionalized 12 nm gold nanoparticles on cell membrane interactions (1-propanethiol, 2-mercaptoethanol, 2-aminoethanethiol, or 3-mercaptopropionic acid). Regardless of hydrophobicity and electrostatic charge, all of the functionalized gold nanoparticles decreased the rigidity of the lipid bilayer by increasing the dissipation and decreasing the mass associated with the adsorbed film. These results help in the design of nanocarriers for drug delivery and consumer applications.

COLL 298

WITHDRAWN

COLL 299

Nanosecond time-resolved studies of gold nanoparticle nucleation

James D Gaynor, *gaynor13@up.edu, Steven G Mayer.Department of Chemistry, University of Portland, Portland, OR 97203, United States*

Fundamental spectroscopic studies of gold nanoparticles (AuNPs) using simple synthetic protocols with highly reproducible AuNP size distributions has facilitated their successful use in applied studies of catalysis, energy storage, and cancer treatment. However, our understanding of nanoparticle (NP) nucleation - which largely controls the size, shape, and desired properties of the NP – is still in the nascent stages. Few studies of NP nucleation mechanisms are reported in the literature and these papers cite the lack of experimental techniques to directly measure NP nucleation, thereby resulting in contradictory mechanisms being published in the literature. Fast (10^{-9}s) and ultrafast ($\leq 10^{-12}$s) spectroscopic techniques utilize pulsed lasers to obtain light scattering information on timescales sufficient for studying NP nucleation that occurs within the first *micro*- to *milli*seconds of synthesis. We report what we believe is the first demonstration of using a 10Hz, pulsed Nd:YAG laser with a 10 nanosecond pulse width

to measure particle size distributions at 50 nanosecond time intervals during the nucleation period of gold nanoparticles via the citrate-reduction method.

COLL 300

Preferential attachment and surface interaction of amines on modified Si(111) terminations

Tatiana Peixoto[1]*, tati@utdallas.edu, Peter Thissen*[2]*, Yves Chabal*[1]*.Â (1) Department of Materials Science and Engineering, University of Texas at Dallas, Richardson, Texas 75080, United StatesÂ (2) Karlsruhe Institute of Technology, Karlsruhe, Germany*

Silyl amines are of fundamental interest to the microelectronics, biotechnology and nanotechnology communities, with its ability to enhance the tailoring of surface properties. The presence of amine groups aid in additional functionalization of the surface, enabling the attachment of quantum dots, nanoparticles, and biological molecules thus allowing for the development of new surfaces/devices. Despite these advantages, a clear mechanistic understanding of liquid-phase amino group attachment on Si surfaces and its attachment configuration to different surface terminations has not been completely developed.

In this work using wet chemical functionalization, several Si(111) oxide-free terminations (SiH. SiCl and SiF) were reacted with both an anhydrous solution of ammonia in dioxane and neat anhydrous ethylenediamine (NH_2-CH_2-CH_2-NH_2) to achieve amine terminated surfaces. Ethylenediamine reacts with Si-Cl surfaces and attaches in a bridge configuration characterized by the lack of the (NH_2) deformation mode in IR and dominance of the Si-N binding energy in the XPS N1s peak. On the 1/3 Si-F terminated surface it attaches via monodentate termination observed by the (N-H) stretch and deformation modes in IR and the XPS N1s binding energies attributed to Si-N bonds as well as the C-NH_2 unreacted tail. On the Si-H surface only physisorption is observed as evidenced by an undetectable (N-H) stretch and weak deformation mode further confirmed by the peak features present in the N1s peak of XPS.

In contrast, the ammonia solution showed less variability in attachment to the different terminations. High intensity (N-H) stretch and deformation modes attributed to ammonia H-bonding are observed for the SiCl surface with XPS N1s binding energies confirming some attachment to the surface. The 1/3 SiF surface exhibits lower amounts of ammonia H-bonding also confirmed by the N1s peak of the XPS. The SiH surface showed the least amount of ammonia H-bonding via IR with the XPS corroborating this evidence. The ammonia- treated terminations all contained IR modes belonging to the solvent, indicating the solvent could be the cause of the observed ammonia H-bonding on the surface.

In conclusion, there is a clear difference in interaction between the primary amine and its parent molecule, ammonia, thus showing a difference in attachment depending not only on surface termination but also on the chemical environment (ie. dioxane solvent) of the molecule.

COLL 301

Using time evolution of contact angle of evaporating droplets for estimation of chemical agent permeation through barrier materials

***Molly Clay**, Molly.N.Clay.ctr@mail.mil, Rajagopalan Srinivasan, Ramanathan Nagarajan.Molecular Sciences and Engineering Team, Natick Soldier Research, Development & Engineering Center, Natick, MA 01760, United States*

Knowledge of the diffusivity of chemical agents and toxic chemicals through materials is important for the development of barrier materials (for clothing, face masks, gloves, etc) to protect against chemical and biological threats. Robust experimental methods such as immersion testing that are routinely used to measure liquid diffusion into polymer membranes typically require large volumes of the liquid chemicals, and handling such volumes is not desirable because of the extreme toxicity and lethality of many of these compounds. We have used a sessile drop which requires only 1 or 2 ml of liquid volume and have monitored the time evolution of the contact angle of the sessile drop on the surface of candidate barrier materials and also on an impermeable surface. The contact angle-time data were analyzed using approximate analytical methods to estimate the diffusivity of the agent in air (based on contact angle data on impermeable surface) and diffusivity of agent into the barrier material (based on contact angle data on barrier material). We compare the diffusivity estimates for a number of toxic chemicals obtained from the analytical approximation against estimates obtained by other methods in the literature.

COLL 302

Topography and enzymatic activity of bovine serine albumin and carbon nanotube incorporated nanofibers

***Ericka N. J. Ford**, ericka.n.ford.ctr@mail.mil, Nisaraporn Suthiwangcharoen, Paola D'Angelo, Ramanathan Nagarajan.Molecular Sciences and Engineering Team, Natick Soldier Research, Development & Engineering Center, Natick, MA 01760, United States*

To combat the threat of chemical and biological warfare agents, there is currently active research on the use of proteins/enzymes as biosensors and as catalysts in remediation textiles. Protein sensing can result from the enzymatic degradation of analytes to colorful, molecular byproducts. Ultraviolet-visible spectroscopy can be used to monitor these reactions. In this study, biologically active membranes were prepared by the electrospinning technique. Nanofiber meshes were spun from aqueous mixtures of poly(vinyl alcohol), protein esterase bovine serine albumin (BSA), and carbon nanotubes (CNTs)- at ~0.25 weight percent of the polymer. The effects of CNTs and pH of spinning dopes on the topography and activity of BSA fiber mats were investigated.

COLL 303

Characterization of surface-engineered nanoparticles and their assembly

***De-Hao Tsai**, dhtsai@mx.nthu.edu.tw, Jui-Ting Tai, Chao-Shun Lai.Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan Republic of China*

We study ligand-nanoparticle interactions and their assembly processes using a combination of physical [electrospray-differential mobility analyzer (ES-DMA)], microscopic (SEM, TEM), and spectroscopic (FT-IR, ICP-MS) approaches. Silica nanoparticle (SiO_2-NP) and gold nanoparticle (AuNP) are chosen as representatives due to their attractiveness in biomedical applications. Material properties, and the corresponding interactions of nanoparticles with ligands, and/or between the particles, can be obtained through a complementary characterization: ES-DMA provides the information of high-resolution particle size distribution, colloidal stability, and the degree of aggregation of SiO_2-NPs and AuNPs in the media; SEM and TEM are employed to present the morphology of nanoparticles, and the efficiency of the nanoparticle assembly process; ICP-MS and FT-IR are used to investigate the elemental composition and the extent of ligand conjugation on nanoparticle's surface. The binding affinity between SiO_2-NP and AuNP is shown to be tunable, based on a combination of silane treatment on SiO_2-NP's surface plus surface PEGylation to the AuNP. A Brownian dynamic simulation model is employed as support to our experimental work, providing a further fundamental understanding to the process of nanoparticle assembly over different extent of surface functionalization.

COLL 304

Thermally stable molecular self-assembly in an aqueous solution of mixture of anionic surfactant and triblock copolymers

***Zhe Zhang**[1], zhangz2@ornl.gov, Tae-Hwan Kim[2], Changwoo Do[1].Â (1) Biology and Soft Matter Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United StatesÂ (2) Research Reactor Utilization Department, Korea Atomic Energy Research Institute, Yuseong-gu, Daejeon 305353, Republic of Korea*

Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) type triblock copolymers have wide variety of applications in biological, chemical, and pharmaceutical areas. Specifically, thermally stable nano- and meso-structures formed by these triblock copolymers in aqueous solutions have great potential applications in drug delivery systems. Here, we report a molecular self-assembly of triblock copolymers (L62) with anionic surfactant Dioctyl sodium sulfosuccinate (AOT). The microstructures of L62, AOT and their mixtures, as a function of the temperature and concentration, were studied by using small-angle neutron scattering (SANS). While individual components exhibit various nano structures including micelles and lamellar structure,

thermally stable micelle formation was observed with the addition of AOT to L62 solution.

COLL 305

Enhanced cytotoxic activity of LbL coated camptothecin for cancer treatment

Gaurav Parekh[1], *gpa005@latech.edu, Pravin P. Pattekari*[1], *Chaitanya Joshi*[1], *Tatsiana G. Shutava*[1], *Mark A. DeCoster*[1], *Yuri M. Lvov*[1], *Tatyana Levchenko*[2]*.Â (1) Institute for Micromanufacturing and Biomedical Engineering Program, Louisiana Tech University, Ruston, LA 71272, United StatesÂ (2) Department of Pharmaceutical Sciences, Northeastern University, 360 Huntington Ave., Boston, MA 02115, United States*

Encapsulation of poorly soluble anti-cancer drugs in self-assembled nanoshell structure is a promising strategy for efficient delivery via intravenous administration. Stable dispersion of nanoparticles with an average size of 150 nm diameter and drug loading capacity of 60 wt. % was synthesized by using washless layer-by-layer (LbL) assembly to form camptothecin (CPT) cores coated with 8 bilayers of alternating heparin and block-copolymer of poly-L-lysine and polyethylene glycol (PEG). The outermost layer of nanoparticle was covered with PEG of 5 kDa and 20 kDa to resist serum protein adsorption and prolong systemic circulation due to sustained release kinetics. The advantage of LbL coated nanoparticle is to preserve active lactone form of CPT by initial 3.5 bilayers of the shell at acidic pH. Increasing active form of CPT was achieved by incorporation of bovine serum albumin (BSA) along with drug core as compared to the drug itself. In conclusion cytotoxicity activity of LbL coated CPT nanoparticles against *CRL2303* glioblastoma cancer cells was found 20-25% higher than uncoated drug. IC_{50} of CPT was decreased from ca. ~146 nM to ~103 nM after encapsulation of drug using LbL coated nanoshell.

COLL 306

Biocompatible shaped particles from dried multilayer polymer capsules for cellular uptake

Jun Chen[1], *cj1016@uab.edu, Eugenia Kharlampieva*[1], *Veronika Kozlovskaya*[1], *Allison Goins*[1], *Mohammad Saeed*[2], *Javier Campos-Gomez*[2]*.Â (1) Department of Chemistry, University of Alabama at Birmingham, Birmingham, Alabama 35205, United StatesÂ (2) Department of Biochemistry and Molecular Biology, Drug Discovery Division, Southern Research Institute, Birmingham, Alabama 35205, United States*

We present a simple and facile approach to fabricate biocompatible hollow microparticles of controlled geometry undergoing shape-dependent cellular uptake. The hemispherical, spherical and cubical microparticles were obtained by drying multilayer capsules of hydrogen-bonded poly(N-vinylpyrrolidone)/tannic acid $(PVPON/TA)_n$. That shape transformation was controlled by capsule stiffness which was regulated by the layer number, capsule diameter, and PVPON molecular weight. The hemispherical

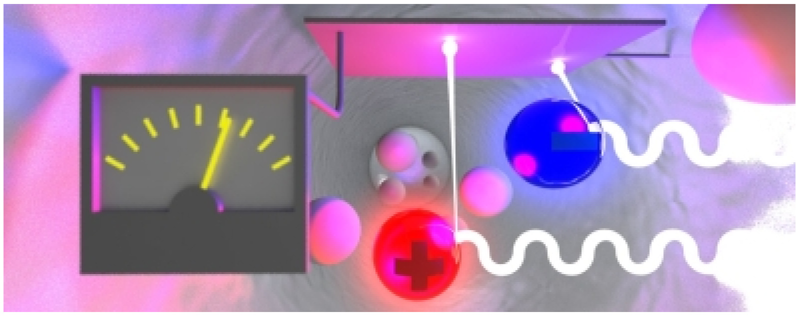
particles were produced from spherical capsules when this ratio was in the range from 0.041 to 0.055. Opening in the hemispherical particles was modulated by the initial shell thickness which was controlled by the number of deposited polymer layers in the initial multilayer shell. We also found that increase in capsule wall thickness prevented cubical and spherical capsules from collapsing upon drying. These structures maintained their three-dimensional shapes in the dry state and upon rehydration. The cell growth and viability studies using human cancer cells showed noncytotoxic properties of the capsules. Finally, we revealed that spherical and hemispherical capsules were internalized by macrophages with the uptake of the hemispherical particles per cell two times more efficient. The method presented here allows for a robust preparation of biocompatible shaped particles whose shape and dimensions can be easily tuned by controlling capsule size and wall thickness. The reported structures can be potentially useful for biomedical applications such as shape-controlled cellular uptake and flow dynamics.

COLL 307

Measure of surface potential at the water-oxide nanoparticle interface by XPS from a liquid microjet

***Matthew A. Brown**[1], matthew.brown@chem.ethz.ch, Jeroen A. van Bokhoven[1,2].Â (1) Institute for Chemical and Bioengineering, ETH Zurich, Zurich, SwitzerlandÂ (2) Swiss Light Source, Paul Scherrer Institute, Villigen PSI, Switzerland*

Gaining molecular level insight into the liquid-solid interface is considered one of the next great challenges for the surface science community. Here we show that the surface potential at a water–oxide nanoparticle (NP) interface, long considered an immeasurable direct quantity, can be measured through apparent binding energy shifts by X–ray photoelectron spectroscopy (XPS) from a liquid microjet. This new method does not require a priori knowledge of the particles' surface structure or of the ion distribution throughout the electrical double layer for its interpretation, and can be applied to any colloidal suspension independent of composition, particle size and shape, and solvent. We demonstrate the application for aqueous suspensions of 9 nm colloidal silica (SiO_2) at pH 0.3 and 10.0, where the surface potential changes from positive to negative, and at pH 10.0 in different cation chloride electrolytes, Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ba^{2+}, and Al^{3+}. The experimental results are compared with calculated surface potentials based on Guoy-Chapman theory, and are shown to be in good agreement.



COLL 308

Cationic oligo(p-phenylene ethynylenes) (OPEs) induce germination of spore-forming *B. atrophaeus*

Harry C Pappas, *hpappas@unm.edu, David G Whitten.Center for Biomedical Engineering, University of New Mexico, Albuquerque, NM 87131, United States*

A wide range of oligo(*p*-Phenylene ethynylenes) has been shown to exhibit good biocidal activity against both Gram-negative and Gram-positive bacteria. In the current studies, the interactions of a specific cationic OPE with spore-forming *Bacillus atrophaeus* are investigated. In agreement with our previous findings, this compound effectively kills *B. atrophaeus* vegetative cells, presumably by severe perturbations of the bacterial cell wall and cytoplasmic membrane. However, electron microscopy imaging and flow cytometry assays reveal that this compound also strongly induces germination of *B. atrophaeus* spores in the dark. Additional work in progress is shedding light on mechanisms by which germination occurs upon exposure to OPEs and similar polymeric biocides. These studies will monitor induced germination of *B. anthracis*, whichis notorious for its role as the causative agent of anthrax: an acute, life-threatening disease that infects mammals and humans by cutaneous, pulmonary, and gastrointestinal pathways. Previous work conducted by Lu *et al.* (2005) suggests that OPEs and other light-activated compounds should be lethal biocides to *B. anthracis* Sterne, in addition to acting as a germinant.

COLL 309

Non endocytotic intracellular delivery of luminescent quantum dots mediated by a lytic peptide

Hedi Mattoussi[1]*, mattoussi@chem.fsu.edu, Malalk Safi*[1]*, Tatiana Domitrovic*[2]*, Naiqian Zhan*[1]*, Fadi Aldeek*[1]*, John E. Johnson*[2]*.Â (1) Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FLorida 32306, United StatesÂ (2) Department of Integrative Structural and Computational Biology, The Scripps Research institute, La Jolla, CA 92037, United States*

A major hurdle that has slowed the integration of quantum dots into biology has been the inability to efficiently deliver them into the cytosol of live cells. Thus far, most if not all the strategies relying on passive delivery have largely resulted in uptake via endocytosis. Here, we describe a new conjugate design using a lytic-peptide, derived from a virus known to infect insects, capable of bypassing the endocytotic pathways, while delivering large amounts of QD-conjugates. We combined that with the design of zwitterion ligand to allow polyhistidine-driven self-assembly. We found that the efficacy of uptake by mammalian cells was substantial even for short incubation times and at moderate concentrations. Upon internalization the conjugates were primarily distributed outside the endosomes. These findings suggest an intracellular entry mechanism that does not involve endocytosis, but likely involves the perforation of the cell membrane by the lytic peptide presented on the QD surfaces.

COLL 310

Characterizing DANPY-1 binding to biological substrates

***Conner S Kummerlowe**, csk22012@mymail.pomona.edu, Juliah Kim, Lewis E Johnson, Malkiat S Johal.Department of Chemistry, Pomona College, Claremont, CALIFORNIA 91711, United States*

DANPY-1 is a fluorescent dye with high affinity for DNA that has potential applications as an alternative option for commonly used nucleic acid stains. We used a Quartz Crystal Microbalance (QCM) to characterize binding between DANPY and several biological substrates, as well as comparing it with binding data for control dyes DAST and Ethidium Bromide. DANPY proved to bind irreversibly to double stranded DNA, single stranded DNA, and RNA and reversibly to the disordered anionic control polystyrene sulfonate.

Â	Â Ethidium brtomide	Â DAST Â Â Â	Â DANPY-1
Â dsDNA	Â Irrevesrible Binding	Â No binding	Â Irreversible Binding
Â ssDNA	Â Irreversible Binding	Â Irreversible Binding	Â Irreversible Binding
Â tRNA	Â No Binding	Â Reversible Binding	Â Irreversible Binding
Â PSS	Â Irreversible Binding	Irreversible BindingÂ	Â Reversible Binding
Â SiO_2	Â Irreversible Binding	Â Reversible Binding	Â Reversible Binding

These results indicate that DANPY may be an effective cell stain for nucleic acids due to its strong and irreversible binding mode. QCM studies on DANPY binding to Bovine Serum Albumin, anionic proteins, lipid membranes, and other biological substrates will be carried out to further understand DANPY binding to biological substrates and evaluate its efficacy for cellular staining.

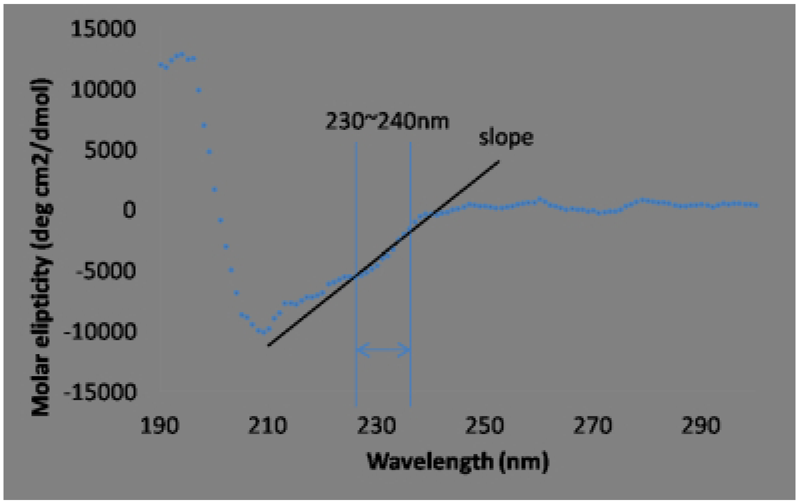
COLL 311

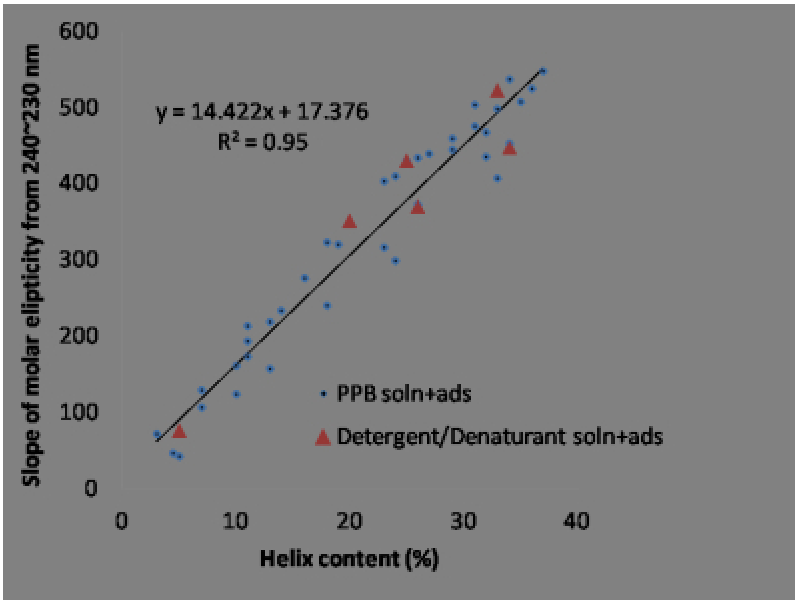
Empirical approaches using circular dichroism spectroscopy to study protein structural transitions from detergent or denaturant solutions with high concentration

Yang Wei, *wei2@g.clemson.edu, Aby A Thyparambil, Robert A Latour.Bioengineering, Clemson University, Clemson, SC 29634, United States*

Circular dichroism is a technique widely used for the evaluation of the secondary conformation and stability of proteins under various environmental conditions. Many algorithms have been developed for the empirical analysis of CD spectra below 220 nm using reference databases derived from proteins of known structures due to the different absorption signatures of alpha-helices and beta-sheets in this spectral range. However, detergent and denaturant solutions are generally incompatible with CD unless used under extremely dilute conditions (e.g., 10-50 mM range) due to the fact that these chemical agents tend to strongly absorb in the same CD spectral range of 220 nm and below. To overcome this limitation, we determined that the slopes of CD spectra acquired from the 230-240 nm region strongly correlate with the alpha-helix content of protein calculated by commercial algorithms, thus providing an effective means to determine the alpha-helix content within proteins under high detergent/denaturant solutions conditions.

Acknowledgement: Funding from DTRA grant HDTRA1-10-1-0028.





COLL 312

Interaction of bacterial cellular membrane with Ag nanoparticles-decorated silica microsphere

***Kyoungja Woo**[1], kjwoo@kist.re.kr, Mihwa Seo[1], Yun Haeng Joe[2], Jungho Hwang[2].Â*
(1) Molecular Recognition Research Center, Korea Institute of Science and Technology, Seoul, not applicable 136-791, Republic of KoreaÂ (2) School of Mechanical Engineering, Yonsei University, Seoul, Republic of Korea

Ag nanoparticles have been known as an efficient antimicrobial agent. However, their aggregation and environmental release have retarded their practical utilization. An inorganic composite microsphere decorated with Ag nanoparticles can be an alternative to resolve the problems and facilitate their practical utilization.

Recently, we reported the magnetic silica microspheres decorated with Ag nanoparticles with ~10, ~20, and ~30 nm sizes and their applications as an antimicrobial agent in the contaminated water. The ~30 nm Ag nanoparticles-decorated magnetic silica microspheres showed the highest toxicity against the tested microorganisms, *E. coli* CN13 and Bacteriophage MS2. After use, they could be magnetically collected due to an encapsulated cluster of superparamagnetic nanoparticles at the center. The cellular membrane of *E. coli* CN13 began to be destroyed as soon as the microspheres were added and was totally ruptured at 30 minutes.

In this study, for a scale-up synthesis of ~30 nm Ag nanoparticles-decorated silica microspheres, Ag nanoparticle-growth was performed on the silica microspheres without magnetic center using the same seeded growth method. Their surface is exposed directly to the medium containing target material and so, they can show an abnormal surface activity of nano-sized material toward the target while restraining from aggregation due to their hybridized overall micron-size effect and electrostatic repulsion caused by the protonated amine moieties which are not decorated. The microspheres can be easily collected by a conventional centrifugation.

The colloidal solution containing Ag nanoparticles-decorated silica microspheres was applied for an antibacterial coating on the air purification filter. Antibacterial efficacy was tested against gram-negative bacteria *E. coli* (ATCC11775) and gram-positive bacteria *Staphylococcus epidermidis* (ATCC 14990), resulting in a removal rate over 95% in both cases. The bacterial capture image on the coated filter will be presented with a suggested mechanism.

COLL 313

Targeted polymer-nanoparticle based therapies to treat secondary degeneration following partial injury to the CNS

Ivan Lozić[1,2]*, ivan.lozic@uwa.edu.au, Carole A Bartlett*[2]*, Nicole M Smith*[1,2]*, Matt R Kilburn*[3]*, Swaminathan K Iyer*[1]*, Sarah A Dunlop*[2]*, Melinda Fitzgerald*[2]*.Â (1) School of Chemistry and Biochemistry, The University of Western Australia, Crawley, Western Australia 6009, AustraliaÂ (2) Experimental and Regenerative Neurosciences, School of Animal Biology, The University of Western Australia, Crawley, Western Australia 6009, AustraliaÂ (3) Centre for Microscopy, Characterisation and Analysis, The University of Western Australia, Crawley, Western Australia 6009, Australia*

Oxidative stress in the astrocytic syncytium adjacent to the primary injury is believed to play a vital role in the spread of secondary degeneration following injury to the Central Nervous System (CNS). In order to stem the spread of secondary degeneration, we have developed a targeted nanoparticle-based therapy designed to deliver the anti-oxidant resveratrol to astrocytes overexpressing aquaporin 4 (AQP4) following neurotrauma. Nanoparticles (NPs) containing 6 nm magnetite particles, rhodamine B dye and resveratrol were synthesised using a spontaneous emulsion method from a highly functionalised poly(glycidyl methacrylate) polymer [141 nm]. A custom-made anti-AQP4 antibody was attached to the nanoparticles via a maleimide-thiol reaction [NP size: 581 nm]. *In vitro*, antibody conjugated resveratrol encapsulating NPs appeared to be taken up by a larger proportion of mixed retinal cells than non-antibody conjugated resveratrol encapsulating NPs, or antibody conjugated NPs without resveratrol [antibody conjugated resveratrol encapsulating NPs = 0.31 ± 0.05; non-antibody conjugated resveratrol encapsulating NPs = 0.19 ± 0.03; antibody conjugated NPs without resveratrol = 0.20 ± 0.03, data expressed as the proportion of cells with NP uptake]. PVG rats that underwent partial optic nerve transection and had antibody conjugated resveratrol encapsulating NPs nano-injected into the injury site at the time of injury, made a greater number of responses in the optokinetic nystagmus visual reflex test, than similarly injured animals treated with non-antibody conjugated resveratrol

encapsulating NPs ($P \leq 0.05$). NPs containing resveratrol targeted to astrocytes may serve as an effective therapy for secondary degeneration following neurotrauma.

COLL 314

Rapid aerosol-based synthesis of hollow silica particles as templates for hollow-nanostructured lithium ion battery anodes

Olasehinde G Owoseni, *oowoseni@tulane.edu, Jibao He, Vijay John.Department of Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana 70118, United States*

Hollow particles are promising in various applications such as rechargeable batteries, sensors, catalyst supports, biomedical imaging agents and controlled delivery systems. However, the synthesis of hollow particles typically requires building a desirable material layer around a solid core, followed by removal of the core by dissolution or high temperature calcination. These multistep operations and complex components often leads to difficulties in scaling up to commercially viable quantities. Here, we integrate fundamental understanding of surfactant self-assembly in solution with sol-gel chemistry for the rapid and scalable synthesis of hollow silica particles using a surfactant-aided aerosol process. The utility of these hollow silica spheres for the fabrication of hollow-nanostuctured tin oxide/iron oxide composite spheres is described. The results of this work is significant in the rapid and scalable synthesis of hollow anode materials for lithium ion batteries.

COLL 315

Millifluidic dispensing of compound drops

Jihye Kim, *zhay0809.kim@ttu.edu, Siva A. Vanapalli.Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, United States*

Recently, millimeter-scale fluidic devices are gaining interest as tools to manipulate fluid volumes because of their ease of fabrication and assembly. In this study, we demonstrate a millifluidic dispensing device which exploits gravity-driven pinch-off of compound-emulsion drops into multiwell plates. This strategy can be an inexpensive alternative to conventional automated pipetting systems, with the flexibility of controlling sample volumes and reagent concentrations for applications in drug screening and cell-based assays.

The millifluidic device consists of a T-junction to produce aqueous drops in a continuous oil phase which subsequently flow through a vertical tube. We manipulate the aqueous and oil flow rates at T-junction and investigate how drop size, production frequency and spacing affect the number of encapsulated aqueous droplets in the dispensing compound drop. We find that the number of encapsulated aqueous droplets is directly dictated by the ratio of the aqueous droplet production rate at T-junction to the

compound drop dispensing rate at vertical tube. We observe that compound drop gets pinched off when it reaches a critical volume determined by the balance of gravitational and capillary forces. Furthermore, dispensing rate can be predicted with the total volumetric flow rate injected divided by the critical volume.

To manipulate reagent concentration in each dispensing compound drop, we adjust the flow rates of the reagent and water prior to drop production at T-junction. We study the effect of system parameters on the concentration profiles generated and the maximum dilution-fold achievable. We find that larger increment of the mixing flow rate ratio of reagent to water results in higher dilution fold with narrow dilution step size between consecutive dispensing drops. Lastly, more is the number of aqueous droplets accumulated in a single compound drop smaller is the dilution fold. We will discuss the significance of our results for drug screening applications.

COLL 316

Detection of nanoparticle aggregation in complex, biological environments

***Samir V. Jenkins**[1], svjenkin@email.uark.edu, Jingyi Chen[1], Yongbin Zhang[2].Â (1) Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Ar 72701, United StatesÂ (2) NCTR/ORA Nanotechnology Core Facility, National Center for Toxicological Research, Jefferson, AR 72079, United States*

Plasmonic metal nanomaterials are promising candidates for future theranostic platforms that are in various stages of translation from the benchtop to clinical use. They are typically administered intravenously and, therefore, immediately encounter blood—an extremely complex fluid with many active components. These components may cause aggregation or dissolution of the particles, thus changing their properties. Determining a material's response to blood is crucial, particularly from a regulatory standpoint, to the development of new, clinically available materials. Most commonly-used characterization methods have limited capabilities for monitoring the status of NPs *in situ* following their introduction to the blood. In this study, a new methodology is developed to reveal the changes of spherical Au and Ag nanoparticles in complex biological solutions (e.g. blood) using reflectance hyperspectral imaging coupled with Raman spectroscopy. The aggregation of the NPs is monitored based on the changes of the optical resonance of the particles by hyperspectral imaging. These results are further correlated with the Raman enhancement of the protein adsorbed on the NPs. Using this method, the fate of the citrate-capped gold NPs in the blood is examined and compared with that of the silver NPs, and little aggregation was observed for either sample. Some particle aggregation is observed following uptake and sequestration in endosomes of macrophages, but the NPs generally remained nonaggregated. The methodology is adaptable to a wide range of materials of varying shapes, compositions, and functions.

COLL 317

Injectable hydrogel with oxygen-generating microsystem for tissue regeneration

***Wei Lv**, wei.lv@coyotes.usd.edu, Ying Deng.Department of Biomedical Engineering, University of South Dakota, Sioux Falls, SD 57107, United States*

Oxygen deprivation is one of the formidable challenge in the tissue engineering field. Delayed tissue healing, cell apoptosis as well as tissue necrosis can occur due to the limited oxygen delivery. In order to address this issue, an oxygen-generating injectable hydrogel system was fabricated by incorporating calcium peroxide-based (1 wt%, 5 wt% and 10 wt%) polycaprolactone (PCL) microparticles into catalase-containing poly(N-isopropylacrylamide)-methacrylic acid-chitosan (PNIPAM-MAA-CS) hydrogel. A dosage-dependent trend of oxygen releasing was observed and the media oxygen concentration was maintained at approximate 1 mg/L to 10 mg/L for 10 days when incubated under normal conditions. Fibroblasts were seeded in the oxygen-generating PCL microparticles-containing PNIPAM-MAA-CS hydrogel and control hydrogel without oxygen-generating PCL microparticles for biocompatibility test on the center section of the hydrogel. Cell viability and cell proliferation were characterized under normal culture conditions. Confocal images showed that cell viability was significantly improved in the center of the oxygen-generating gel compared to the cells in the center of the control. MTT test for cell proliferation revealed that hydrogel containing 5 wt% calcium peroxide microparticles showed a significantly higher cell number compared to the control and other groups. Our results demonstrate that a catalase-contained hydrogel with oxygen-generating PCL microparticle system can be designed and developed to provide a long-term (up to 10 days) oxygen delivery for tissue regeneration.

COLL 318

Controlled release of hydrophobic drugs from poly(ethylene glycol) covered gold nanocages

***Jingyi Chen**[1], chenj@uark.edu, Samir Jenkins[1], Avinash Srivatsan[2], Kimberly Reynolds[1], Ravindra Pandey[2].Â (1) Chemistry and Biochemistry, University of Arkansas, Fayetteville, AR 72701, United StatesÂ (2) Photodynamic Therapy Center, Roswell Park Cancer Institute, Buffalo, NY 14263, United States*

Two strategies, exterior and interior loading, are demonstrated to entrap and controllably deliver hydrophobic drugs based on a poly(ethylene glycol) (PEG) monolayer covered gold nanocage (AuNC) platform. A protein-rich in vivo environment was imitated to study the release kinetics during delivery. To facilitate monitoring, a hydrophobic photosensitizer, 3-(1'-hexyloxyethyl)-3-devinylpyropheophorbide-a, was used for this study. For exterior loading, the release rate was found to increase with PEG terminus in the order of positively charged (cationic terminus) > neutral (methoxy terminus) > negatively charged (anionic terminus). Using a surface cross-linking approach, the release was largely inhibited. External stimuli (e.g. light irradiation) led to a burst release due to the photothermal effect of the AuNCs. In the case of interior loading, no release was observed. The study is extended to in vivo for image-guide

enhanced photodynamic therapy. The short-term toxicity of the nanoparticles is also examined.

COLL 319

Dendron-based PEGylated micelles: Structure, stability and interactions with lipid membranes

***Soumyo Sen**, ssen5@uic.edu, Niladri Patra, Petr Kral.Chemistry, University of Illinois at Chicago, Chicago, Illinois 60607, United States*

In collaboration with experimentalists, we study the self-assembly of PEGylated dendron-based
copolymers (PDCs) with different end-groups functionalities (-OMe, -NH2, -COOH, and -Ac) into
dendron micelles. We use classical molecular dynamics simulations to model these systems to compare
the morphologies of PDC micelles with PEGylated linear copolymers micelles, and analyze the effects of
the monomer architecture on the micelle size, aggregation number, and structure of its individual
regions1,2. We also investigate how different PDC micelles with charged end groups interact with lipid
bilayer membranes to figure out under which conditions the micelles enter into cellular systems. Finally,
we study the interactions of mixed PDC micelles with membrane proteins. The highly stable PDC
micelles have a great potential to provide novel drug delivery platforms.

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2. R. M. Pearson, N. Patra, H.-J. Hsu, S. Uddin, P. Král, and S. Hong. ACS Macro Lett. 2, 77 (2013).

COLL 320

Toxicity measurements of quantum dot nanoparticles in cell cultures and Daphnia pulex

***Jennifer Holland**, jennifer-holland@utulsa.edu, Amanda Rightler, Kevin Thomas, Robert Sheaff, Kenneth P Roberts.Department of Chemistry and Biochemistry, The University of Tulsa, Tulsa, OK 74104, United States*

Nanomaterials are becoming widely used in technology, medicine, and industry. However, the potential toxicity of nanomaterials to humans remains unclear, which leads to uncertainties in establishing proper safety guidelines for individuals that come into contact with nanomaterials. In particular, it is unclear as to whether the size and/or the chemical compositions of the nanomaterials dictate toxicological effects. To partially address this debate, we have conducted studies on various cell cultures, using quantum dots with varied surface chemistries and nanoparticle size. In addition to cellular studies, the toxicity of quantum dots was tested with daphnia pulex as a whole organism comparison. Assay methods included fluorescence microscopy, cell viability assays, and inductively coupled-plasma mass spectrometry to determine the degree of degradation within cells and daphnia. It is anticipated that these results will further clarify the mode of toxicity of quantum dot nanoparticles and provide a framework for future studies of cell cultures coupled to whole organism studies.

COLL 321

Synthetic high-density lipoprotein mimic for treatment of atherosclerosis

Sean Marrache[1]*, sm186@uga.edu, Shanta Dhar*[1,2]*.Â (1) Department of Chemistry, University of Georgia, Athens, GA 30602, United StatesÂ (2) Department of Physiology and Pharmacology, University of Georgia, Athens, GA 3060, United States*

Atherosclerosis continues to be one of the leading causes of death in the United States despite numerous advances in treatment and prevention. Amongst these treatments, there is growing interest in the early identification and treatment of vulnerable plaques, which is a plaque that is at high risk of disruption followed by thrombosis. However, there is no accepted method for the early detection of such plaques. Recently, we developed a synthetic high-density lipoprotein (HDL)-mimicking nanoparticle (NP)[1] that demonstrates excellent biocompatibility, serum stability, physicochemical and non-immunogenic properties, and has the ability to sense apoptotic macrophages which can be used in imaging vulnerable plaques. These NPs show potential in rerouting cholesterol away from plaque macrophages to help prevent or slow the progression of vulnerable plaques. Here we present further optimization in order to better mimic of natural HDL. In vitro cholesterol binding and efflux of cholesterol from macrophage derived foam cells will be discussed.

1. Marrache, S. and Dhar, S. "Biodegradable synthetic high-density lipoprotein nanoparticles for atherosclerosis, *Proc. Natl. Acad. Sci. USA*, **2013** , *110*, 9445-9450.

COLL 322

Seeded co-reduction of Cu-containing bimetallic nanostructures and their catalytic applications

Jingyi Chen*, chenj@uark.edu, Shutang Chen, Samir Jenkins, Emily Miller.Chemistry and Biochemistry, University of Arkansas, Fayetteville, AR 72701, United States*

A general strategy to synthesize Cu-M (M=Au, Pt, or Pd) bimetallic nanorods is reported which is based on a seeded co-reduction method. In this approach, noble metal nanoparticles serve as seeds, and newly reduced Cu atoms are subsequently nucleated on one side of the seeds, resulting in heterodimmer nanoparticles with an M-rich and a Cu-rich portion. The elongation of the particles originates from the site-specific deposition of Cu clusters on Cu-rich side of these Janus nanoparticles by retarding reduction kinetics of Cu through galvanic replacement. Using this approach, Cu-M alloyed nanorods can be conveniently synthesized with tunable composition, crystal structure, and aspect ratio. These nanorods provide a unique system for investigation of the structural and compositional effects on their optical and catalytic properties.

COLL 323

Influence of thiol protected gold nanoparticles on the catalytic activity of the first generation Grubbs catalyst

Isaias B Aragão, *isaias.aragao@iqm.unicamp.br, Regina Buffon, Daniela Zanchet.Department of Inorganic Chemistry, University of Campinas, Campinas, Sao Paulo 13083-970, Brazil*

Thiol-protected gold nanoparticles (AuNPs) are well-known particles that show enhanced stability and properties compared to non-protected particles. Grubbs-type ruthenium complexes are also well-studied catalysts for olefin metathesis. This Ru complex is widely used in organic synthesis due to its remarkable activity and functional group tolerance. That way, binding a Grubbs like complex to the AuNP could give both brand new properties and applications. Firstly, it is indispensable to evaluate the stability of both components in the presence of each other. Nevertheless, the ring opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene (COD) was chosen because it is an olefin metathesis model reaction. Reactions were conducted under argon atmosphere, at 308 K, with 0.1 mol% of Ru catalyst, in dry $CH_2Cl_{2,}$ with methylcyclohexane as internal standard, under Schlenk techniques and with the addition of the desired mass of AuNPs (synthesized by the $NaBH_4$/EtOH one-phase method). Reaction yield measurements were obtained comparing the methylcyclohexane/COD peak ratio obtained by gas chromatography (GCFID). The reaction was also followed by ^{1}H NMR in C_6D_6 with 1 mol% of Ru complex in a 400 MHz instrument. Yield measurements were obtained comparing the poly(COD) peaks (2.00-2.15 and 5.35-5.53 ppm) with the COD ones (2.12 and 5.58 ppm). The reactions analyzed by GCFID in the presence of AuNPs showed lower yields towards blank reactions, even showing null results because of thiol interactions with the ruthenium alkylidenes, depicted by additional peaks in the ^{31}P NMR, indicating formation of new phosphorus species and catalyst deactivation. The ^{1}H NMR reactions showed concordant results, with fast activation in the presence of AuNP related to phosphine abstraction. It has been shown that besides its high group tolerance, Grubbs first generation catalyst is not stable enough toward free thiols, other studies are being made to assure the reproducibility of these results.

COLL 324

Surface patterning of silver nanoparticles using spiropyran-functionalized surfaces and spiropyran-functionalized nanoparticles assemblies

Gavin F Kirton[1,2], *gavin.kirton@rocky.edu, William J Brittain*[1], *Christopher Reyes*[1]*.Â*
(1) Chemistry and Biochemistry, Texas State University, San Marcos, Texas 78666, United StatesÂ (2) Chemistry, Rocky Mountain College, Billings, Montana 59102, United States

The ability to control growth and organization of nanoparticles on a surface using light would have numerous applications in materials science. Towards this aim, spiropyran was chosen as the photochromic center for surface patterning, where a large change in polarity and conformation occurs when spiropyran is converted by UV photon absorption to the colored merocyanine form. We propose the generation of silver nanoparticles based on the following methodology: 1) surface attachment of spiropyran moities, 2) photochemical formation of the merocyanine form of spiropyran (“UV activation”), 3) electrostatic binding of Ag^+ ions to the merocyanine moity, and 4) reduction of Ag^+ to adsorbed Ag^0. We will compare the approaches of directly functionalizing glass and silicon surfaces with covalent attachment of spiropyran, and the assembly of spiropyran-functionalized silica nanoparticles onto the same substrates. The loading, patterning, and nanoparticle dimensions will also be discussed.

COLL 325

Metal-enhanced fluorescence of photosynthetic complexes

Maria Olejnik[1], *marysia8@doktorant.umk.pl, Dorota Kowalska*[1], *Guanhua Lin*[1], *Bartosz Krajnik*[1], *Eckhard Hofmann*[2], *Sebastian Maćkowski*[1]*.Â (1) Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Torun, PolandÂ (2) Department of Biology and Biotechnology, Ruhr-University Bochum, Bochum, Germany*

Knowledge of the basics properties of individual nanostructures is essential to create a hybrid system exhibiting improved properties over the constituents. In particular, by combining organic emitters with metallic nanoparticle it is possible to enhance the fluorescence intensity of the emitter.

In this work, we combine photosynthetic complexes responsible for absorbing solar energy, and after isolation exhibit emission in the res spectral region, with metallic nanoparticles, in order to establish conditions for observing metal – enhanced fluorescence (MEF).

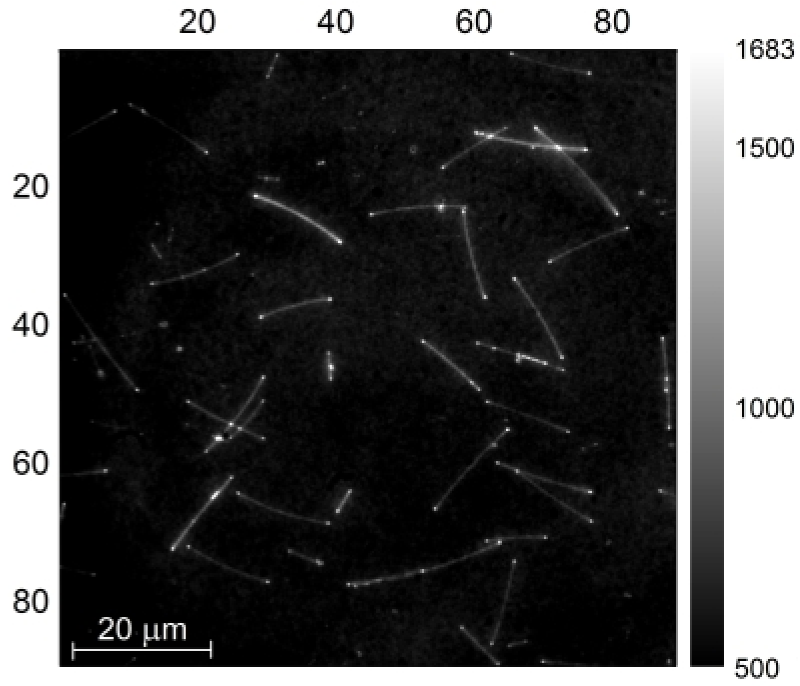


Figure 1. Fluorescence map of photosynthetic complexes coupled to silver nanowires.

We coupled photosynthetic complexes to metallic nanoparticles with varied plasmonic character, in either random or more controlled geometry, utilize strong non-covalent binding. Combination of wide-field and confocal fluorescence microscopy as well as time-resolved fluorescence techniques enabled demonstration of strong influence of plasmon excitation in metallic nanoparticles upon the fluorescence of photosynthetic complexes (Fig.1).

Coherent information of mechanisms playing key roles in fluorescence or excitation enhancements in photosynthetic complexes can results in finding attractive solution for a concept of artificial photosynthesis.

Financial support from the WELCOME program “Hybrid nanostructures as a stepping-stone towards efficient artificial photosynthesis” awarded by the Foundation for Polish Science is gratefully acknowledged.

COLL 326

Immunomodulatory properties of hydrogen-bonded multilayer capsules of polyphenol

***Veronika Kozlovskaya**[1], vkozlovs@uab.edu, Hubert M Tse[2], Eugenia Kharlampieva[1].Â (1) Department of Chemistry, University of Alabama at Birmingham,*

Birmingham, Alabama 35294, United StatesÂ (2) Department of Microbiology, University of Alabama at Birmingham, Birmingham, Alabama 35294, United States

We report on immunomodulatory properties of multilayer capsules based on hydrogen-bonded interactions of a natural polyphenol (tannic acid) with poly(N-vinylpyrrolidone) (TA/PVPON). The immunomodulatory properties of the (TA/PVPON) capsules were investigated on three types of pro-inflammatory cytokines synthesized by stimulated macrophages and diabetogenic autoreactive CD4$^+$ T cells. Our results on immunomodulatory properties of the hydrogen-bonded capsules indicate that the shells themselves are not immunogenic, as they do not induce synthesis of the cytokines in the absence of stimulators. Importantly, the (PVPON/TA)$_4$ capsules drastically suppress synthesis of lymphocyte maturation factor IL-12p70 (twenty-fold) which can produce IFN-γ by promoting formation of T helper type 1 effector cells from naïve CD4$^+$ T cells, and IFN-γ (three-fold), indicative of T cell adaptive immune activation, in stimulated macrophages and diabetogenic BDC-2.5 T cells, respectively. In contrast, no significant change in synthesis of IL-2 cytokine indicative of T cell proliferative capacity was found under the same conditions. We also demonstrate the capability of TA/PVPON multilayers to scavenge reactive oxigen species (ROS) which are produced in the cell surroundings and act as signaling molecules for activation of macrophages and T cells. Potentially,transplantation with (TA/PVPON)-coated islets of pancreatic cells should significantly decrease the risk of graft rejection due to attenuation of IL-12p70 and IFN-γ, while the unaffected synthesis of IL-2 would not promote the T cell apoptosis undesirable due to increased risks of infections.

COLL 327

Tuning the redox coupling in quantum dot-dopamine assemblies

***Xin Ji**, xj09@fsu.edu, Wentao Wang, Hedi Mattoussi.Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida 32306, United States*

We explored the charge transfer interactions between CdSe–ZnS quantum dots (QDs) and redox active dopamine. For this, we synthesized four different size CdSe–ZnS QDs with core/shell radius that vary between 2.8 nm, emitting at 520 nm, to 3.9 nm, emitting at 610 nm. These nanocrystals were rendered water-compatible via ligand exchange, followed by covalent coupling to a controlled number of dopamine isothiocyanate via a fixed length linker. Combining steady-state/time-resolved fluorescence, we found that the highest quenching efficiency is measured for the QDs with the largest band gap (smallest size) but progressively decreases for those with narrower band gap. In addition, transient absorption measurements probed at 800 nm and at the first exciton peak of different QDs were carried out to investigate the changes of dynamic relaxation rates between QDs and redox active dopamine in both acidic and alkaline solutions. We will discuss the mechanism of size/pH-dependent photoluminescence quenching behaviors within the framework of photoinduced charge transfer interactions.

COLL 328

Cyclic azasilanes: Efficient monolayer deposition and their applications

Janis G Matisons, *jmatisons@gelest.com, Annalese F Maddox, Kevin Alpaugh, Mani Singh, Youlin Pan, Joel Zazyczny, Barry Arkles.Gelest Inc, MORRISVILLE, Pennsylvania 19067, United States*

Silane coupling agents, such as alkoxy and chlorosilanes, are frequently used to link inorganic surfaces with organofunctional substituents with applications in microelectronics, optoelectronic devices etc. Even though these conventional silane coupling agents remain the most versatile surface modifiers, they do release alcohol or HCl byproducts on coupling to surfaces. Their low vapor pressure also poses challenges during surface modification especially when this is applied to nanoparticles. Any byproducts can remain on the substrate surface, thereby interfering with the targeted chemical properties. Furthermore, alkoxy silanes require hydrolysis prior to deposition on the surface, leading to water at the interface and the potential deposition of cage-like silane condensation products.

Gelest Inc., a leader and innovator of silane chemistry/technology, has developed an efficient alternative to conventional silane coupling agents. Cyclic azasilanes afford inherent structural properties that would eliminate the need for any hydrolysis step and offer no byproducts on surface coupling. These silanes contain Si–N bonds in a ring structure that opens very quickly when it meets any hydroxyl functionality forming a covalent bond to a surface. It has been described as 'click chemistry on surfaces' by those that have used this approach. Both Si-N and Si–O bond energies thermodynamically favor ring opening and reaction with a hydroxyl surface; a reaction that occurs in under a minute. Gelest has monitored the kinetics of this process which shows a first order reaction with respect to ring opening. Our investigation of cyclic azasilane reactivity and the resultant treated surfaces will be presented using ^{1}H NMR, FTIR, XPS, and AFM data to provide an understanding of the surface interaction, topography, and durability of the monolayer. The application of cyclic azasilanes as additives in surface treatment formulations will also be presented.

COLL 329

Study of Nile red exchange between nanodiscs: A kinetics study of hydrophobic molecular transportation

Ying Liu, *YING.4.LIU@UCONN.EDU, Paul Molinaro, Mu-Ping Nieh.Department of Chemical and Biomolecular Engineering, UNIVERSITY OF CONNECTICUT, Storrs, CT 06269, United States*

Monodispersed nanodiscs can be self-assembled in an aqueous lipid mixture of 1,2-dipalmitoyl-sn-glycero- 3-phosphocholine (DPPC), 1,2-dihexanoyl-sn-glycero-3-phosphocholine (DHPC) and 1,2-dipalmitoyl-sn-glycero-3-phospho- (1'-rac-glycerol) (sodium salt)(DPPG) and 1,2-distearoyl-sn-glycero- 3-phosphoethanolamine-N-[methoxy(polyethylene glycol)-2000] (ammonium salt) (PEGylated DSPE). The stability

of the nanodiscs and the effect of PEG (molecular chain length and concentration) on the disc morphology are characterized by dynamic light scattering, negative staining transmission electron microscopy and small angle neutron scattering. Furthermore, the nanodiscs are found capable of entrapping hydrophobic molecules such as cholesterol, Nile red, hydrocarbon chains. Fluorescent spectroscopy was applied to study the loading capacity of the nanodiscs through the fluorescence of the entrapped Nile red.. The exchanging rate of Nile red between discs is characterized by the time-resolved fluorescence measurement. The approach allows us to experimentally determine the exchange rate of the molecules from one to another nanoparticle, thus providing the insight to the stability of entrapped molecules in nanoparticles.

COLL 330

Poly-(3-hexylthiophene) aggregate formation in binary solvent mixtures: An excitonic coupling analysis

David S Boucher*, boucherds@cofc.edu, Calynn E Johnson.Department of Chemistry and Biochemistry, College of Charleston, Charleston, SC 29424, United States*

We have studied the aggregation behavior of P3HT [M_n ~ 28.2 kDa, regioregularity > 96 %, PDI ~ 1.3] in 96 solvent mixtures is studied using UV-Vis absorption spectroscopy. We used Hansen solubility parameters (HSPs) and Spano excitonic coupling analyses to identify correlations between the properties of the solvent mixtures and the extent of structural order of the aggregates. It is clear that the identity of the poor solvent used to drive aggregation has a significant impact on the excitonic coupling behavior and, hence, the structural order of the P3HT aggregates. However, solubility parameter theory does not account nor provide a predictive theory for the observed trends. Instead, qualitative arguments based on the nature of the interactions between the solvents and the polythiophene and hexyl side chain motifs are used to rationalize the kinetics of formation and the observed excitonic coupling characteristics of the P3HT aggregates.

COLL 331

Magnetic nanocomposites for cell growth

Vania B Bueno, Luiz Henrique Catalani, ***Denise F S Petri****, dfsp@usp.br.University of Sao Paulo, Brazil*

In this paper we present a ten minutes' synthesis to obtain magnetite nanoparticles by co-precipitation under sonication (MP-US) at room temperature in the absence of any stabilizer and their characterization. For comparison magnetite particles were synthesized by co-precipitation under heat (MP-Heat). The magnetite nanoparticles were characterized and the colloidal stability of magnetite dispersions was evaluated. MP-US particles presented mean diameter of 15 nm and isoelectric point (pI) of 6.5, while MP-Heat particles were sub-micrometric and presented pI at 5.4. At pH 6 these

characteristics made the aqueous MP-US dispersions more stable than the aqueous MP-Heat dispersions. Further cross-linked xanthan films were immersed for ten seconds in the aqueous dispersion at pH 6 and room temperature. Scanning transmission electron microscopy revealed that the MP-US nanoparticles assumed a spatial distribution in the xanthan matrix, resulting in scaffolds with improved coercivity in comparison to bare MP-US particles and suitable for the proliferation of fibroblasts, particularly when exposed to external static magnetic field[1].

1. Bueno, VB; Silva, AM; Barbosa, LRS; Catalani, LH; Teixeira-Neto, E.; Cornejo, DR; Petri, DFS, *Chem Commun.* **2013** , *49*, 9911.DOI: 10.1039/c3cc42277a

COLL 332

Negative impact of functionalization of Cu/CeO_2 catalysts for hydrogen production

*Tathiana Midori Kokumai, **Daniela Zanchet**, daniela@iqm.unicamp.br.Institute of Chemistry, Campinas State University, Campinas, SP 13083-970, Brazil*

Functionalization of oxides with chemical groups such as $–NH_2$, -CN, -COOH, is an interesting route to prepared metal-supported catalysts since it favors a firmly attachment of the metal species and improvement of metal loading and dispersion. In this work we explore the functionalization of $CeO\text{-}_{2\text{-}}$ nanorods (~11 x 70 nm^2) with 3-aminopropyltrimethoxysilane (APTMS) to address its impact on catalytic activity of Cu/CeO_2 catalysts under water-gas shift reaction (WGS). The WGS refers to the conversion of CO with steam producing CO_2 and H_2 and copper catalysts are usually under low temperature regime, below 230 ^oC. Interestingly, the studies revealed a negative effect of the functionalization, decreasing by half the CO conversion under the same conditions. A set of characterization techniques were used to address this result. We found that the functionalization decreased the surface area (from 96 to 53 m^2/g) and truncated the length of the CeO_2 nanorods (from ~70 to 40 nm), but did not affect the mean nanorod diameter. The APTMS totally covers the CeO_2 surface and after calcination created a thin silica layer, detected by nuclear magnetic resonance. Cu^{2+} was well dispersed on the CeO_2 nanorod surfaces, and we did not find a significant improvement due to the functionalization. A minor population of large Cu nanoparticles (~13 nm) was detected by X ray diffraction but it was similar to bare and functionalized nanorods. The results suggest that the thin silica layer formed between metallic copper and CeO_2 nanorod hinders the $Cu\text{-}CeO_x$ interaction that favors H_2O activation, decreasing the catalyst performance.

COLL 333

Folic acid-modified laponite nanodisks as targeted carriers for doxorubicin delivery

*Yilun Wu, **Rui Guo**, ruiguo@dhu.edu.cn, Xueyan Cao, Mingwu Shen, Xiangyang Shi.Department of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai, China*

In this report, we synthesized folic acid-modified laponite (LAP) nanodisks as a targeted drug delivery system for efficient loading and delivery of anticancer drug doxorubicin (DOX) to cancer cells overexpressing folate receptors (FR). The surface modification of LAP was successfully accomplished through step-by-step coupling reactions with 3-aminopropyldimethylethoxysilane and then folic acid by the aid of 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide. The formed folic acid-modified LAP (LM-FA) was characterized by UV-Vis spectroscopy and thermogravimetric analysis, and used as a carrier to encapsulate and release DOX. We show that DOX is able to be encapsulated within the interlayer space of LAP with a high loading efficiency of 92.1% and be released at a quicker rate at acidic pH condition (pH = 5.4) than at physiological pH condition. The specific therapeutic efficacy of LM-FA/DOX to FR-overexpressed cancer cells will be demonstrated by 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide cell viability assay and laser scanning confocal microscopy observation in future work. Therefore, cancer-cell-specific ligand modified laponite may be used as drug carriers to encapsulate cancer drugs for potential targeting therapy of different types of cancer.

COLL 334

Prodrug strategy to achieve lyophilizable, high drug loading micelle formulations through diester derivatives of β-lapachone

***Xinpeng Ma**, xinpeng.ma@utsouthwestern.edu, Xiumei Huang, Gang Huang, Yiguang Wang, Xiuquan Luo, David A Boothman, Jinming Gao.Departments of Oncology, Pharmacology, and Radiation Oncology, University of Texas Southwestern Medical Center, Dallas, TX 75390, United States*

β-Lapachone (β-Lap) is a promising anticancer agent that kills many cancer cells with elevated expressions of NAD(P)H:quinone oxidoreductase-1 (NQO1). Despite the therapeutic promise, clinical translation of b-lap is hampered by the lack of an effective formulation to overcome the limitations in solubility and pharmacokinetics. In this study, we investigated a prodrug strategy to improve the formulation properties of β-lap therapeutics. Diester derivatives of β-lap were synthesized and found to increase the compatibility with PEG-b-PLA copolymer in a micelle formulation (30-40 nm in diameter). Our data show that diester prodrugs (except for the diacetyl derivative) greatly improved the drug loading density and efficiency in PEG-b-PLA micelles, which led to high apparent drug solubility (>7 mg/mL), physical stability, and ability for reconstitution after lyophilization. In the presence of esterase, β-lap prodrugs (e.g. dC_3) can be efficiently converted into parent drug, resulting in NQO1-specific killings of lung cancer cells. The established β-lap prodrug micelles allow for further evaluation of safety and antitumor efficacy in preclinical animal tumor models.

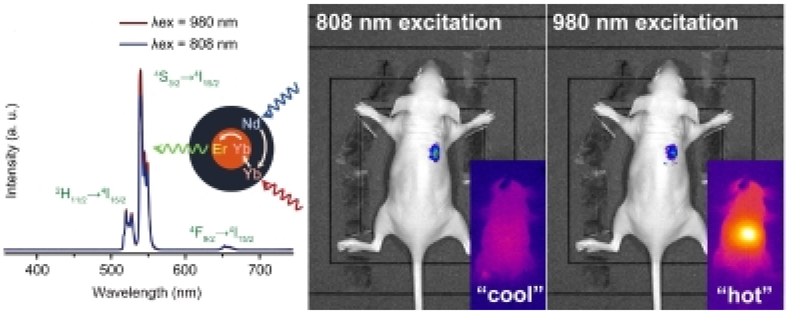
COLL 335

"Cool" and efficient: Nd^{3+}-sensitized upconversion emission

Ye-Fu Wang[1,2,3]*, koei@pku.edu.cn, Ling-Dong Sun*[1,2,3]*, Chun-Hua Yan*[1,2,3]*.Â (1) Beijing National Laboratory for Molecular Sciences, Beijing, ChinaÂ (2) State Key Laboratory of Rare Earth Materials Chemistry and Applications & PKU-HKU Joint Laboratory in Rare Earth Materials and Bioinorganic Chemistry, Beijing, ChinaÂ (3) College of Chemistry and Molecular Engineering, Peking University, Beijing, China*

Upconversion (UC) process is a unique two-photon fluorescence phenomenon. For lanthanide-based UC process, the sensitizer (usually Yb^{3+}) absorb the two or more near-infrared (NIR) photons and via transfer energy modes to activators ($Er^{3+}/Tm^{3+}/Ho^{3+}$) to result upconverted emissions. It features high tissue penetration depth and low background interference, and attracts great research interest for imaging *in vivo*.

However, the absorption of Yb^{3+}ions are efficient at ~980 nm, which is coincidently at the maxim absorption of water. Intense absorption of excitation light by water may induce risk of tissue overheating or even burn wound. Thus, to ensure the biosafety of UC-involved in vivo applications, it is of great importance to shift the excitation wavelength of UC process away from 980 nm.



Here in this work, we report a new excitation way with Nd^{3+} sensitization at 808 nm by constructing $NaGdF_4$:Yb,Er@$NaGdF_4$:Nd,Yb nanoparticles. The large absorption cross section of Nd^{3+} at 808 nm, along with the efficient Nd^{3+}-to-Yb^{3+} energy transfer, result in high UC excitation efficiency at 808 nm, which is comparable with that at 980 nm. More importantly, as water absorbs much less at around 808 nm, the tissue overheating effect is dramatically alleviated. This result might help rational design of UC materials, especially when high excitation power density or long irradiation duration is required.

COLL 336

Designing a nontoxic liposomal delivery system to enhance oncolytic viral therapy

***Natalie Mendez**, nmendez@ucsd.edu, Andrew C Kummel.Department of Material Science and Engineering, University of California, San Diego, San Diego, CA, United States*

Oncolytic viruses can exploit validated genetic pathways known to be deregulated in many cancers and are directly cytolytic. Viral gene therapy holds great promise due to the approach which takes advantage of the virus' ability to replicate within cancer cells to levels that are many logs higher than the input dose, lyse the infected cell and subsequently spread to adjacent cells. In particular, the oncolytic adenovirus TAV-255 has shown viral replication attenuation in normal cells while retaining cytolytic activity in tumor cells by taking advantage of defects in the p53-tumor suppressor pathway. Despite its several advantages, the utility of OVs for cancer therapy is limited by neutralization by antibodies mediated by the immune system, rapid clearance by the reticuloendothelial (RE) system in the liver, and the lack of expression of surface receptors (CAR) in certain cancers necessary for OV transduction. With the aim to overcome an immune response and to enhance its potential use to treat primary and metastatic tumors, a method for liposomal encapsulation of adenovirus has been developed. The encapsulation of Adenovirus in an anionic non-toxic liposome has been prepared by self-assembly of Lecithin around the viral capsid. The developed method has shown that encapsulated viruses retain their ability to infect cancer cells and serum stability. PEGylated liposomes have the potential to increase the circulation time of Adenovirus after systemic delivery which can enhance the efficacy of OV therapy. Furthermore, an immunoprecipitation (IP) technique has shown to be a fast and effective method to extract non-encapsulated viruses and homogenize the liposomes remaining in solution. Extracting non-encapsulated viruses from solution may prevent an adverse immune response when used in an in vivo model and may enhance treatment for multiple administrations.

COLL 337

Nanoparticle-based strategy for the broad detection and imaging of tumours by nonlinear amplification of microenvironment signals

***Yiguang Wang**[1], wangyiguang1980@hotmail.com, Kejin Zhou[1], Gang Huang[1], Christopher Hensley[2], Xiaonan Huang[1], Xinpeng Ma[1], Tian Zhao[1], Baran D. Sumer[3], Ralph J. DeBerardinis[2], Jinming Gao[1].Â (1) Simmons Comprehensive Cancer Center, UT Southwestern Medical Center, Dallas, Texas 75235, United StatesÂ (2) Children’s Medical Center Research Institute, UT Southwestern Medical Center, Dallas, Texas, United StatesÂ (3) Department of Otolaryngology, UT Southwestern Medical Center, Dallas, Texas 75390, United States*

Stimuli-responsive nanomaterials are increasingly important in a variety of applications such as biosensing, molecular imaging, drug delivery and tissue engineering. For cancer detection, a paramount challenge still exists in search of methods that can illuminate tumors universally regardless of their genotypes and phenotypes. Here we capitalized on the acidic, angiogenic tumor microenvironment to achieve broad detection of tumor tissues in a wide variety of mouse cancer models. This was accomplished using ultra-pH sensitive fluorescent nanoprobes that have tunable, exponential fluorescence activation upon encountering subtle, physiologically relevant pH transitions. These nanoprobes were silent in the circulation, then dramatically activated (>300 fold) in response to neovasculature or to the low extracellular pH in tumors. Thus, we have established non-toxic, fluorescent nanoreporters that can non-linearly amplify tumor microenvironmental signals, permitting identification of tumor tissue independently of histological type or driver mutation, and detection of acute treatment responses much more rapidly than conventional imaging approaches.

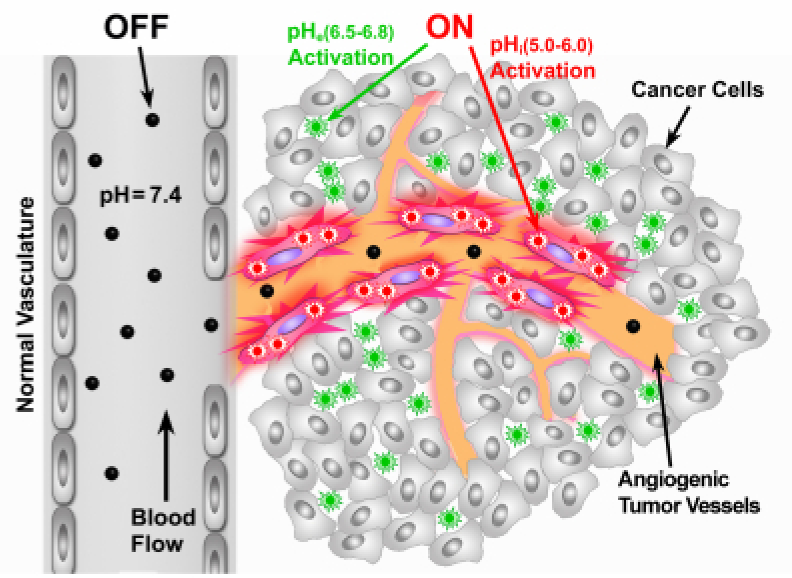


Figure 1. Schematic of imaging tumor microenvironment by ultra-pH sensitive (UPS) nanoprobes. The UPS nanoprobes stay 'OFF' at pH 7.4 during blood circulation. After reaching tumors, the UPS nanoprobes are turned ON by acidic extracellular pHe (6.5-6.8) in the tumor milieu, or endocytic organelles (pHi, 5.0-6.0) in the tumor endothelial cells after receptor-mediated endocytosis.

COLL 338

c-Met: A new target for nanoparticle therapeutics

*Alesha Harris, Amanda Phelps, **Robby A Petros**, petros@unt.edu.Department of Chemistry, University of North Texas, Denton, TX 76203, United States*

c-Met, a member of the tyrosine kinase family of proteins, is over-expressed in well-differentiated pancreatic endocrine neoplasms as well as many carcinomas including pancreatic, lung, breast, colorectal, head and neck, ovarian, renal, prostate, glioma, melanoma, gastric, hepatocellular, and a number of sarcomas. c-Met plays a role in several oncogenic pathways (PI3K-PDK1-AKT-mTor, Ras-Rac-Pak, Ras-Raf-MEK-ERK, and PLC-γ) that regulate cell migration, invasion, angiogenesis, morphogenic differentiation, cell proliferation and survival. An underappreciated aspect of c-Met's role in oncogenesis is its potential exploitation in nanoparticle therapeutics. The external domain of c-Met provides a prime target for directing therapeutic nanoparticles to metastatic tumor cells. We have conjugated c-Met binding ligands to the surface of fluorescently labeled polymeric nanoparticles. Cells that exhibit low, medium, or high levels of c-Met expression were then exposed to our targeted particles where uptake was examined by flow cytometry and fluorescence microscopy. Details of the conjugation chemistry, characterization, and uptake studies will be discussed along with future opportunities.

COLL 339

Raidiotherapy enhancement with hollow gold nanoparticles

Sina Moeendarbari[1], *sina.moeendarbari@mavs.uta.edu*, ***Yaowu Hao***[1], *yhao@uta.edu*, *Chienwen Huang*[1], *Preston Christensen*[2], *Vasant Kearney*[3], *Xiankai Sun*[2], *Weihua Mao*[3]*.Â (1) Department of Materials Science and Engineering, University of Texas at Arlington, Arlington, TX 76019, United StatesÂ (2) Department of Radiology, University of Texas Southwestern Medical Center at Dallas, Dallas, TX 75390, United StatesÂ (3) Department of Radiation Oncology, University of Texas Southwestern Medical Center at Dallas, Dallas, TX 75390, United States*

In the last decade, gold nanoparticles have been explored as radiation sensitizers to enhance radiotherapy. It has been reported that the energy deposition due to nanoparticles is geometrically dependant and that hollow shell-shaped nanoparticles may lead to higher radiation enhancement than solid nanoparticles. In this work we report in vitro study on radiotherapy enhancement of hollow gold nanopartilces. Hollow gold nanoparticles with a diameter of approximately 120 nm, termed as Au-NanoCapsules, were synthesized by bubble template synthesis method [2]. Au-NanoCapsules have a 50 nm hollow core and a 30 nm thick polycrystalline shell. A clonogenic cell survival assay protocol was used in this study to assess radiation dose enhancement on breast cancer MDA-MB-231 cells. The Au-NanoCapsules were sterilized in 70% IPA and then re-suspended in the cell culture medium at different concentrations. After 48 hours, cell colonies were irradiated using x-rays from a small animal irradiator (Precision X-ray), or a 6 MV x-rays from a commercial linear accelerator (Truebeam, Varian Medical Systems). 8 days following irradiation, the cell colonies were fixed, stained, and then counted visually. Using the same protocol but without irradiation, cytotoxicity studies were performed, which also acted as control groups. The result shows that there was no notable cytotoxicity of Au-NanoCapsules up to an Au concentration of 350 µM. The enhancement at radiation dosages up to 6 Gy was investigated. With 140 µM Au-NanoCapules at a dose of 4Gy, the survival fraction, defined as the ratio between the numbers of survival colonies of irradiated samples and control samples, dropped from 0.37 to 0.24 for the Truebeam and from 0.17 to 0.03 with the small animal irradiator. It can be concluded that this novel hollow nanoparticle has excellent radiotherapy enhancement and could potentially be used to significantly reduce prescription dosage when they are uptaken prior to radiation therapy.

COLL 340

Gold nanoparticle-polyplex enhanced electroporation-based therapeutic strategies in leukemia

*Shuyan Huang[2], Yingbo Zu[1], Yang Lu[1], **Shengnian Wang**[1], swang@latech.edu.Â (1) Department of Chemical Engineering, Louisiana Tech University, Ruston, Louisiana 71272, United StatesÂ (2) Department of Biomedical Engineering, Louisiana Tech University, Ruston, Louisiana 71272, United States*

DNA or RNA-based non-viral therapy methods (including chemical or physical approaches) have been developed to serve as favorable alternative in cancer therapy to their virus-mediated counterparts while still suffer some unsatisfied performance (e.g., low cellular uptake, high cytotoxicity, and/or low efficiency). We hypothesize that the combination of some of these methods could improve therapy performance. Specifically, we evaluated two novel therapeutic strategies. In strategy I, gold nanoparticles (AuNPs) were used to enhance electroporation-based delivery of DNA (e.g., pGFP & pLuc) and RNA probes (e.g., miR29b): free AuNPs of high conductivity help reduce the electroporation solution resistance so that the pulse strength on cells is enhanced; transferrin grafting AuNPs (Tf-AuNPs) were brought to leukemia cell membrane through affinity binding with TfR receptors and served as virtual microelectrodes to locally polarize cells from various sites, each affected only limited area. The enhancement was found dependent on the size, concentration, and the mixing ratio of free AuNPs/Tf-AuNPs. An equivalent mixture of free AuNPs and Tf-AuNPs exhibited the best enhancement with the transfection efficiency increased 2-3 folds at minimum sacrifice of cell viability. In strategy II, polyplex (e.g., polyethylenimine-DNA or-RNA complex) were internalized through electroporating the leukemia cells after conjugating with AuNPs. The formed Au-NPs-polyplex complex became more uniform in size and less toxicity as cationic polymers were fixed on the surface of AuNPs. Electroporation helps directly introduce nanoparticles into the cell cytoplasm, avoiding slow and inefficient internalization routes like endocytosis. We found that AuNP polyplex showed significant enhancement on the transfection efficiency while no obvious increase of toxicity. These new delivery strategies, the combination of nanoparticles and electroporation technologies, may stimulate *in vitro* and *in vivo* delivery of various DNA/RNA probes, anticancer drugs, or other therapeutic materials.

COLL 341

Metal-organic coordination networks for surface-supported transition metal catalysts

***Daniel Skomski**, dskomski@indiana.edu, Benjamin E. Draper, Christopher G. Williams, Christopher D. Tempas, Kevin A. Smith, Steven L. Tait.Department of Chemistry, Indiana University - Bloomington, Bloomington, Indiana 47405, United States*

The control of surface reactivity has major economic implications in heterogeneous catalysis. For the chemical tuning of catalytic metal centers, redox-active, on-surface coordination to a diverse repertoire of ligands is of great interest for the self-assembly of

ordered supramolecluar networks and control of the metal oxidation state. It is necessary to extend strategies for surface coordination from model systems towards those of a practical interest. We are working to study applications of C-H bond activation resulting from the interaction of small alkanes and oxygen with single-site catalysts under ultra-high vacuum conditions. Our experiments utilize several complementary analysis methods, including a pulsed supersonic molecular beam, X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), high-resolution electron energy loss spectroscopy (HREELS), low-energy electron diffraction (LEED), temperature programmed desorption (TPD), and scanning tunneling and atomic force microscopy (STM/AFM). New measurements into surface structure and reactivity on metal supports and supported catalyst compounds will be presented.

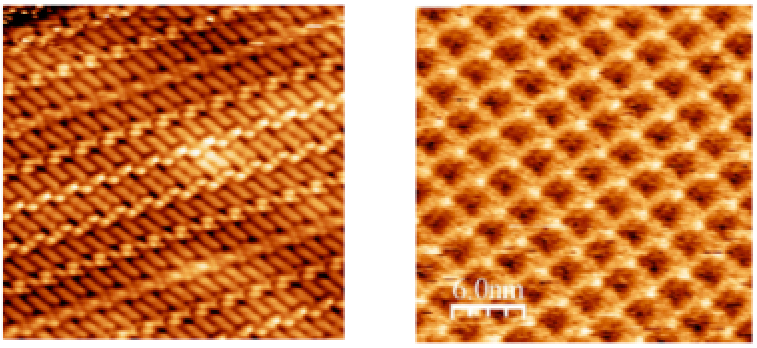
COLL 342

Supramolecular networks on a silicon surface or on insulators

Matthieu Beyer[1], Younes Makoudi[1], Simon Lamare[1], Judicael Jeannoutot[1], Frank Palmino[1], ***Frederic Cherioux[1]****, frederic.cherioux@femto-st.fr, Ania Amrous[2], Franck Bocquet[2], Laurent Nony[2], Franck Para[2], Christian Loppacher[2].Â (1) Institut FEMTO-ST, Besancon, France 25044, FranceÂ (2) IM2NP, Aix-Marseille UniversitÃ©, Marseille, France 13397, France*

The aim of this work is to understand and to control the adsorption of organic molecules on ionic substrates and silicon surface by means of a joint work of molecular synthesis, nc-AFM or STM imaging. The influence of the substrate lattice constant was also investigated by depositing the molecules on different substrates. The chosen molecule (CDB) consists of a central part with three phenyl rings and two lateral alkyl chains $(CH_2)_9$-CH_3.

The alkyl chains were added to the molecule in order to facilitate the two-dimensional (2D) growth by interdigitation between alkyl chains of adjacent molecules. The central part of the molecule is ended by cyano groups on the one hand to modify the molecule-substrate (MS) interaction and, on the other hand, to favour the molecule-molecule (MM) interaction. Nc-AFM or STM high resolution images acquired at room temperature and under ultra high vacuum show highly ordered organic layers and confirm that our strategy to obtain 2D molecular assembly on ionic substrates and silicon surface is successful.



Our work shows that the ordered growth is driven by the conformational adaptability of the molecule, the commensurability between the molecular layer and the substrate, and the proper choice of polar end-groups which enforce both, the MM as well as the MS interaction.

COLL 343

Experimental and theoretical studies of supramolecular self-assemblies on a silicon surface

*Guillaume Copie[2], Christophe Krzeminski[2], Fabrizio Cleri[2], Bruno Grandidier[2], Younes Makoudi[1], Frank Palmino[1], **Frederic Cherioux**[1], frederic.cherioux@femto-st.fr.Â (1) Institut FEMTO-ST, Besancon, FranceÂ (2) IEMN, Lille, France*

We report the experimental and theoretical study of the self-assembly of planar organic molecules of the type tris-1,3,5-(4'-X-biphenyl)benzene (with X=H, Br and CN) on a passivated, boron-doped Si(111)-B √3x√3R=30° surface. Ordered molecular structures are observed by high-resolution STM. We perform multi-scale atomistic simulations, by DFT structure relaxation (Gaussian03), metadynamics, molecular dynamics (MD) with empirical forces, and kinetic Monte Carlo with condensed degrees of freedom. At low coverage, we identify by metadynamics the lowest-energy adsorption sites consistently with the STM images. Upon increasing molecular coverage, structural phase transitions of the molecular network are observed, in excellent agreement with experimental STM data. Our theoretical models allow to elucidate the subtle interplay between dispersion forces and hydrogen bonding, leading to some unexpected phenomena. Biasing the MD by a simple elastic-band constraint method, we identify the kinetic path leading from a high-density to a low-density ordered phase. Next, kinetic Monte Carlo simulations over a frozen Si(111)-B surface, with energy parameters derived from the MD, help explaining the apparently striking experimental observations, according to which lower-density phases are favored over higher-density phases.

COLL 344

STM study of halogen bonded self-assembled supramolecular structures at the solution/solid interface

*Riccardo Gatti[1], **Jennifer MacLeod**[1], macleod@emt.inrs.ca, Josh Lipton-Duffin[1], Andrey Moiseev[2], Dmitrii Perepichka[2], Federico Rosei[1].Â (1) Ã‰nergie, MatÃ©riaux et TÃ©lÃ©communications, Institut National de la Recherche Scientifique, Varennes, Quebec J3X 1S2, CanadaÂ (2) Department of Chemistry, McGill University, Montreal, QC H2W 2J4, Canada*

The self-assembly of organic molecules on surfaces is a potential driving force for the creation of bottom-up bidimensional (2D) nanostructures. The resulting self-assembled molecular networks (SAMNs) exhibit appealing properties that can be tailored by properly tuning the features of the single molecules, as well as the interactions governing their self-assembly.

Here, we describe a detailed scanning tunneling microscopy (STM) study of the self-organization of halogen-terminated molecules at the solution/solid interface. In ambient conditions these molecules form stable organized arrangements, with intermolecular halogen bonding as the main stabilizing force. By changing the halogen terminations and the kind of substrate onto which these molecules assemble, interesting insights into the energetic of the system can be obtained. We will present data obtained from Br- and I- terminations of a threefold symmetric molecule that self-assembles on both graphite and Au(111) surfaces, considering the effects of different substituents on the molecular arrangement within the SAMN. Furthermore, the surface symmetry can induce different phases or domains if energetically degenerate configurations are allowed.

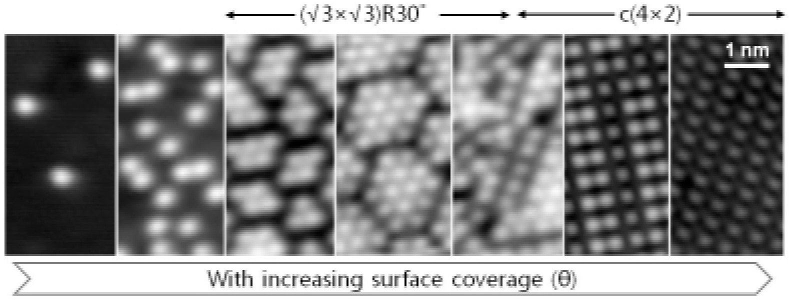
A deep understanding of the formation of such organized molecular layers is an essential step towards the future incorporation of these molecular materials into devices. Although SAMNs can be stabilized by other weak forces, e.g. van der Waals or hydrogenbonding, halogen bound 2D structures are interesting thanks to the peculiar double polarisation of the carbon-halogen (C-X) bond, which allows the formation of geometrical stable structures with the halogen termination participating in more than one interaction.

COLL 345

CO chemisorbed on Pt(111): Coverage-dependent overlayer structures and intermolecular interaction

***Hyun Jin Yang**[1,2], hjyang@riken.jp, Maki Kawai[1], Yousoo Kim[2].Â (1) Department of Advanced Materials Science, The University of Tokyo, Kashiwa, Chiba 277-8561, JapanÂ (2) RIKEN, Wako, Saitama 351-0198, Japan*

In terms of the intermolecular interaction, carbon monoxide (CO) adsorbed on a metal surface is generally considered to be repulsive due to the dipole-dipole interaction. Here we report the existence of more complex intermolecular interaction rather than simple repulsive one in CO chemisorbed on Pt(111) surface, by means of the real-space investigation of various coverage-dependent overlayer structures[1] and relevant dynamics in the overlayer structure, using scanning tunneling microscopy(STM) at liquid helium temperature (4.7 K) under ultra-high vacuum. Formation of anti-phase islands with local (√3×√3)R30˚ geometry at 0.1 ~ 0.3 monolayer (ML) surface coverage indicates not only short-range repulsive interaction between adjacent ontop-adsorbed molecules, but also the complex interaction to limit the number of molecules in each island and to form anti-phase boundary. Bridge-site adsorbed CO, which appears at the boundary of (√3×√3)R30˚ islands and c(4×2) domain, exhibit the intermolecular interaction between ontop CO and bridge CO by reducing the height of neighboring ontop CO in topographic STM image. Moreover, the bridge CO occupying at the center of local rectangular geometry (c(√3×2)rect) shows switching behavior with neighboring ontop site, and the relative energetic state of the ontop site is under influence of relevant geometry outside the rectangular unit, implying the intermolecular interaction between nonadjacent adsorbates. The origin of each intermolecular interaction will be discussed.



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COLL 346

Dynamic exchange in mixed supramolecular networks at the liquid-solid interface

Yuan Fang[1], *yuan.fang@student.kuleuven.be, Iris Destoop*[1]*, Kazukuni Tahara*[2]*, Yoshito Tobe*[2]*, Steven De Feyter*[1]*.Â (1) Department of Chemistry, Devision fo Molecular Imaging and Photonics, KU Leuven, Leuven, BelgiumÂ (2) Department of Graduate School of Engineering Science, Division of Frontier Materials Science, Osaka university, Toyonaka, Osaka 560-8531, Japan*

For self-assembly at the liquid/solid interface, the liquid phase acts as a reservoir of dissolved species which can diffuse towards the substrate, adsorb, diffuse laterally and desorb. These dynamic processes are highly sensitive to changes of the exact experimental conditions (solute concentration, choice of the solvent, deposition temperature *etc.*) and are on par with the proper supramolecular design for the formation of high quality monolayers at the liquid/solid interface. To get insights into the kinetics and thermodynamics of various processes occurring in surface self-assembly, we have studied bicomponent model systems based on dehydrobenzo[12]annulene (DBA) derivatives in which carefully designed marker molecules not only facilitate STM identification and analysis but also induce chirality and have well defined adsorption energies relative to the reference component. Here we report our preliminary findings on the effect of temperature and solution composition for the adsorption/desorption dynamics and monolayer growth in these systems.

COLL 347

Formation of regenerable light-harvesting complexes on SnO_2 nanocrystalline films via “on-surface” assembly

Rebecca Putans, *bputans@chem.wisc.edu, Robert J Hamers.Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706, United States*

A novel two-step “on-surface” assembly method has been designed to build a $Ru(bpy)_3$ complex directly onto a nanocrystalline metal oxide surface. This was achieved by first grafting a “building-block” ligand (2,2'-bipyridine) to the surface through a Williamson ether synthesis like reaction utilizing organo-halide compounds. A solution of $[Ru(bpy)_2(CH_3CN)_2](PF_6)_2$ was then exposed to the surface under UV irradiation to obtain the full $Ru(bpy)_3$ complex tethered to the surface. The stability of the complex in water and the charge transfer characteristics were then measured. After dissociation in water, the molecules were shown to be regenerable when re-exposed to the $[Ru(bpy)_2(CH_3CN)_2](PF_6)_2$ solution. The two-step method can be extended to other metal-containing light-harvesting complexes, including those containing Cu.

COLL 348

Cu underpotential deposition on Au(111) confined by a hydrogen bonded network

Baharan Karamzadeh[1], *bk27@st-andrews.ac.uk, Izabela Cebula*[2], *Minna Räisänen*[3], *Hervé Menard*[4], *Manfred Buck*[1]*.Â (1) Department of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, United KingdomÂ (2) Department of Experimental Physics, University of Wroclaw, Wroclaw, PolandÂ (3) Department of Chemistry, University of Helsinki, Helsinki, FinlandÂ (4) Sasol Technology (UK) Ltd, St Andrews, Fife KY16 9ST, United Kingdom*

Ultraprecise templating on the sub-5 nm scale is one of the attractive features of two-dimensional networks on surfaces. Mostly demonstrated for molecular guest species in ultrahigh vacuum experiments and at the liquid-solid interface [1], network controlled deposition in an electrochemical environment has, so far, been limited to the intercalation of metal monolayers at the interface between nanoislands of thiols corralled by a network and the underlying substrate [2,3].

However, extending electrodeposition of metal monolayers to empty network pores is of interest due to the catalytic properties of metallic nanostructures as well as the possibility of orthogonal self-assembly of molecules through tailoring of molecule-substrate interactions.

Here we present results on the underpotential deposition (UPD) of Cu templated by a supramolecular honeycomb network. Consisting of 3,4:9,10-perylenetetracarboxylic diimide (PTCDI) and melamine, the network is, in contrast to a self-assembled monolayer/network hybrid structure [2,3], not sufficiently stable under the acidic environment usually employed in Cu-UPD. However, deposition at higher pH improves the stability of the network to the extent that Cu-UPD becomes feasible. Scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) show that the network structure is preserved upon metal UPD and that the UPD is confined to the pore area. Atomically resolved STM images of anions adsorbed on the UPD islands and on uniform UPD layers exhibit significant differences in height contrast, thus, indicating an influence of the network confinement on the structure of the UPD layer.

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COLL 349

On-surface synthesis and application of covalent organic frameworks

Jan Plas, *jan.plas@chem.kuleuven.be, Oleksandr Ivasenko, Steven De Feyter.Department of Chemistry, KU Leuven - University of Leuven, Leuven, Belgium*

The decoration of surfaces through the self-assembly of molecules has received much attention over the past decade. These supramolecular systems allow one to nanostructure the surface in a straightforward fashion with great control over composition and functionality. The self-assembled nanoporous systems in particular are a promising sub-domain in this field of research. They have one disadvantage however, namely their lack of stability.

To solve this problem, the most straightforward approach seems to be the substitution of the non-covalent interactions by strong, covalent bonds. In this work, we present the synthesis of such a covalently linked 2D surface-confined polymer composed out of boronic acid building blocks and its potential application in molecular electronics by the incorporation of suited guest molecules. Scanning tunneling microscopy (STM) is an important tool in the visualization of these films.

COLL 350

Induction of chirality in an achiral monolayer at the liquid/solid interface: Temperature and concentration effects

Hai Cao[1]*, Hai.Cao@chem.kuleuven.be, Iris Destoop*[1]*, Kazukuni Tahara*[2]*, Yoshito Tobe*[2]*, Steven De Feyter*[1]*.Â (1) Department of Chemistry, KU Leuven - University of Leuven, Leuven, BelgiumÂ (2) Division of Frontier Materials Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan*

The fabrication of chiral self-assemblies, no matter from chiral building blocks or achiral ones, has been widely investigated and is still of great interest nowadays. STM has been proven to be a powerful tool for the understanding of chiral effects at molecular level. In our experiments, we found that deposition of achiral DBA solution on hot substrate can produce large scale high density patterns. The introduction of small amounts of chiral DBA led to the formation of homochiral surface, surprisingly without the presence of chiral DBA on surface. With increasing molar ratio of chiral molecules, morphological transformation from high density pattern to porous pattern was observed. Moreover, the surface chirality was inversed. All these findings can be ascribed to the relative poor stability of the chiral molecules on surface at high temperature. The chiral molecules were found capable of inducing homochiral self-assemblies with opposite handedness.

COLL 351

Examining ternary complex formation through cucurbit[n]uril on functional surfaces

Zarah Walsh*, zpw21@cam.ac.uk, Paul E. Williams, Samuel T. Jones, Yang Lan, Roger Coulston, Eric A. Appel, Oren A. Scherman.Department of Chemistry, Melville Laboratory for Polymer Synthesis, University of Cambridge, Cambridge, United Kingdom*

Curcurbit[8]uril (CB[8]) complexes have been or have the potential to be exploited in a wide variety of applications such as energy storage, plasmonics and logic gates on surfaces, to name a few. From capacitors and sensors to biomimetic and reversible adhesives, careful selection of the guest molecules or interactions at the cucurbit[n]uril portals can allow for many, useful applications.

CB[8], a barrel-shaped macromolecular host molecule, is unique amongst the CB[n] family (where n = 5, 6, 7, 8, 10) in its ability to hold two guests within its internal cavity simultaneously. This allows for the formation of a supramolecular “handcuff”, holding two functionalised units together. The ability to reversibly draw together units such as synthetic polymers and peptides on functionalised surfaces and in solution in a controlled manner has revolutionised applications of assembly at interfaces.

Exploiting these systems to their fullest potential requires understanding of the formation of these complexes at interfaces. The effect of the environment (counter-ions,

buffer solutions, electrolytes) plays a key role in how these macromolecular complexes can form.

Atomic force microscopy has been used extensively in this work to probe and understand the effect of the environment on the formation and application of CB[n] complexes. In particular force-distance spectroscopy allows the estimation of the interaction force between the components in a complex, giving an indication of its stability. Meanwhile topographic-recognition imaging has allowed the direct visualisation of complex formation on surfaces, enabling quantification of packing or surface functionalisation efficiency.

AFM studies have been verified with solution state (isothermal titration calorimetry) and gas phase (mass spectrometry) binding measurements to further understand *how* or *if* the complex formation on a surface and the environment around the surface affects the binding strength. Detailed characterisation of the materials and several applications, current and potential, of these systems will be presented.

COLL 352

Observing the effects of temperature and surface roughness on cetyltrimethylammonium bromide (CTAB) adsorption using quartz-crystal microbalance with dissapation

***Joshua Hamon**, joshua.hamon-1@ou.edu, Brian Grady, Alberto Striolo.Chemical, Biological and Materials Engineering, University of Oklahoma, Norman, OK 73019, United States*

The effects of temperature and surface roughness on mass and viscoelasticity of an adsorbed surfactant layer were monitored using the quartz crystal microbalance with dissipation (QCM-D). Adsorption isotherms at 20, 30, 40, 50 and 60°C and at two different roughnesses on gold were measured using cetyltrimethylammonium bromide (CTAB). All isotherms displayed an increase in mass and dissipation as surfactant concentration was increased to its CMC and, for isotherms above the Krafft temperature of CTAB, roughly 25°C, adsorption reached a peak followed by a slight decrease to a plateau at the equilibrium adsorption value. As the temperature was increased the same trend observed with increasing concentration was seen, but adsorbed mass was decreased at equilibrium. Adsorbed mass was decreased further by increasing substrate roughness, where a decrease in the peak height above the equilibrium value was also observed, while the dissipation was increased. Previously, our group reported a large peak at the CMC for rough surfaces at room temperature which was attributed to impurities; in this work the peak is much smaller which we attributed to the fact that helium sparging and ultrasonic degassing of the surfactant solution was performed prior to contact with the substrate surface in this series of experiments.

COLL 353

Ordered macromolecular assembly: Understanding peptoid behavior at an oil-water interface

Ellen J. Robertson[1]*, eroberts@uoregon.edu, Gloria K. Oliver*[2]*, Menglu Quan*[2]*, Rebecca Pizano*[1]*, Caroline Proulx*[2]*, Ronald N. Zuckermann*[2]*, Geraldine L. Richmond*[1]*.Â (1) Department of Chemistry, University of Oregon, Eugene, Oregon 97403, United StatesÂ (2) The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States*

Macromolecular assembly at the interface between two immiscible fluids is important for a variety of applications including biological processes, targeted drug delivery, enhanced oil recovery, water remediation, and interfacial catalysis. It has recently been discovered that fluid interfaces are essential catalysts for the self-assembly of peptoid nanosheets, yet the molecular level details of peptoid interfacial behavior are not well understood. Through a combination of vibrational sum frequency spectroscopy and interfacial tension studies of peptoid monolayers at an oil-water interface, we show that sequence specific peptoids self-assemble in an ordered fashion and that electrostatic interactions play a key role in this assembly. These oil-water interfacial studies have implications for increasing the complexity and functionality of peptoid nanosheets.

COLL 354

Tuning noncovalent interactions to guide orientation and surface density of covalently bound peptides on self-assembled monolayers

Annette F Raigoza*, araigoza@austin.utexas.edu, Kristeen Onyirioha, Lauren J. Webb.Department of Chemistry, The University of Texas at Austin, Austin, Tx 78712, United States*

Properly integrating the highly specific catalytic and sensing functionality of proteins with non-biological materials is challenging because proteins can unfold, aggregate, or lose their overall structure when they are placed in the harsh structural and electrostatic environment that occurs near surfaces. To improve protein-surface interactions, we have created a surface composed of peptides on an alkanethiol scaffold, attached via a Huisgen cycloaddition ("Click") reaction. Peptide functionalization produces homogeneous surfaces with high surface coverages, while maintaining secondary structure. Here, we show that the peptide-tethering chemistry can be synchronized with the alkanethiol monolayer formation, generating a peptide-functionalized surface in a significantly shorter time period of 4 hours. Furthermore, the incorporation of alternate functional groups at the surface provides an additional means for controlling the peptide-tethering chemistry through non-covalent interactions.

COLL 355

"Soft” epitaxy at the nanoscale: The role of size, shape, and strain

Sara M Rupich[1], *sara.rupich@utdallas.edu, William T.M. Irvine*[2], *Dmitri V. Talapin*[1]*.Â*
(1) Department of Chemistry, University of Chicago, Chicago, Illinois 60637, United StatesÂ (2) Department of Physics, University of Chicago, Chicago, Illinois 606137, United States

Colloidal nanocrystals (NCs) are used as building blocks for LED's, solar cells, transistors and other devices with semiconductor junctions. Recent fundamental studies on the energy, chargeand heat transport provide the foundation for the rational design of NC-based materials and devices. At the same time, little is known about structure of the interfaces formed between different NC layers. For example, NC solar cells require stacked NC layers with n- and p-type conductivity for efficient separation of charge carriers. Performance of NC devices should depend on the perfection of homo- and heteroepitaxial interfaces formed between the NC layers, in a similar way as it occurs in traditional electronics and optoelectronics. In this work, we study the epitaxial growth of NCs arrays that revealed an exceptional strain tolerance. It followed a universal island size scaling behavior and showed a strain-driven transition from layer-by-layer to Stranski-Krastanov growth regime with non-trivial island height statistics. We found that kinetic bottlenecks played an important role in NC epitaxy, especially in the transition from sub-monolayer to multilayer coverage and the epitaxy of NCs with anisotropic shape.

COLL 356

Supramolecular interactions in the first and second layers at the organic/metal interface

Steven L. Tait, *tait@indiana.edu.Department of Chemistry, Indiana University, Bloomington, Indiana 47405, United States*

Various supramolecular interactions have been explored for the growth of highly-ordered organic molecules at metal surfaces. An understanding of how these interactions balance with molecule – substrate interactions is essential to developing rational design rules for supramolecular architectures at surfaces. Here, we present results from scanning tunneling microscopy studies, couples with high-resolution electron energy loss spectroscopy, which allows insight into vibrational modes and structure, as well as X-ray photoelectron spectroscopy, which provides chemical information about the surface. This will include several examples of the interactions between small organic species at metal surfaces, as well as transitions to different chemical states and new structures in the second layer. This raises questions about the character of the first few layers at the organic / metal interface, which is essential for charge transfer and energy level alignment in organic devices.

COLL 357

Mesoporous magnetic carbon nanocomposite fabrics toward highly efficient Cr(VI) removal

Jiang Guo[1], *zhanhu.guo@lamar.edu, Jiahua Zhu*[1,2], *Huige Wei*[1], *Suying Wei*[1,3], ***Zhanhu Guo***[1], *zhanhu.guo@lamar.edu.Â (1) Department of Chemical Engineering, Lamar University, Beaumont, TX 77710, United StatesÂ (2) Chemical and Biomolecular Engineering Department, The University of Akron, Akron, OH 44325, United StatesÂ (3) Department of Chemistry and Biochemistry, Lamar University, Beaumont, TX 77710, United States*

Magnetic carbon nanocomposite fabrics prepared from microwave assisted heating have been demonstrated as an advanced adsorbent to remove Cr (VI) with a much higher removal capacity of 3.74 mg/g than 0.32 mg/g for cotton fabrics and 0.46 mg/g for carbon fabrics. The enhanced Cr(VI) removal is attributed to the highly porous structure of the nanocomposites. The adsorption kinetic follows the pseudo-second-order model, which reveals a very large adsorption capacity and high adsorption rate. The removal process takes only 10 min, which is much faster than conventional adsorbents such as activated carbon and biomass that often requires hours of operation. The significantly reduced treatment time and the large adsorption capacity make these nanocomposite fabrics promising for the highly efficient removal of heavy metals from polluted water.

COLL 358

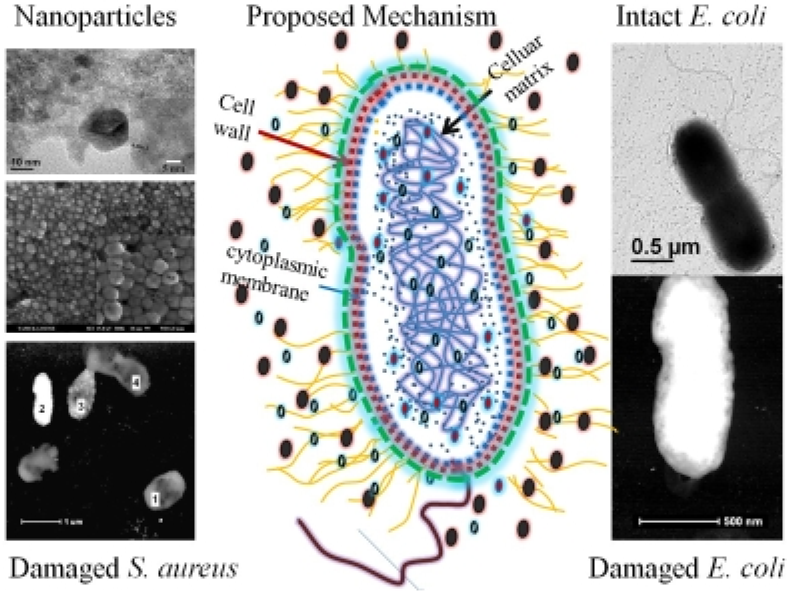
Green synthesis of nanocomposites used as effective bactericidal agents

Rudolf Flores[1], *rudolf.flores@students.tamuk.edu,* ***Madalyn Mendoza***[1], *Madalyn.Mendoza@students.tamuk.edu, Sajid Bashir*[1,2], *Jingbo Liu*[1,2]*.Â (1) Department of Chemistry, Texas A&M University-Kingsville, Kingsville, Texas 783638204, United StatesÂ (2) Advanced Light Sources, Lawrence Berkeley National Laboratory, Berkeley, California 94720-8226, United States*

The outbreak of a deadly strain of *Escherichia coli* (*E. coli*) bacteria motivates us to conduct extensive research on the development of new bactericidal agents. Transition metal oxides (TMO) offer one possible disinfection strategy and are pursued due to a number of advantages, such as low cost, engineering control, tunability which is difficult with other approaches coupled with generation of less disinfection by-products than other methods. In this study, we will present a generation process of TMO nanocomposites through facile green-chemical approach. Several steps are shown as follows: (1) A complex between a metal ion and a ligand, that is the functional group of a protecting polymer, is formed in an aqueous solution; (2) The metal ion is reduced to a metal atom with a reducing agent; and (3) The metal atoms aggregate and grow into a nanoparticle.

The effect of the nature and concentration of reducing agents have been evaluated. TMO-based disinfectants offer an effective approach in water purification. This discovery found that silver (Ag) decorated titania (TiO_2) nano-composites displayed high potency at 2.5 ppm within 4 hr co-incubation, proved to be effective at 100 % inactivation. The composite disinfectant was effective against both Gram-negative and

Gram-positive bacteria, *Escherichia coli* and *Staphylococcus aureus*. The mechanism of action is through nanocomposite catalysed photocatalytic oxidation and possible depolarization of the bacterial outer membrane, resulting in disinfection under visible-light conditions.



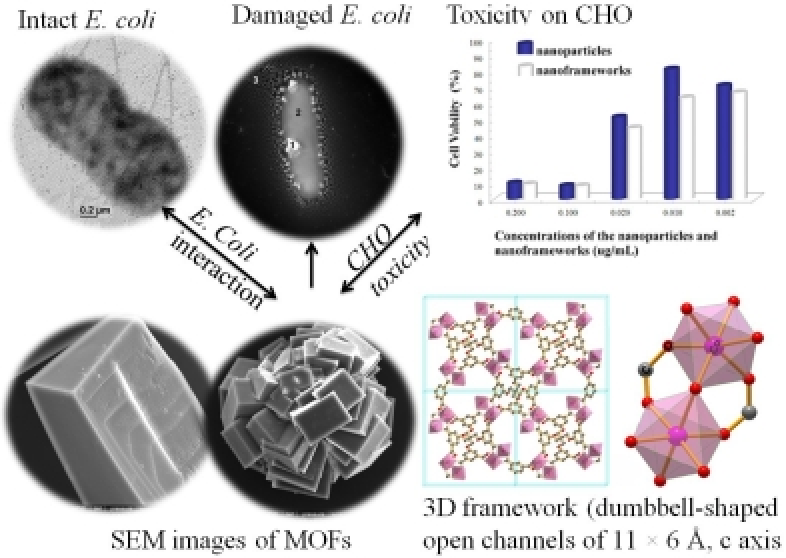
COLL 359

Porous metal-organic frameworks and their biological application

Baldemar Martinez[1], *Baldemar.Martinez@students.tamuk.edu, Madhuri Maganti*[1], *Sajid Bashir*[1,2], *Jingbo Liu*[1,2,3]*.Â (1) Department of Chemistry, Texas A&M University-Kingsville, Kingsville, Texas 783638204, United StatesÂ (2) Advanced Light Sources, Lawrence Berkeley National Laboratory, Berkeley, California 94720-8226, United StatesÂ (3) Department of Chemistry, Texas A&M University, College Station, Texas 783638204, United States*

A novel cobalt (Co) based metal-organic framework (MOF) was tested and shown to be highly effective at inactivating model microorganisms. Gram-negative bacteria, *Escherichia coli* (*E. Coli*, strains DH5alpha and XL1-Blue) were selected to determine the antibacterial activities. In this MOF, the Co serves as a central element and an octa-topic carboxylate ligand, tetrakis [(3,5-dicarboxyphenyl)-oxamethyl] methane (TDM^{8-}) as a bridging linker. X-ray crystallographic studies indicated that Co-TDM crystallizes in tetragonal space group $P2_1m$ with porous 3D framework. The high potency of the Co-TDM disinfectant was evaluated using minimal bactericidal concentration (MBC) benchmark and was determined to be 10-15 ppm, within a short incubation time period (< 60 min). The Co active sites rapidly catalyzed the lipid peroxidation, causing rapture of the bacteria membrane followed by inactivation, with 100 % recycling and high persistence (> 4 weeks). Additionally, the MOFs also displayed high potency to inactivate the cancer cells, which was tested using Chinese Hamster Ovary cell lines.

In-vitro toxicity data indicated that MOFs IC_{50} (0.02 ppm) is comparable to, or lower than the current first-line drug formulations; at higher doses, the kinetics of action were approximately ten-fold higher.



This MOF-based approach may lead to a new paradigm of MOF applications in diverse biological fields due to the unique porous structure, tunable surface functional groups, and adjustable metal coordination environments.

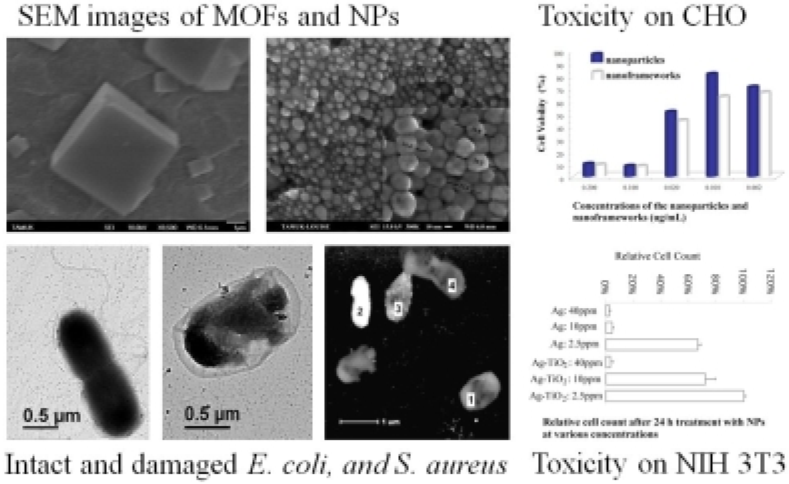
COLL 360

Colloidal chemistry derived ultrafine nanoparticles and their biological application

***Eduardo Hernandez**[1], Eduardo.Hernandez@students.tamuk.edu, Sreevardhan Reddy Posa[1], Sajid Bashir[1,2], Jingbo Louise Liu[1,2].Â (1) Department of Chemistry, Texas A&M University-Kingsville, Kingsville, Texas 783638204, United StatesÂ (2) Advanced Light Sources, Lawrence Berkeley National Laboratory, Berkeley, California 94720-8226, United StatesÂ (3) Department of Materials Science, Lanzhou University of Technology, Lanzhou, China 130 050, China*

Series of nanomaterials (NMs), including nano-metal, nano-oxides and nano-frameworks were produced via a green bottom-up colloidal synthesis using natural products as reducing and dispersing agents. The fabrication variables of the synthesis were optimized to obtain NMs with tuneable architecture and potency. The use of water-soluble natural products, such as *Salvia hispanica* and traditional Chinese medicine (*Cordyceps extracts*), coffee and tea offer a variety of water-soluble components to enhance the reduction of noble metal aimed to increase the fluorescent intensity of those NMs in a cancer treatment. The NMs were modified and characterized to determine their crystalline phase structure, particle size and distribution. The cytotoxicity on Chinese hamster ovary (CHO) cells, human blood cells and bacteria showed these NMs possessed high potency to kill cancer cells and bacteria.

An effective dose at 50% of 20 ppb (cytotoxicity at 100 ppm) indicating that Fe_3O_4 based MNs with amphiprotic functionalization would facilitate targeting of tumour cells as demonstrated *in vitro* by the 3-[4,5-dimethylthiazol-2-yl]-2,5 diphenyl tetrazolium bromide) assay. The silver, titania and cobalt based NMs displayed high potency in inactivating gram-negative and gram-positive bacteria. The potency was found to be at 2.5 ppm within 4 hr co-incubation at 100 % inactivation.



The mechanism on bactericidal activity indicated that four steps are: a: K^+ leakage and membrane depolarization; b: protein aggregation and DNA fragmentation; c: membrane-NP interaction; and d. inhibition of respiratory protein.

COLL 361

Synergistic interactions between activated carbon fabric and toxic hexavalent chromium

*Cuixia Xu[1,2], Bin Qiu[1,3], Hongbo Gu[1], Xingru Yan[1], **Suying Wei**[1,2], suying.wei@lamar.edu, **Zhanhu Guo**[1], zhanhu.guo@lamar.edu.Â (1) Department of Chemical Engineering, Lamar University, Beaumont, TX 77710, United StatesÂ (2) Department of Chemistry and Biochemistry, Lamar University, Beaumont, TX 77710, United StatesÂ (3) College of Environmental Science and Engineering, Beijing Forestry University, Beijing, Beijing 100083, China*

The synergistic interactions between the as-received activated carbon fabric (ACFs) and the toxic hexavalent chromium (Cr(VI)) were investigated aiming to functionalize the carbon fabric and to remove the toxic Cr(VI) by X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), Raman spectroscopy and scanning electron microscopy (SEM). The effects of varying parameters such as pH, treatment time, initial Cr(VI) concentration and ACFs dose on the adsorption behavior of ACFs were discussed. Results revealed that ACFs could be used for an effective absorbent for Cr(VI) removal from aqueous solutions and different pH values had different effects on ACFs, pH=1.0 was found to be the optimum pH value for the Cr(VI) removal. For the pH=1.0 solution, the Cr(VI) in the aqueous solution was reduced to Cr(III) and were adsorbed onto the ACFs, and the C-O and C=O functional groups were found to form on the ACFs surface. The redox kinetic in the pH=1.0 solution could be described by the pseudo-first-order model and the typical value of the pseudo-first-order rate constant was calculated to be 0.0872 min^{-1}. Langmuir, Freundlich, and Temkin adsorption isotherm models were applied to describe isotherm constants, the Cr(VI) equilibrium data agreed well with the Langmiur isotherm model, with the maximum adsorption capacity of 5.59 mg g^{-1}. The ACFs was found to be easily regenerated by 1.0 mol L^{-1} sodium hydroxide (NaOH) and could be effectively recycled 7 times with the removal percentage decreased by 16.5%, the decreased adsorption behavior was caused by the formation of oxygen functional groups on the surface of ACFs which was irreversible.

KEYWORDS: Activated carbon fabrics; Synergistic interactions; Oxygen functional groups; Redox reaction; Chromium removal

COLL 362

Chemical behavior of Cu, Zn, Cd, and Pb in a eutrophic reservoir: Speciation and complexation capacity

Ana Teresa Lombardi[1]*, lombardi@ufscar.br, Alessandra Emanuele Tonietto*[1]*, Rodrigo Brasil Choueri*[2]*, Armando Augusto Henriques Vieira*[1]*.Â (1) Department of Botany, Federal University of SÃ£o Carlos, SÃ£o Carlos, SÃ£o Paulo, BrazilÂ (2) Departament of Marine Sciences, Federal University of SÃ£o Paulo, Santos, SÃ£o Paulo, Brazil*

This research aimed at evaluating cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) speciation and interactions with natural dissolved organic materials in a eutrophic reservoir. Water samples were obtained in dry and rainy seasons, and PCA identified seasonal influences of metal input sources into the reservoir. The results showed higher labile Zn (Znlabile) and Pb (Pblabile) in the dry season, but complexed Zn (ZnL) dominated during the rainy season. Total dissolved Cu (CuTD) and Pb (PbTD) concentrations were higher in the dry season, with the concentration order Zn > Cu > Pb > Cd. In general, higher percentile of Cu and Zn remained complexed to the dissolved fraction, while Pb was associated with particulate materials. Chemical equilibrium modeling (MineqL+) showed that Zn^{2+} and Cd^{2+} dominated labile species, while Cu and Pb remained associated with carbonates. Cu and Zn complexes, labile Zn and Pb concentrations were directly proportional to each respective metal concentration in its dissolved form. Cd, Cu, Pb and Zn complexation capacity indicated higher ligand concentration for Cu, followed in decreasing amounts for Pb, Zn and Cd. Nevetheless, the strength of association for all metals and the respective ligands were similar. We conclude that in eutrophic environments, metals that otherwise would sink to the bottom in oligotrophic environments, in organic rich ones, these metals are likely to remain as the dissolved form in the water column. An exception to this was observed for Pb, which

mostly related to particulate material and sinked to the sediments. The results revealed a high degree of deterioration of the reservoir regardless of sampling location.

COLL 363

Effects of clay spacing in nanobrick wall gas barrier thin films

Morgan A Priolo[1], ***David A Hagen***[1], *david_hagen@tamu.edu, Kevin M Holder*[1], *Stephen M Greenlee*[1], *Bart E Stevens*[1], ***Jaime C Grunlan***[1,2], *jgrunlan@neo.tamu.edu.Â (1) Department of Mechanical Engineering, Texas A&M University, College Station, Texas 77843, United StatesÂ (2) Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843, United States*

Thin films of sodium montmorillonite clay and polyelectrolytes, created via layer-by-layer assembly, were designed with varying polymer thickness between clay layers to investigate the influence of clay spacing. The alternate deposition of polymers and clay leads to the assembly of a nanobrick wall structure that creates a tortuous pathway for gasses and proves to be highly impermeable. In an effort to tailor the thickness (or spacing) between clay layers, films with differing numbers of polymer layers between clay depositions were examined. Films were analyzed for their thickness, clay concentration, transparency, nanostructure, and oxygen barrier as a function of layers (or spacing) between clay depositions, revealing linear growth, optical clarity, and low OTR at 100 nm thick and containing only four clay layers. An optimal thickness between clay layers appears to exist for achieving the highest oxygen barrier LbL films (O_2 Permeability $< 1 \times 10^{-21}$ cc(STP)·cm/(cm^2·s·Pa)). This knowledge can ultimately minimize deposition steps, material use, and thin film fabrication times.

COLL 364

Programmable crafting of PS-b-P4VP micelles via flow enabled self-assembly

Bo Li, *cactuslibo@gatech.edu, Wei Han, Zhiqun Lin.School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States*

Hierarchical assembly of diblock copolymer micelles was successfully crafted into parallel stripes by flow enabled self-assembly (FESA). The micelles were precisely and programmably patterned at desired positions on a silicon substrate. Remarkably, a minimum spacing between two adjacent stripes was observed and a model was, for the first time, proposed to understand the relationship between the width of stripe and the minimum spacing between two adjacent stripes. Moreover, arrays and networks of inorganic nanoparticle were also produced by FESA of diblock copolymer/precursor solution, followed by selective removal of the diblock copolymer template. Such flow enabled self-assembly of diblock copolymer micelles is facile to implement, offering opportunities to create hierarchical structures and materials for potential applications in nanoelectronics.

COLL 365

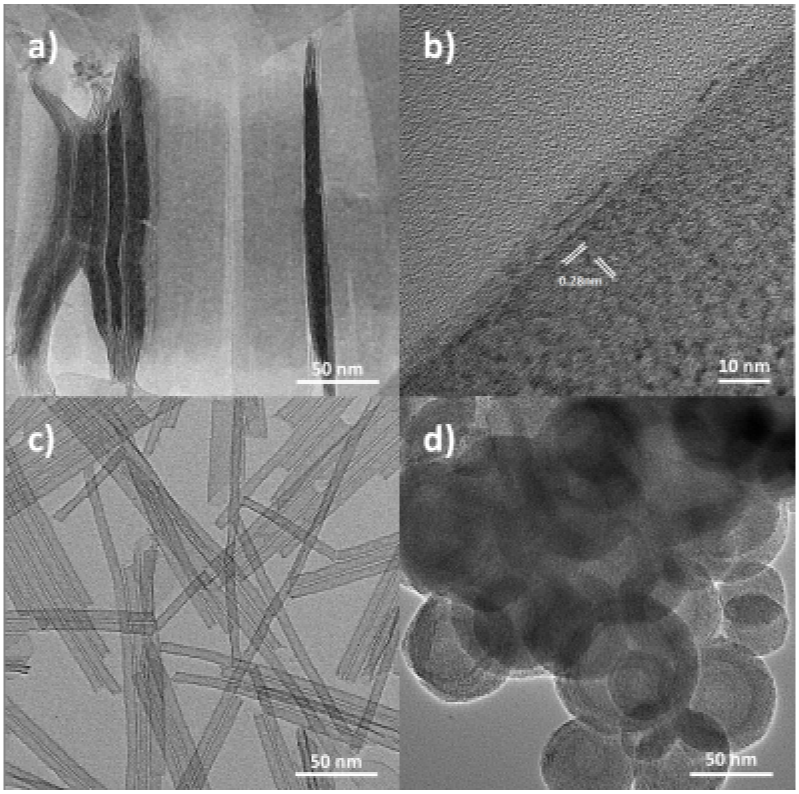
Synthesis of CeO_{2-x} nanoplates, nanotubes, and fullerene-like nanoparticles with high Ce^{3+} concentration

Rui Liu[1,2,3]*, plain364@126.com, Chun-Hua Yan*[1,2,3]*.Â (1) Beijing National Laboratory for Molecular Sciences, Beijing, ChinaÂ (2) State Key Laboratory of Rare Earth Materials Chemistry and Applications & PKU-HKU Joint Laboratory in Rare Earth Materials and Bioinorganic Chemistry, Beijing, ChinaÂ (3) College of Chemistry and Molecular Engineering, Peking University, Beijing, China*

Ceria is one of the most important rare earth functional materials. It is widely used in catalysis, SOFC, mechanical polishing material, gas sensor and so forth. Among all these fields, people are especially interested in its catalytic performance.

The high catalytic capacity of nanoceria originates from its high level of Ce^{3+} and oxygen vacancy concentration. Lots of research works aim at controlling these parameters so as to improve the catalytic activity. In previous works, researchers have found that morphology and size control are quite important. Among the low miller-index surfaces, nanoceria with (100) or (111) surfaces has the highest catalytic capacity. Ce^{3+} and oxygen vacancy mostly reside on the surface of nanoceria because of coordination unsaturation. Small nanoparticles have high specific surface, and thus usually have more Ce^{3+} and oxygen vacancy on the surface and higher catalytic capacity.

In our previous work, we have synthesized ceria nanoparticles with different morphologies and sizes by hydrothermal method, and confirmed that small nanoceria exposing (100) facets have higher CO catalytic oxidation capacity. In the current work, we synthesized CeO_{2-x} nanoplates, nanotubes and fullerene-like nanoparticles by a simple pyrolysis method. All of these nanostructures have a thickness less than 1.2 nm, and among them the CeO_{2-x} nanoplates expose (200) facet. XPS proved that all of them have a high Ce^{3+} concentration (40% - 90%). These nanostructures may be promising candidates in the related catalysis field.



COLL 366

Self-assembly of tunable protein nanoclusters with molecular crowding agents (depletants)

Jessica J Hung, *jhung4@utexas.edu, Aileen K Dinin, Ameya U Borwankar, Barton J Dear, Brian K Wilson, April Twu, Jingyan Yue, Jennifer A Maynard, Thomas M Truskett, Keith P Johnston.Department of Chemical Engineering, University of Texas at Austin, Austin, TX 78712, United States*

Stabilizing proteins at high concentration is of broad interest in drug delivery for the treatment of cancer and many other diseases. Proteins have a tendency to undergo irreversible aggregation, gelation or precipitation at high concentrations due to unfolding caused by specific short ranged forces. We create highly concentrated antibody dispersions comprising dense equilibrium nanoclusters of protein molecules, which upon dilution *in vitro* reversibly dissociate to individual protein molecules. The nanocluster hydrodynamic diameter, determined by DLS, is tuned by manipulation of the electrostatic, van der Waals and depletion forces. Molecular crowding agents (depletants) are added to create sufficient depletion attraction to overcome electrostatic repulsion between individual protein molecules and drive assembly into clusters. We demonstrate that the size, polarity and charge of the depletant influence the thermodynamic self-assembly process, which is based on a free energy model. A hierarchy of intracluster and intercluster interactions is shown to produce self-limited growth of the clusters to a controllable size and to provide colloidal stability. The advancing understanding of the relationship between crowder structure, protein structure, pH and nanocluster formation and colloidal properties will be highly beneficial for developing novel drug delivery technologies.

COLL 367

Effects of a phage-display peptide on the growth of thiamethoxam (TMX) organic crystals

Whirang Cho[1]*, chorang@udel.edu, Lina Liu*[2]*, James Forrest*[2]*, Jeffrey D. Fowler*[2]*, Eric M. Furst*[1]*.Â (1) Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, United StatesÂ (2) Syngenta Crop Protection, Greensboro, NC 27409, United States*

Controlling the shape and size of crystalline solids is critical for the production of many fine chemicals, pharmaceuticals and foods, and is also important in drug delivery and release, and for technologies as diverse as bio/photo catalysis, thin-film solar cells, and antibacterial fabrics.We report the preparation of organic crystals of thiamethoxam (TMX) with a regular, micron-sized, tetragonal bipyramid shape by combinations of directed biological additives that specifically bind to the crystal surface and change the degree of supersaturation during crystal growth. Filamentous M13 bacteriophage was used as a versatile platform for presenting and selecting material-specific peptides with high affinity for TMX. Crystal morphology was manipulated with TMX-binding M13 bacteriophage displaying heptapeptide ASTLPKA coat proteins as a biological adsorbant. The mechanism by which crystal morphology was altered suggests an influence of the phage on the driving force for crystallization (an equilibrium effect) and/or the rate at which dissolved molecules precipitate on growing crystal faces (a kinetic effect). We also present data from de-supersaturation experiments suggesting that both phenomena were affected by the presence of the phage additives. Further, we varied the concentration of M13 type bacteriophage expressing heptapeptide ASTLPKA coat proteins to understand the characteristics of the adsorption behavior of phage to TMX crystals. It is shown that a modified Langmuir isotherm describes the adsorption isotherm of phage onto TMX crystals by introducing a concentration dependent factor. The phage adsorption data was also well-fitted to Satake-Yang model, which quantifies the extent of binding in terms of the binding constant (*Ku*) and the cooperativity parameter (*u*) via least-square-error fitting. This analysis suggested a cooperative binding between neighboring phage as well as site-specific binding with TMX surface. Such specific binding of M13 bacteriophage to solid surfaces could lead to the targeted manipulation of surface chemistry in colloidal suspensions in potentially complex mixtures.

COLL 368

Nanoscale carbon dots: From energy conversion to photocatalysts and mechanistic implications

***Sushant P Sahu**, sushans@clemson.edu, Ya-Ping Sun.Chemistry, Clemson University, Clemson, South Carolina 29634, United States*

The increasing demand for clean energy technology has generated tremendous amount of research in the development of nanostructured materials for efficient solar harvesting to address current global energy related concerns, particularly that of CO_2 conversion to hydrocarbon fuels and solar water splitting for hydrogen (H_2) generation,which were recently identified as one of the world's emerging key research fields for energy applications.[1-4] Of which, the increasing level of carbon dioxide (CO_2) in the atmosphere has become an important environmental issue, for which a number of carbon sequestration strategies have been pursued.[1,3] Among more desirable yet challenging option is the photocatalytic conversion of CO_2, especially with solar irradiation. While nanosized wide-band gap semiconductor-based systems were largely employed in such studies,[1,3,4] carbon nanoparticles have recently emerged as a new class of semiconductor equivalent photoactive materials, owing to some of its excellent optical figures of merit.[5-7] In this meeting, we would like to present the possibility of using quantum sized carbon particles as chromophores for energy conversion and visible-light photocatalysts for carbon dioxide conversion to organic acids such as formic acid (HCOOH), etc. as well as results supporting photoinduced redox behavior of carbon dots.[8-10] Very recent results obtained in our group will be briefly summarized and possible future directions will be proposed. Our results demonstrate that nanoscale carbon particles represent a highly promising new platform for visible-light photocatalysis of CO_2 conversion and beyond, competitive to that obtained with classical nanoscale semiconductor-based systems.

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COLL 369

Crystallization of lysozyme using metal-assisted and microwave-accelerated evaporative crystallization

*Kevin Mauge-Lewis, Adeolu Mojibola, **KADIR ASLAN**, kadir.aslan@morgan.edu.CHEMISTRY, MORGAN STATE UNIV., BALTIMORE, Maryland 21251-0001, United States*

In this study, the proof-of-principle application of the newly developed Metal Assisted – Microwave Accelerated Evaporative Crystallization (MA-MAEC) technique to the crystallization of lysozyme is demonstrated. Polyethylene glycol monomethyl ether was used as the solvent of choice for both room temperature crystallization and the MA-MAEC technique. At room temperature, complete crystallization of lysozyme occurred at 1,560 minutes with crystal sizes ranging between 15-440 µm. Using the MA-MAEC technique, complete crystallization of lysozyme was achieved at 555 minutes, and the same defined hexagonal crystal morphology as that of lysozyme crystallized at room temperature was observed. Crystal sizes using this technique ranged between 41-1630 µm. MA-MAEC was demonstrated to be a more effective technique in the rapid crystallization of macromolecules in comparison to room temperature crystallization

COLL 370

Dual-modal nanoprobes: Hybrid superparamagnetic iron-oxide and ultrasmall luminescent gold nanoparticles

***Rodrigo Vinluan**[1], rvinluan3@utdallas.edu, Jinbin Liu[1], Mengxiao Yu[1], Chen Zhou[1], Shengyang Yang[1], Amit Kumar[2], Orathai Thumthan[3], Shasha Sun[1], Andrew Dean[1], Yaowu Hao[3], Xiankai Sun[2], Jie Zheng[1].Â (1) Department of Chemistry, University of Texas at Dallas, Richardson, Texas 75080, United StatesÂ (2) Department of Radiology, University of Texas at Southwestern Medical Center, Dallas, Texas 75390, United StatesÂ (3) Department of Materials Science and Engineering, University of Texas at Arlington, Arlington, Texas 76019, United States*

While small-molecule based contrast agents have been widely used in the clinics, one major limitation is that they are only suitable for single modality imaging. As a result, the strengths of different imaging techniques are hardly integrated together for better disease management. To address this challenge, we recently synthesized a dual modal nanoprobe by integrating supermagnetic iron oxide nanoparticles with ultrasmall luminescent gold nanoparticles, which shows high physiological stability and can serve as contrast agents in both MRI and fluorescence imaging.

COLL 371

Cellular uptake and intracellular dynamics of luminescent plasmonic silver nanoparticles with different surface chemistries

***Shasha Sun**, sxs116020@utdallas.edu, Sishan Chen, Jinbin Liu.Chemistry, University of Texas at Dallas, Richardson, TX 75080, United States*

PEGylation and active targeting are two most common surface chemistry strategies used in enhancing tumor targeting efficiencies of inorganic nanoparticles (**NPs**). However, how these two strategies quantitatively influence their follow-up interactions with cancer cells such as membrane binding, cellular uptakes and intracellular dynamics have not been thoroughly and quantitatively investigated under the same conditions. To address these questions, we compared the cellular uptake and intracellular dynamics of luminescent silver NPs (AgNPs) coated by a PEG molecule modified and a c-RGD peptide, respectively. The c-RGD-AgNPs showed 20 times higher cellular uptake efficiency than the PEG coated one in the first three hour incubation and intracellular dynamics of c-RGD-AgNPs is also faster than that of PEG-AgNPs. This study helps quantitatively understand the surface chemistry effects on the in vitro behavior of NPs and is of fundamental importance of their applications as imaging agents or drug delivery vectors.

COLL 372

Design and application of novel PMMA platform for microwave-accelerated bioassays

***Muzaffer Mohammed**, mumoh1@morgan.edu, KADIR ASLAN.MORGAN STATE UNIV., BALTIMORE, Maryland 21251-0001, United States*

Microwave energy is being used to accelerate chemical and biological reactions including application in immunochemistry. Currently available 96 well High Throughput Screening (HTS) plate are ill-suited for microwave heating applications due the presence of sharp edges where microwaves tend to aggregate their energy, thereby causing uneven heating across the wells. We use COMSOL mutliphysics software to design a novel circular PMMA platform deposited with metal nanoparticles on surface for use in Microwave-Accelerated Bioassays (MAB) technique. We show the results of two ELISA based assays of wild type p53 and Glial Fibrillary Acidic Protein (GFAP) performed using our constructed platform and compare the results obtained at room temperature and using microwave heating

COLL 373

Frictional additivity of lateral diffusion on supported bilayers: Influence of linker length in Synaptotagmin 7 C2A-C2B tandem domains

***Joseph K Vasquez**, joseph.vasquez@ucdenver.edu, Kan Chantranuvatana, Jefferson Knight.Department of Chemistry, University of Colorado Denver, Denver, Colorado 80217, United States*

The synaptotagmin (Syt) family of proteins contains tandem C2 domains, C2A and C2B, which bind membranes in the presence of Ca^{2+}. The precise mechanism by which Syt participates in membrane fusion events is not completely understood, and the role of interactions between C2A and C2B in membrane binding and fusion is unclear. To test whether the two domains interact with each other on a planar lipid bilayer, diffusion constants of fluorescent-tagged C2A, C2B, and tandem C2AB domains from Syt7 were determined using total internal reflection fluorescence microscopy with single-particle tracking. As expected, the tandem domain diffuses significantly more slowly than the single domains. However, the diffusion constant of the C2AB tandem is significantly faster than predicted by simple summation of the individual domains' frictional coefficients. This result suggests that either (a) the short interdomain linker holds the two domains in close proximity to each other in the plane of the bilayer, at a separation distance shorter than the free draining limit, and/or (b) the two domains directly interact with each other when membrane-bound. In order to distinguish between these two possibilities, several mutant versions of the tandem domain with extended C2A–C2B linker regions were purified. Preliminary results indicate these mutants continue to diffuse similarly to the native C2AB tandem and faster than predicted based on frictional additivity, even at linker distances expected to exceed the free draining limit. These results suggest that C2A and C2B interact with each other when bound to a membrane in a manner that is independent of C2A−C2B linker length. Current experiments in this ongoing project probe the nature of the C2A–C2B interaction and may provide insight into the membrane fusion activity of this protein.

COLL 374

Signaling in cell membranes at the single molecule level

***Jay T Groves**, jtgroves@lbl.gov.Chemistry, UC Berkeley, Berkeley, CA 94720, United States*

The majority of intracellular signaling reactions take place on membrane surfaces, however the role of the membrane in modulating these chemical processes remains largely unknown. Using the supported lipid bilayer platform, we have developed several experimental systems that allow direct visualization of signaling reactions on membrane

surfaces at the single molecule level, both in vitro and in live cells. From these studies, a rich chemistry of regulated conformational dynamics along with membrane-induced structures and assemblies are emerging. This has significant consequences for the way we need to think about the chemical processes of signal transduction in living systems as well as they ways in which these may be therapeutically modulated.

COLL 375

Molecular drill bits as antibiotics

*Brian Murray[1], Zachary Kloos[2], C. Seth Pearson[1], Kathleen A. McDonough[2], **Georges Belfort**[1], belfog@rpi.edu.Â (1) Chemical and Biological Engineering and Center for Biotechnology and Interdisciplinary Studies, Rensselaer Polytechnic Institute, Troy, NY 12159, United StatesÂ (2) Infectious Diseases, Wadsworth Center, NY State Health Department, Albany, NY 12201, United States*

Antibiotic resistance is increasing at an alarming rate. Disrupting bacterial but not mammalian outer membrane integrity with peptides is an alternate strategy to destroy toxic bacteria and assess selectivity. New potent stable antimicrobial peptides (AMPs) together with a fundamental understanding of their mechanism of cell disruption are urgently needed. By combining a new *de novo* design approach, Database Filtering, protein engineering and rational design with several complementary measurement methods, we synthesize and test AMPs and derive structure-activity relationships for the most potent stable AMPs. Our first generation AMPs are toxic to both *M. smeg*matis and *Mycobacterium tuberculosis.* We also investigate the mechanism of membrane disruption of another class of AMPs, picidin 1 and 3, and discuss these finding.

COLL 376

Effect of surfaces on protein folding and assembly

***Joan-Emma Shea**, shea@chem.ucsb.edu.Chemistry and Biochemistry, UC Santa Barbara, Santa Barbara, CA 93106, United States*

The folding of a protein to its native state is critical for the correct functioning of the cell. Under cellular conditions, proteins encounter a variety of surfaces, from chaperones to membranes, that can alter folding pathways. In this talk, I will present atomistic and coarse-grained simulations to probe the effect of surfaces on protein folding and assembly.

COLL 377

Simulations of the folding/unfolding of proteins under different solvent and confinement conditions

***Angel E Garcia**, angel@rpi.edu.Physics, Applied Physics and Astronomy, Rensselaer Polytechnic Institute, Troy, NY 12180, United States*

Proteins exhibit marginal stability, determined by the balance of many competing effects. This stability can be perturbed by changes in temperature, pH, pressure, confinement and other solvent conditions. Osmolytes are small organic compounds that modulate the conformational equilibrium, folded (F) and unfolded (U), of proteins as cosolvents. Protecting osmolytes such as trimethylamine N-oxide (TMAO), glycerol, and sugars that push the equilibrium toward F play a crucial role in maintaining the function of intracellular proteins in extreme environmental conditions. Urea is a denaturing osmolyte that shifts the equilibrium toward U. Here we report the reversible folding/unfolding equilibrium, under various solution conditions that include urea, high pressure, and different charge states of the Trp-cage miniprotein. The folding/unfolding equilibrium is studied using all-atom Replica exchange MD simulations. For urea, the simulations capture the experimentally observed linear dependence of unfolding free energy on urea concentration. We find that the denaturation is driven by favorable direct interaction of urea with the protein through both electrostatic and van der Waals forces and quantify their contributions. Though the magnitude of direct electrostatic interaction of urea is larger than van der Waals, the difference between unfolded and folded ensembles is dominated by the van der Waals interaction. We also find that hydrogen bonding of urea to the peptide backbone does not play a dominant role in denaturation. The unfolded ensemble sampled depends on urea concentration, with greater urea concentration favoring conformations with greater solvent exposure. The m-value is predicted to increase with temperature and more strongly so with pressure.

We also study the equilibrium folding/unfolding thermodynamics of the Trp-cage that is confined to the interior of a 2 nm radius fullerene ball. The interactions of the fullerene surface are changed from non-polar to polar to mimic the interior of the GroEL/ES chaperonin that assists proteins to fold in vivo. We find that non-polar confinement stabilizes the folded state of the protein due to the effects of volume reduction that destabilize the unfolded state, and also due to interactions with the fullerene surface. For the Trp-cage, polar confinement has a net destabilizing effect that results from the stabilizing confinement and the competitive exclusion effect that keeps the protein away from the surface hydration shell, and stronger interactions between charged side chains in the protein with the polar surface that competes against the formation of an ion pair that stabilizes the protein folded state. We show that confinement effects due to volume reduction can be overcome by sequence specific interactions of the protein side chains with the encapsulating surface.

This work has been done in collaborations with graduate students D R Canchi, Camilo Jimenez, Charles English and Jianhui Tian. This research has been supported by grants from NSF MCB-0543769 and MCB-1050966.

COLL 378

Influence of guandinium on interface fluctuation

***Shuching Ou**, ousc@udel.edu, Di Cui, Sandeep Patel.Department of Chemistry & Biochemistry, University of Delaware, Newark, Delaware 19716, United States*

The guanidinium cation (C(NH2)3+) is a highly stable cation in aqueous solution due to the efficient resonance stabilization of the charge and efficient solvation by water molecules.
It is one of the strongest denaturants used in biophysical studies of protein folding.
Recently studies imply a connection between the ion-induced surface fluctuation and the ion stability at the interfaces.
The presence of guanidinium with different orientation has also shown distinct ability to pertubate the interfaces.
We therefore investigate the behavior of single guanidinium at the various surfaces (air-water, protein-water, oil-water), using atomistic molecular dynamics (MD) simulations and calculation of potentials of mean force.
Calculations of surface fluctuations demonstrate that near the surface, the parallel-oriented guanidinum generate significantly greater interfacial fluctuations compared to other orientations, which induces more long-ranged perturbations and solvent density redistribution.
This study serves as a bridge to understand the distinction (and similarity) between different types of interfaces.

COLL 379

Protein corona of nanoparticles

***Wolfgang J. Parak**, wolfgang.parak@physik.uni-marburg.de.Physics Department, Philipps UniversitÃ¤t- Marburg, Marburg, Germany*

The protein corona that forms on the surface of colloidal nanoparticles plays an important role in their interaction with living matter. For this reason the characterization of the protein corona is of utmost importance for understanding how exposure to nanoparticles affects the biological responses of cells and organisms. Although a lot of experimental work has been reported in this direction, a comprehensive picture is still missing, in particular due to the high number of different scenarios under which experiments have been performed. It will be reviewed how existing simple analytical models such as the adopted Hill model may help to extract quantitative data from such experiments such as equilibrium dissociation and kinetic coefficients of "in test tube" scenarios. However, once exposed to cells (in vitro), the protein corona of the nanoparticles can change, in particular upon incooperation of the nanoparticles by cells. Upon internalization, NPs typically reside in endocytic vesicles (e.g. endosomes, lysosomes), in which the conditions are completely different to those outside the cell; that is, NPs are exposed to a lower pH, different salts, and also different kinds of proteins and enzymes. It will be demonstrated how these enzymes can (at least partly) digest the original protein corona. Indications will be presented that the same is true also for in vivo scenarios.

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COLL 380

Interactions of gold nanoparticles with cells

***Catherine J. Murphy**, murphycj@illinois.edu.Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

Gold nanoparticles are emerging as possible in vivo agents, for drug delivery, imaging, or therapeutic purposes. The first level of interaction of gold nanoparticles with living systems is at the cellular level, and many workers in the field focus on cellular uptake and toxicity of their materials. In contrast, in this talk, I will discuss "nonlinear" effects that gold nanoparticles have on cells. In particular, I will focus on how gold nanoparticles alter cellular behavior, especially with regard to migration, and what possble mechanisms might be for these effects.

COLL 381

Plasmonic waveguide endoscopy

***Hiroshi Uji-i**, hiroshi.ujii@chem.kuleuven.be.Department of Chemistry, KULeuven, Heverlee, Flemish Brabant 3001, Belgium*

Metal nano-structures can be used as waveguides for propagating surface plasmon polaritons (SPPs), allowing the transfer of light over micrometer distance through structures with sub-diffraction limited diameter. This could lead to miniaturized photonics and help us to realize high-resolution microscopy. Alternatively, the use of surface plasmons allows us to concentrate light in nanometer regions, such as a nanogap between metal nanoparticles, leading to a massive enhancement of electromagnetic field that can be used for surface enhanced Raman scattering (SERS) spectroscopy. In this contribution, we introduce a noble endoscopy using the combination of these two concepts – that of SERS detection of bio-molecules and that of sub-diffraction limit SPPs waveguiding. Specifically, we demonstrate that SPPs launched along a silver nanowire (50-150 nm diameter) can excite SERS at an end of the wire due to the SPPs waveguide effect. [1] The ability to transfer SERS excitation over several microns,

through a sub-diffraction limited structure, will be discussed with respect to potential super-resolution SERS endoscopy in a living cell.

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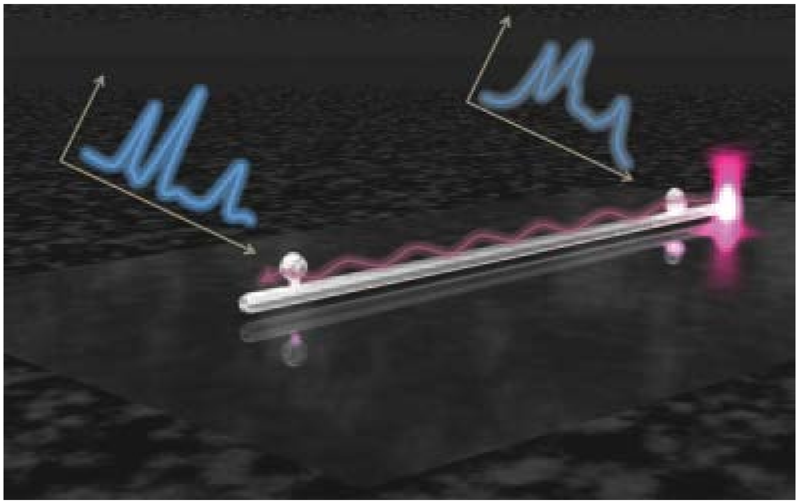

COLL 382

Plasmonic nanoreactors: From remote thermal activation of chemical reactions to intracellular optical monitoring

Miguel Angel Angel Correa-Duarte*, macorrea@uvigo.es.Departament of Physical Chemistry, University of Vigo, Vigo, Pontevedra 36310, Spain*

The synthetic architectures of complex nanostructures, including multifunctional hollow capsules, are expected to play key roles in many different applications, such as drug delivery, photonic crystals, nanoreactors, and sensing. Implementation of novel strategies for the fabrication of such materials is needed because of the infancy of this knowledge, which still limits progress in certain areas. We report herein the design of plasmonic hollow nanoreactors capable of concentrating light at the nanometer scale for the simultaneous performance and optical monitoring of thermal-activated reactions. These reactors feature the encapsulation of plasmonic nanoparticles on the inner walls of a mesoporous silica capsule. A Diels-Alder cy-cloaddition reaction was carried out in the inner cavities of these nanoreactors to evidence their efficacy. Thus, it is demonstrated that reactions can be accomplished in a confined volume without alteration of the temperature of the bulk solvent while allowing a real time monitoring of the reaction progress. Additionally, these plasmonic nanoprobes have been shown as an advanced intracellular hybrid SERS sensor for relevant signaling molecules (NO). After their inner functionalization with a NO chemoreceptor, the sensor is quantitative and can perform in-situ, real-time monitoring of the dynamics of intracellular NO in living

cells while remains fully biocompatible. Its sophisticated design prevents the interaction of cytosolic macromolecules within the active optical material and the enzymatic degradation of the sensor. It additionally facilitates the diffusion of small molecules between the interior and exterior thanks to the plasmonic thermal gradients generated upon their illumination.

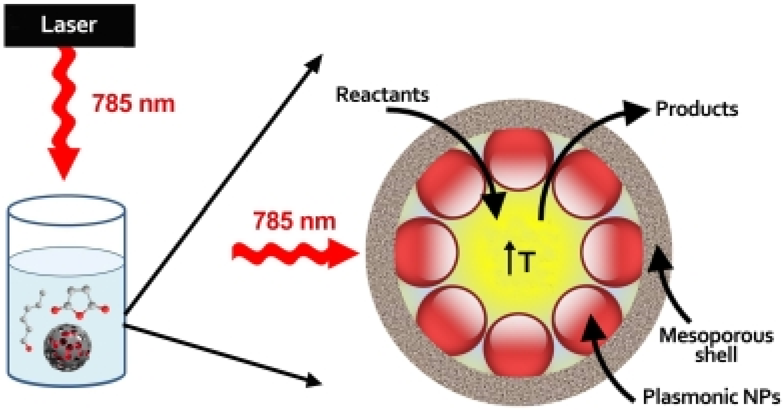

Figure 1. Schematic cross-section view of the plamonic nanoreactors developed in this work where reactants and products diffuse through the mesoporous silica shell and a NIR-laser irradiation promotes the chemical reaction allowing a simultaneous in situ SERS monitoring of the process.

COLL 383

Controlling the interactions of mesoporous silica nanoparticles with cells through multiple functionalities

*Alexandra Schmidt, Veronika Weiss, Stephan Mackowiak, Christian Argyo, Constantin von Schirnding, Stefan Niedermayer, Christoph Bräuchle, **Thomas Bein**, bein@lmu.de.Department of Chemistry, University of Munich (LMU), Munich, Germany*

Mesoporous silica core-shell nanoparticles (MSN) with high colloidal stability attract growing attention as targeted drug delivery systems. These types of nanoparticles can feature a well-defined and tunable porosity at the nanometer scale, high loading capacity, and the option to introduce multiple molecular functionalities. We will discuss the challenges associated with key functionalities needed to control the nanoparticle-cell interactions, including cell targeting, stimuli-responsive enclosure/release systems, and endosomal escape. For example, we have employed folate and epidermal growth factor (EGF) for successful cell-targeting with 70 nm MSNs, as well as pH-, redox-, or temperature-responsive release systems. To induce endosomal escape, we have covalently attached a red-light sensitive phthalocyanine photosensitizer surrounded by a lipid bilayer.[1] Photoactivation leads to endosomal membrane rupture in cells causing cargo release from the mesopores. These and other examples demonstrate that mesoporous silica nanoparticles constitute a promising and flexible platform for numerous biomedical applications.

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COLL 384

Tailoring the surface of inorganic nanoparticles

Beatriz Pelaz[1]*, beatriz.pelazgarcia@physik.uni-marburg.de, Mahmoud Gamal*[1]*, Pablo del Pino*[2]*, Wolfgang J. Parak*[1]*.Â (1) Physic Department, Philipps UniversitÃ¤t Marburg, Marburg, GermanyÂ (2) CIC biomaGUNE, San SebastiÃ¡n, Spain*

Colloidal stability of nanoparticles (NPs) in aqueous solutions is crucial for their use in bioapplications. One of the widest use methodologies to stabilize NPs in water solutions is the use of amphiphilic polymers. Despite, this methodology has been extensively used, it is working to transfer small organic-soluble NPs to water solution. One of advantages of this methodology is the generation of a universal nanoparticle surface when any kind of particle (size, shape or material) is coated using a common polymer. In this work, we demonstrated that the use of a phase transfer to organic solvent of the water-soluble NPs makes this methodology completely universal. This new phase transfer approach allows us transfer NPs of different materials, sizes and shapes.

COLL 385

Interactions between plasmonic nanoparticles and proteins investigated by correlation spectroscopy with single particle sensitivity

Stephan Link*, slink@rice.edu.Department of Chemistry, Rice University, Houston, TX 77005, United States*

We present *in situ* studies on the adsorption of proteins to plasmonic nanoparticles. We have implemented luminescence and scattering correlation spectroscopy with single particle sensitivity as an optical tool to quantify changes in the nanoparticle Brownian motion resulting from protein adsorption onto the nanoparticle surface. We are able to measure changes in the hydrodynamic radius of only a few nanometers corresponding to protein monolayer coverages. Nanoparticle aggregation can be distinguished by analyzing the collected photon trajectories for the intensity and number of individual bursts caused by single objects passing through the confocal excitation volume. We also measure adsorption isotherms to elucidate the thermodynamics of protein binding. For an accurate implementation of correlation spectroscopy methods it is furthermore necessary to understand how the collected optical signal scales with nanoparticle size and shape. We are able to obtain this information by correlated electron microscopy and single particle spectroscopy of immobilized plasmonic nanoparticles.

COLL 386

Effect of surface coatings on the cytotoxicity and cellular uptake of gold nanorods

***Jianfang Wang**, jfwang@phy.cuhk.edu.hk.Department of Physics, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong Special Administrative Region of China*

With the development of gold nanorods for versatile biomedical applications, understanding of their interactions with cells has become increasingly important. We prepared six types of surface coatings and investigated their effect on the cellular responses of gold nanorods. Cytotoxicity, cellular uptake, and photothermal effect in six different cell lines were examined. The coatings exhibit distinct cytotoxicities. The cell type plays a vital role for the cellular uptake of gold nanorods. The silica- and titania-coated gold nanorods show significantly higher amounts of cellular uptake than the PEG- and PSS-coated ones, which leads to better photothermal ablation effects for the silica- and titania-coated gold nanorods. Our studies indicate that the coatings on gold nanorods and the cell type determine the cellular responses. The inorganic coatings can bring improved biocompatibility, cellular uptake, as well as photothermal therapeutic effect to gold nanorods.

COLL 387

Insights into the cellular response following photothermal therapy

***Pablo del Pino**[1], pdp.glez@googlemail.com, Beatriz Pelaz[5], Marta Perez-Hermandez[4], Eva Galvez[3], Jesús Martinez de la Fuente[2], Julian Pardo[4].Â (1) Biofunctional Nanomaterials, CIC biomaGUNE, San Sebastian, SpainÂ (2) INA, Universidad de Zaragoza, Zaragoza, SpainÂ (3) Instituto de CarboquÃmica, CSIC, Zaragoza, SpainÂ (4) Department of Biochemistry, Universidad de Zaragoza, Zaragoza, SpainÂ (5) Department of Biophotonics, Philipps-UniversitÃ¤t Marburg, Marburg, Germany*

Among many distinct nanomaterials, plasmonic metal nanoparticles are very prolific in literature, mainly due to their fascinating optical properties. Importantly, the NIR activity of plasmonic materials such gold nanoprisms (NPRs) makes them very useful materials for many relevant applications in vivo such as photothermal therapy and optoacoustic imaging, among others. In vitro studies are however a priority in order to assess their biosafety. Herein, we report a multiparametric investigation on the impact of surface modified NPRs on mice and human primary and transform cell lines. Upon exposure of NPRs to cells, and following uptake, most important parameters such as generation of reactive oxygen species (ROS), mitochondrial hyperpolarization, proliferation, cell morphology and apoptosis features were systematically assayed. Results clearly demonstrate a significant impact of the internalized NPRs in the cell morphology and mitochondria, which however do not translate into impartment of cell viability. Under NIR illumination, these nanoprobes can cause apoptosis. Herein, molecular details following photothermal therapy are described.

COLL 388

Probing scavenger receptor mediated endocytosis in a macrophage model system through plasmon coupling microcopy

Bjoern Reinhard, *bmr@bu.edu.Department of Chemistry and The Photonics Center, Boston University, Boston, Massachusetts 02446, United States*

Macrophages belong to the mononuclear phagocyte system (MPS), which plays a prominent role in the clearing of pathogens and debris from the body. To that end, macrophages are equipped with a broad range of pattern recognition receptors that enable the cell to recognize specific surface features. These functionalities play a key role in regulating the interactions between macrophages and colloidal particles, but the intricate mechanisms between artificial colloidal nanoparticles (NPs) and the responding cellular machinery as well as the intracellular fate of non-degradable colloidal nanoparticles still raises important questions. We investigated the scavenger receptor mediated uptake and subsequent intracellular spatial distribution of 60 nm diameter silver NPs in the murine macrophage cell line J774A.1 through plasmon coupling microscopy (PCM). This optical technique facilitates a monitoring of the nanoparticle association level in living cells in real time. We found that the NPs exhibit an overall red-shift of the plasmon resonance wavelength in the cell ensemble as function of time and concentration, indicative of intracellular NP agglomeration. A detailed analysis of the NP clustering in individual cells revealed, however, a strong phenotypic variability in the intracellular NP organization on the single cell level. Throughout the observation time of 24h cells containing non- or low-agglomerated NPs coexist with cells containing NPs with varying degrees of agglomeration, as evinced by distinct spectral shifts of their resonance wavelengths. Additional pharmacological inhibition studies demonstrated that the observed differences in intracellular NP organization result from coexisting actin- and clathrin-dependent endocytosis mechanisms in the J774A.1 macrophage population. Correlation of intracellular NP clustering with macrophage maturity marker (F4/80, CD14) expression revealed that differentiated J774A.1 cells preferentially contain compact NP agglomerates, whereas monocyte-like macrophages contain non-agglomerated NPs. Overall, our studies indicate significant differences in the cellular processing of NPs in the J774A.1 population that arise from different maturation levels.

COLL 389

Preventing the aggregation of colloidal gold nanoparticles with a protein monolayer

Sergio Dominguez-Medina[1], *sd20@rice.edu, Jan Blankenburg*[1], *Jana Olson*[1], *Christy F. Landes*[1,2], *Stephan Link*[1,2]*.Â (1) Department of Chemistry, Rice University, Houston,* *Texas 77005, United StatesÂ (2) Department of Electrical and Computer Engineering, Rice University, Houston, Texas 77005, United States*

Citrate-stabilized gold nanoparticles aggregate and precipitate below the NaCl concentration of many bodily fluids and blood plasma. Our experiments indicate that this is due to complexation of the citrate anions with Na+ cations in solution. We find that monolayer adsorption of bovine serum albumin -the most abundant protein in cow blood and a side product of the cattle industry- completely prevents the aggregation of colloidal gold nanoparticles under harsh environmental conditions where the NaCl concentration is well beyond the isotonic point. Furthermore, we explore the mechanism of the formation of this albumin corona and find that monolayer protein adsorption is most likely ruled by hydrophobic interactions. As for many nanotechnology-based biomedical and environmental applications, particle aggregation and sedimentation are undesirable and could substantially increase the risk of toxicological side effects; the formation of the BSA corona presented here provides a low-cost biocompatible strategy for nanoparticle stabilization and transport in biological fluids.

COLL 390

Tale of tails: Alkyl chain directed formation of 2D porous networks reveals odd–even effects and unexpected bicomponent phase behavior

Oleksandr Ivasenko[1], *oleksandr.ivasenko@gmail.com, Elke Ghijsens*[1], *Kazukuni Tahara*[2], *Hiroyuki Yamaga*[2], *Shintaro Itano*[2], *Tatyana Balandina*[1], *Yoshito Tobe*[2], *Steven De Feyter*[1]*.Â (1) Department of Chemistry, Division of Molecular Imaging and Photonics, KU Leuven, Leuven, BelgiumÂ (2) Graduate School of Engineering Science, Division of Frontier Materials Science, Osaka University, Toyonaka, Osaka 560-8531, Japan*

Supramolecular self-assembly of suitably functionalized building blocks on surfaces can serve as an excellent test-bed to gain understanding and control over multicomponent self-assembly in more complex matter. Here we employ a powerful combination of scanning tunnelling microscopy (STM) and molecular modeling to uncover two-dimensional (2D) crystallization and mixing behavior of a series of alkylated building blocks based on dehydrobenzo[12]annulene, forming arrays of nanowells. Thorough STM investigation employing high-resolution spatial imaging, use of specially designed marker molecules, statistical analysis and thermal stability measurements revealed rich and complex supramolecular chemistry, highlighting the impact of odd–even effects on the phase behavior. The methodology and analysis presented in this work can be easily adapted to the self-assembly of other alkylated building blocks.

E. Ghijsens *et al.*, *ACS Nano,* 2013, 7 (9), pp 8031–8042

COLL 391

Forced to align: Flow-induced long-range alignment of hierarchical molecular assemblies

Shern-Long LEE[1]*, ShernLong.Lee@chem.kuleuven.be, Zhongyi Yuan*[2]*, Kunal S. Mali*[1]*, Long Chen*[2]*, Klaus Müllen*[2]*, Steven De Feyter*[1]*.Â (1) Department of Chemistry, KU Leuven - University of Leuven, Leuven, BelgiumÂ (2) Max Planck Institute for Polymer Research, Mainz, Germany*

We report a two-step flow method for producing a large area hierarchical organization of molecules at the interface of 1, 2, 4-trichlorobenzene and highly oriented pyrolytic graphite (HOPG), as evidenced by scanning tunneling microscopy. The first flow can induce, over millimeter scale, a uniaxial assembly of rod-like molecules of hexarylene diimide (HDI) where some misaligned HDI molecules appear as up-layer can readily be aligned *via* a subsequent flow. The as-prepared superstructure allows more efficient electron transport *via* the π-stacking conjugated cores of molecules revealed by scanning tunneling spectroscopy.

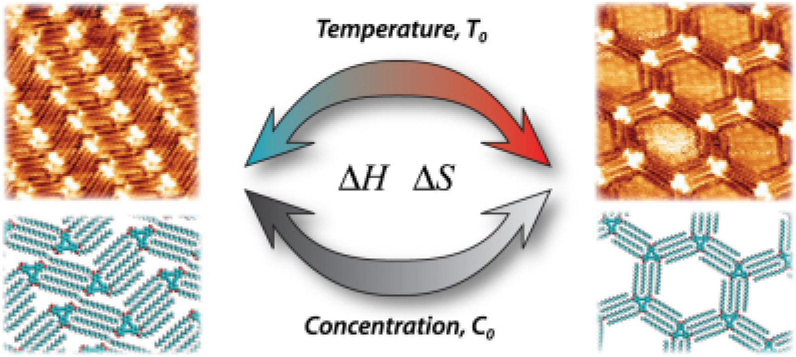
COLL 392

Temperature induced structural phase transitions in a 2D self-assembled network

Matthew O Blunt[1]*, m.blunt@ucl.ac.uk, Jinne Adisoejoso*[2]*, Keisuke Katayama*[3]*, Mark Van der Auweraer*[4]*, Kazukuni Tahara*[3]*, Yoshito Tobe*[3]*, Steven De Feyter*[4]*.Â (1) Department of Chemistry, University College London, London, London WC1H 0AJ, United KingdomÂ (2) Department of Physics, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, ChinaÂ (3) Division of Frontier Materials Science, Graduate School of Engineering Science, Osaka University, Osaka, JapanÂ (4) Department of Chemistry, Division of Molecular and Nanomaterials, KU Leuven, Leuven, Belgium*

Two-dimensional (2D) self-assembly at solid-liquid interfaces can produce a wide array of molecular networks ranging from closely packed to porous structures. Self-assembly under these conditions is a complex process which depends delicately on the strength of interactions between different components of the system; network molecules, solvent molecules and the substrate. Environmental conditions such as the concentration of network molecules in solution and the temperature[1] also play a pivotal role. We report a set of scanning tunnelling microscopy (STM) experiments which study the temperature dependence for the self-assembly of dehydrobenzo[12]annulene (DBA) derivatives at the interface between graphite and an organic solvent. Previous work has shown that DBA switches between two different network arrangements by controlling the concentration[2]with lower concentrations favouring a porous structure. We show that a similar reversible transition between the same two structures can also be achieved by varying the temperature, with the porous network favoured at higher temperatures. By measuring the temperature for the transition at different concentrations and applying this data to a thermodynamic model for the transition we derive values associated with

the change in enthalpy and entropy when DBA molecules adsorb from solution. These experimental values are then compared to theoretically calculated estimates.



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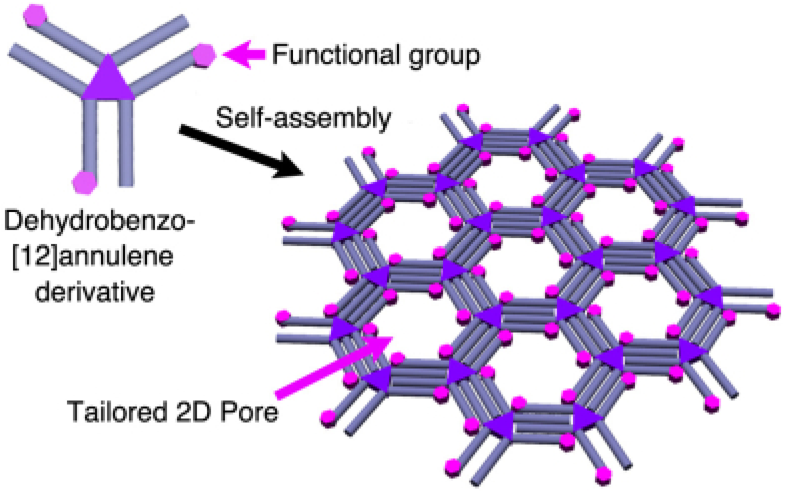
COLL 393

Tailoring surface-confined nanopores within 2D porous molecular networks

Kazukuni Tahara[1], *tahara@chem.es.osaka-u.ac.jp, Koji Inukai*[1], *Keisuke Katayama*[1], *Jinne Adisoejoso*[2], *Matthew O. Blunt*[2], *Steven De Feyter*[2], *Yoshito Tobe*[1]*.Â (1) Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, JapanÂ (2) Department of Chemistry, KU Leuven, Celestijnenlaan 200 F, Leuven, Belgium*

The construction of two-dimensional (2D) porous patterns on solid surfaces using molecular self-assembly has become a subject of great interest because of perspectives in unique applications. Surface confined pores within the 2D porous molecular networks can be used as host space to immobilize guest molecules at the surface. One of the significant challenges in the design of 2D porous system is physical or chemical modification of the interior space of porous networks to construct tailored functional pores. We previously reported that dehydrobenzo[12]annulene (DBA) derivatives formed porous honeycomb structures at the liquid/solid interfaces by van der Waals interactions between interdigitated alkyl chains with adjacent molecules. On the basis of the modification of the alkyl chains attached to DBAs, we herein report the construction of tailored 2D pores, that exhibit an unique recognition toward a guest molecule and the reversible change of the pore size by external stimuli.



COLL 394

STM investigation of interactions in self-assembled organic monolayers

***Yousoo Kim**, ykim@riken.jp.RIKEN, Wako, Saitama 351-0198, Japan*

Well-ordered organic monolayers are expected to play a prominent role in novel technologies beyond Si-based electronics, owing to their versatility in controlling physical and chemical properties. Scanning tunneling microscopy (STM) and density functional theory calculations investigation of self-assembled monolayers (SAMs) is discussed in terms of a subtle balance between molecule−substrate and intermolecular interactions.

Tripod-shaped bromo adamantane trithiol (BATT) molecule forms highly-ordered SAMs with two-tiered hierarchical chiral organization on Au(111) [1]. The self-assembly of achiral BATT monomers produces chiral trimers, followed by forming chiral hexagonal supermolecules. Two structural factors, the S atom (stabilization) and the methylene groups (chirality), induce the chiral ordering of BATT.

Fluorinated fullerene ($C_{60}F_{36}$) with high electron affinity and wide band-gap n-type property forms SAMs on Au(111) [2]. LUMO distribution of the SAMs governs the adsorption orientation due to partial electron transfer from Au to $C_{60}F_{36}$. The intermolecular C-F…π electrostatic interactions determines the lateral orientation of $C_{60}F_{36}$. The LUMO being much closer to the Fermi level than HOMO suggests the potential application for electron transport layer in organic electronic devices.

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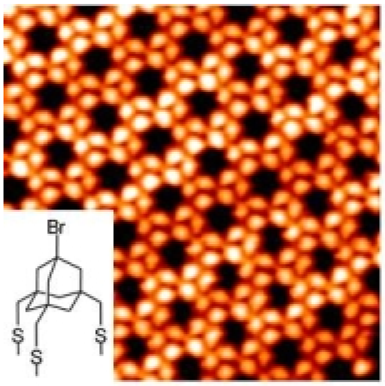
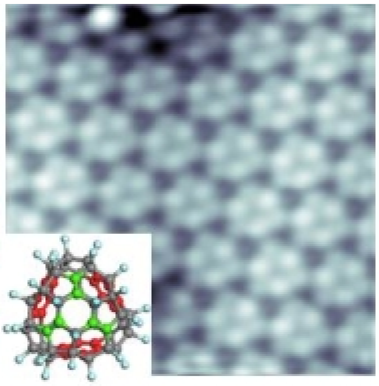


BATT/Au(111)



C60F36/Au(111)

COLL 395

Atomic-scale probing and controlling functional molecular nanostructures

***Klaus Kern**, k.kern@fkf.mpg.de.Max-Planck-Institut fuer Festkoerperforschung, Stuttgart, GermanyEcole Polytechnique FÃ©dÃ©rale de Lausanne - EPFL, Lausanne, Switzerland*

The advent of scanning probe microscopy has provided the unique ability to investigate matter with ultimate precision. Single atoms and molecules can today not only be imaged with unprecedented resolution but also probed by local spectroscopy, manipulated to assemble functional nanostructures and excited to induce chemical change. In the present talk I will present our recent efforts to push the limit of scanning probe microscopy and spectroscopy by exploiting ultralow temperatures and high magnetic fields as well as by developing novel vacuum interfaces for the controlled handling of biomolecules with negligible vapor pressure. The experiments provide unprecedented microscopic details of functional molecular interfaces. Many new perspectives ranging from controlling molecular folding to the development of new concepts in molecular quantum electrodynamics and energy conversion are opened up.

COLL 396

Scanning tunneling microscopy of single and few molecule aggregates of free base and metaled porphyrins on Au surfaces

***Alison Pawlicki**[1], alison.pawlicki@chem.tamu.edu, Bradley Ewers[2], Amanda Schuckman[2], Matthew Jurow[3], Charles Drain[3], James Batteas[1,2].Â (1) Materials Science and Engineering, Texas A&M University, College Station, TX 77843-3003,* *United StatesÂ (2) Chemistry, Texas A&M University, College Station, TX 77842-3012, United StatesÂ (3) Department of Chemistry, Hunter College of the City University of New York, New York, New York 10065, United States*

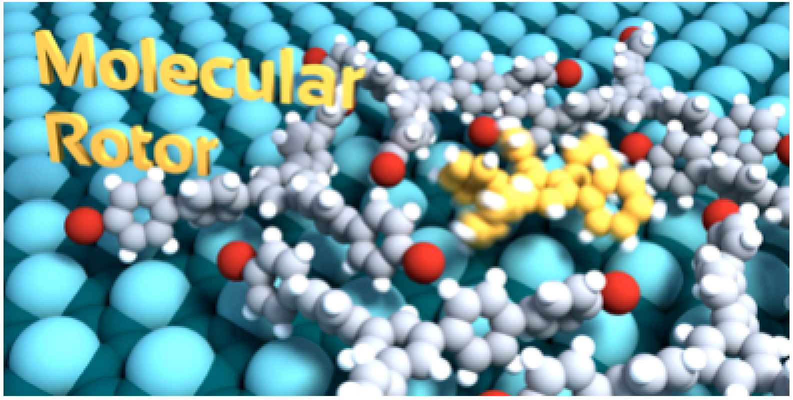
The idea of molecular electronics uses molecules to serve as the building blocks for devices instead of traditional semiconductor materials. One advantage of using molecules arises from the bottom-up way in which such devices can be constructed; one building block at a time, as opposed to conventional top-down device fabrication techniques where devices emerge from macroscopic systems. Other advantages include increased functionality and operating speeds. To profit from these advantages, it is essential to understand the connection between molecular structure and electron conduction in molecules singly and in small clusters. To develop this understanding, we have studied electron transport through a series of porphyrinoid molecules that is composed of a porphyrin macrocycle, pendant phenyl linker, and a thiol theater. The series of molecules is built by altering the choice of metal ion within the macrocycle and the choice of phenyl constituents. These porphyrinoids are examined as part of a mixed self-assembled monolayer (SAM) in which the porphyrinoids randomly insert singly or as small clusters. The electronic structure of the mixed SAM system was modeled by Density Functional Theory and the physical structure was inspected by Atomic Force Microscopy. Electron transport was investigated by Scanning Tunneling Microscopy to obtain the tunneling efficiency, conductance switching behavior, and current-voltage characteristics. We found that the identity of the metal ion impacts the aggregation chemistry of the porphyrins and the phenyl constituents impact the phenyl-macrocycle coupling, thus influencing the conducing/insulating character of the molecule. This study provides integral knowledge necessary for designing molecular electronics devices with intended functions.

COLL 397

Molecular rotators on a silicon surface

***Frederic CHERIOUX**[1], frederic.cherioux@femto-st.fr, Olivier Guillermet[2], Ather Mahmood[1], Jianshu Yang[2], Jorge Echeverria[2], Judicael Jeannoutot[1], Sebastien Gauthier[2], Christian Joachim[2], Frank Palmino[1].Â (1) Institut FEMTO-ST, Besancon, FranceÂ (2) CEMES, Toulouse, France*

The formation and control of rotors adsorbed onto a surface are one of the most promising challenges in nanotechnology. In the present study we demonstrate the remarkable achievement of thermally-activated rotation of pentaphenylbenzene molecules within nanopores formed in a self-assembled supramolecular network on a silicon based surface. Pentaphenylbenzene is composed of five phenyl rings attached to a central aromatic core, where the 6th position on the central ring is vacant. This vacancy works as an excellent marker in STM images for an easy identification of static position, step-by-step rotation and continuous rotation. We have demonstrated by STM experiments, performed from 77 to 150 K, and theoretical calculations that the pore geometry and molecule-surface interaction are key factors in controlling the symmetrical positioning and onset of rotational motion. Furthermore, our ability to control surface temperature allows the determination of activation energy for mobilizing either individual or groups of these 5-lobed rotor structures in the nanoscopic pores. We think that this study opens new avenues for studying the controlled dynamics of molecular machines fabricated on semiconducting surfaces.



COLL 398

Role of benzotriazole in passivating copper surfaces

Federico Grillo, *fg11@st-andrews.ac.uk, Daniel W Tee, Stephen M Francis, Herbert A Früchtl, Neville V Richardson.EaStCHEM and School of Chemistry, University of St Andrews, St Andrews, United Kingdom*

Benzotriazole (BTAH) has been used as a copper corrosion inhibitor since the 1950s. Several adsorption models have been proposed,[1] however the details of how adsorption and surface passivation occur remain a matter of debate. BTAH interaction with a Cu(111) single crystal under UHV conditions has been investigated via vibrational spectroscopy (RAIRS, HREELS) and STM, with support from DFT calculations. At low coverage, BTAH adsorbs as $Cu(BTA)_2$ and CuBTA, which form chains, whose sections diffuse in a concerted manner, while the Cu surface forms a (2×1) reconstruction.[2]Two coexisting extended self-assembled packings are observed at saturation coverage and above, up to desorption at ca. 600 K. The selectivity of BTAH for copper is further investigated by coadsorption of BTAH and copper onto a Au(111) surface, where the topology of the overlayer shows dependency upon preparation conditions and heating treatments. Figure 1 summarizes the different structures observed. This study may contribute to understanding further the interaction between BTAH and Cu, and in turn the mechanism for surface passivation.

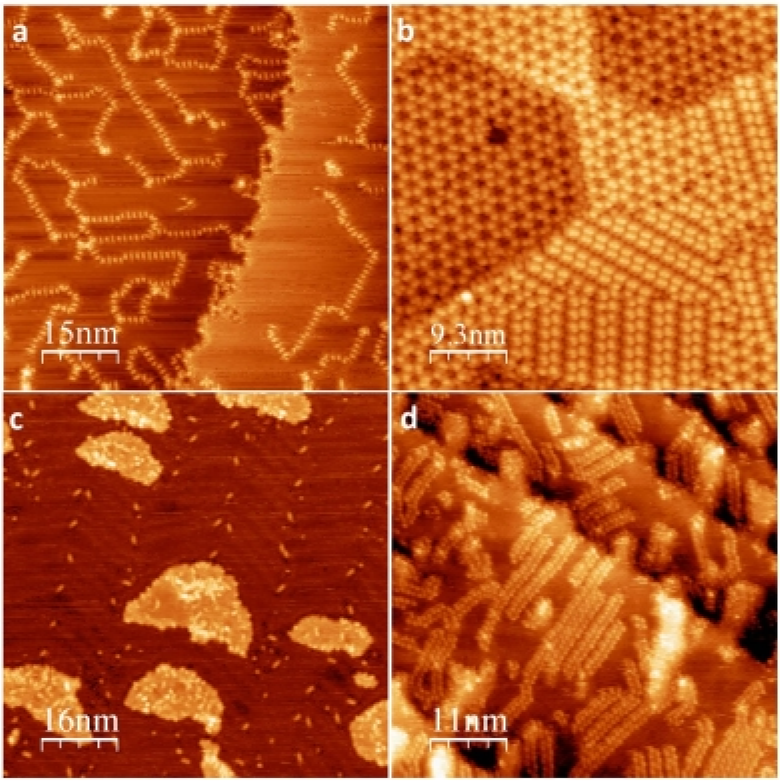


Figure 1. STM images showing: a) ca. 0.05ML BTAH/Cu(111); b) ca. 1ML BTAH/Cu(111); c) BTAH on Cu/Au(111); d) Cu on BTAH/Au(111).

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COLL 399

Systematic nanotoxicity evaluation via zebrafish models

*Gun Hyuk Jang[1,2], Mintai Hwang[1], **Kwan Hyi Lee**[1,2], kwanhyi@kist.re.kr.Â (1) Center for Biomaterials, KIST Biomedical Research Institute, Seongbuk, Seoul 136-791, Republic of KoreaÂ (2) Department of Biomedical Engineering, University of Science and Technology (UST), Seongbuk, Seoul 136-791, Republic of Korea*

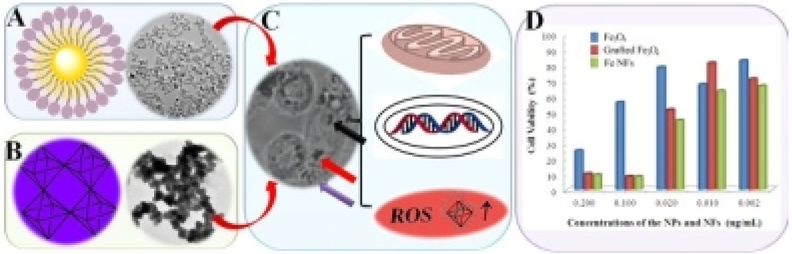
Zebrafish provide many advantages that include, but are not limited to, the following: 1) fast embryonic development, yielding full organ functionality in a short time frame, 2) a transparent body, providing excellent light penetration for a variety of optical and fluorescence microscopy experiments, and 3) an economical and easy maintenance setup, thereby increasing the possible number of samples in a given experimental group. While such zebrafish-specific advantages confer an ideal model for rapid and large-scale toxicity experiments, zebrafish have only been used by others in a limited manner. In this study, we present the *in-vivo* nanotoxicity of nanoparticles by conducting a thorough analysis that includes an examination of phenotypic developmental abnormalities, apoptotic cell death, and heart function.

COLL 400

Evaluation of design and magnetism of nanoparticles and their in vitro cytotoxicity analyses

Eduardo Hernandez[1]*, Eduardo.Hernandez@students.tamuk.edu, Sreevardhan Reddy Posa*[1]*, Xueyan Du*[3]*, Srinath Palakurthi*[2]*,* ***Jingbo Liu***[1,3]*, jingbo.liu@chem.tamu.edu, Sajid Bashir*[1]*.Â (1) Department of Chemistry, Texas A&M University-Kingsville, Kingsville, Texas 783638204, United StatesÂ (2) Department of Pharmacy, Texas A&M Health Science Center, Kingsville, Texas 783638204, United StatesÂ (3) Department of Materials Science, Lanzhou University of Technology, Lanzhou, China 130 050, China*

This research is focused on producing various magnetic nanocomposites (e.g. Fe_3O_4-based MNCs) via a green bottom-up synthesis approach using natural products as reducing and dispersing agents. The fabrication variables of the green synthesis were optimized to obtain MNCs with tuneable architecture and magnetism. The use of water-soluble *Salvia hispanica* and traditional Chinese medicine (*Cordyceps extracts*) offers a variety of water-soluble components to enhance the reduction of inserted noble (such as gold and platinum) metal aimed to increase the fluorescent intensity of those MNCs in a cancer treatment setting. The MNCs were modified, using amphiprotic functionalization and surface grafting chemistries, that successfully maintained high super-paramagnetic behaviour averaged at 60 $A•m^2•kg^{-1}$. Advanced techniques were used to characterise the materials, which demonstrate MNC crystalline structure, uniform paramagnetism and intermediate biological toxicity. The cytotoxicity (cyto) analysis using Chinese hamster ovary (CHO) cells showed an effective dose at 50% of ~20 ppb, (cyto 100 ppm) indicating that amphiproticity of grafted Fe_3O_4-MNCs would facilitate targeting of tumour cells. All class of MNCs displayed EC_{50} activity (11-16% relative to control iron oxide) and can serve as targeting and drug delivery systems as demonstrated *in vitro* by the 3-[4,5-dimethylthiazol-2-yl]-2,5 diphenyl tetrazolium bromide) (MTT) assay



The cytotoxicity (in terms of effective dose at 50%) of our nanomaterials is low (ED_{50} ~20ppb, cyto 100 ppm), indicated that amphiproticity of grafted (**i**) Fe_3O_4-NPs and (**ii**) FeO_4-NFs in itself is low and would facilitate the targeting to the tumour cells (Chinese hamster ovary cells used as a model, CHO), **A**: functionalization scheme for (i) by grafting to maintain magnetism and enhance biological effectiveness; **B**: functionalization scheme for (**ii**) showing high potency against CHO cells; **C**: mechanistic study suggested that the nanomaterials mediated cytotoxicity appears via oxidative damage to the plasma membrane (⟍ lipid peroxidation followed by lysis), DNA fragmentation (⟍ lesions) and degradation of proteins (⟍); and **D**: *in vitro* cytotoxicity analyses demonstrating the high potency of the nanomaterials against CHO cells.

. The mode of inhibition was not thoroughly investigated but appears to involved inhibition of DNA unzipping and replication, as shown by SN-38 standard anti-cancer drug, used as a baseline for efficacy evaluation.

COLL 401

Silver nitrate as a control in silver nanoparticle toxicity tests

Vytas Reipa, *vytas@nist.gov, Steve Rhieu, Sandra daSilva.Biosystems and Biomaterials Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8313, United States*

Antimicrobial properties of silver have been known since ancient times (1). Nanotechnology development vastly expanded silver use in various commercial and biomedical applications and stimulated safety studies. It has been recognized that silver ion release due to the nanoparticle corrosion in aqueous environment is directly related to silver nanoparticle antibacterial potency. Numerous efforts have been directed towards measuring and controlling Ag^+ release rates through nanoparticle engineering and related toxicity assays. Typically a silver nitrate is used in these experiments as a control material to simulate the dissolved silver, given the high solubility of the salt. However, the presence of the nitrate in the test solution is mostly ignored and unaccounted for in the toxicity assay results. Nitrate has been known to pose serious health hazards when consumed by living beings (2). We compare silver nitrate to five alternative soluble silver salts (fluoride, acetate, sulfate, nitrite and bromate) for relative toxicity towards the *E.Coli* using the drop plate method to check cell viability at Ag^+ concentrations up to 40 micrograms/L.

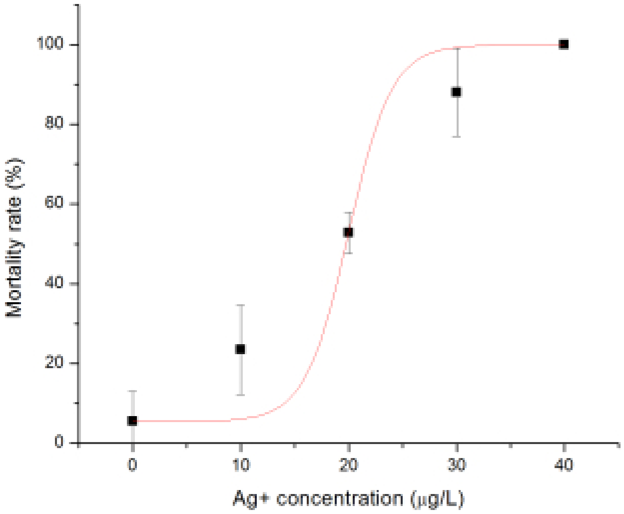


Figure 1. *E.Coli* mortality following a 6h incubation in $AgNO_3$solutions

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COLL 402

Effect of sulfidation and shape on the toxicity of silver nanoparticles

Danielle E Gorka[1,2]*, danielle.gorka@duke.edu, Jie Liu*[1,2]*, Joshua S Osterberg*[2,3]*, Richard T Di Giulio*[2,3]*.Â (1) Department of Chemistry, Duke University, Durham, NC 27708, United StatesÂ (2) Center for the Environmental Implications of NanoTechnology (CEINT), Durham, NC 27708, United StatesÂ (3) Nicholas School of the Environment, Duke University, Durham, NC 27708, United States*

Silver nanoparticles (AgNPs) are increasingly being used due to their unique properties. The most commercially exploited property is their antimicrobial activity. Though most research studying the antibacterial activity has focused on spherical AgNPs, some research has shown that toxicity depends on the shape of the nanomaterial, and materials with different shapes are being used in antibacterial products. The increased use in consumer products has resulted in increased entrance into wastewater and subsequently the environment, where little research has been done to understand the transformations and environmental toxicity. Studies have shown that AgNPs become

sulfidized after entrance into the environment, however the lab and field studies have shown differences in structure.

The aim of this work was to examine the transformations of several shapes of AgNPs through sulfidation and the resulting toxicity to the common annual ryegrass *Lolium multiflorum*. Quasi-spheres, wires, and cubes were synthesized by commonly used polyol methodologies and characterized both before and after partial sulfidation with sodium sulfide. *L. multiflorum* seeds were exposed to the sulfidized and unsulfidized particles at a concentration 10 ppm Ag. After growing in ambient conditions for five days, plants were examined to determine if any toxic effects were present. Exposed plants displayed toxicity in decreased root and shoot length, as well as the absence of root hair. The order of toxicity was semi-spherical AgNPs > silver ions > nanowires ~ nanocubes > control. Plants exposed to unsulfidized NPs showed the greatest toxicity while plants exposed to sulfidized NPs showed little to no toxicity compared to controls. These results indicate that sulfidation after entrance to the environment will greatly decrease the toxicity of AgNPs.

COLL 403

Toxicity of silver nanoparticles: Influence of the particle shape, size, and surface coating

Qingbo Zhang[1], *nanomaterialszh@gmail.com, Zongming Xiu*[2], *Tanya peretyazhko*[1], *Pedro Alvarez*[2], *Vicki L. Colvin*[1]*.Â (1) Department of Chemistry, Rice University, Houston, TX 77005, United StatesÂ (2) Department of Civil and Environmental Engineering, Rice University, Houston, TX 77005, United States*

Silver nanoparticles have extensive application potential in the field of clinic and biomedical devices. The toxicity of silver nanoparticles is highly dependent on their shape, size and surface coating. It is important to systemically evaluate and understand the effect of these particle attributes on the toxicity of the nanoparticles for the responsible application of these nanomaterials.

We synthesized a large library of silver nanoparticles with independently adjustable shape, size and surface coating using solution chemistry method. Using these materials, the influence of the nanoparticle attributes on the toxicity of the nanoparticles was systematically investigated. The mechanism of the toxicity of silver nanoparticles was also studied.

COLL 404

DNA damaging potential of photoactivated P25 titanium dioxide nanoparticles

Elijah J Petersen[1], *elijah.petersen@nist.gov, Vytas Reipa*[1], *Stephanie S Watson*[2], *Deborah L Stanley*[2], *Savelas Rabb*[1], *Bryant Nelson*[1]*.Â (1) Material Management*

Laboratory, NIST, Gaithersburg, MD 20899, United StatesÂ (2) Engineering Laboratory, NIST, Gaithersburg, MD 20899, United States

Titanium dioxide nanoparticles (TiO2 NPs) are found in numerous commercial and personal care products. Thus, it is necessary to understand and characterize their potential environmental health and safety risks. It is well known that photoactivated TiO2 NPs in aerated aqueous solutions can generate highly reactive hydroxyl radicals (•OH) which can damage DNA. Surprisingly, recent in vitro studies utilizing the comet assay have shown that non-photoactivated TiO2 NPs kept in the dark can also induce DNA damage. In this work, we utilize stable isotopedilution gas chromatography/tandem mass spectrometry to quantitatively characterize the levels and types of oxidatively generated base lesions in genomic DNA exposed to NIST Standard Reference Material TiO2 NPs (Degussa P25) under precisely controlled illumination conditions. We show that DNA samples incubated in the dark for 24 h with TiO2 NPs (concentrations ranging from 0.5 >g/mL to 50 >g/mL) does not lead to the formation of base lesions. However, when the same samples are exposed to either visible light from 400 nm to 800 nm (energy dose of ~ 14.5 kJ/m2) for 24 h or UVA light at 370 nm for 30 min (energy dose of ~ 10 kJ/m2), there is a significant formation of lesions at the 50 >g/mL dose for the visible light exposure and a significant formation of lesions at the 5 >g/mL and 50 >g/mL doses for the UVA light exposure. These findings suggest that commercial P25 TiO2 NPs do not have an inherent capacity to oxidatively damage DNA bases in the absence of sufficient photoactivation; however, TiO2 NPs exposed to electromagnetic radiation within the visible portion of the light spectrum can induce the formation of DNA lesions. Based on these findings, comet assay processing of cells exposed to TiO2 should be performed in the dark to minimize potential artefacts from laboratory light.

COLL 405

Detection of carbon nanotubes in biological samples through microwave-induced heating

*Fahmida Irin[1], Mohammad Saed[2], Jaclyn Canas-Carrell[3], **Micah Green**[1], micah.green@ttu.edu.Â (1) Department of Chemical Engineering, Texas Tech University, Lubbock, Texas 79409, United StatesÂ (2) Department of Electrical and Computer Engineering, Texas Tech University, Lubbock, Texas 79409, United StatesÂ (3) Department of Environmental Toxicology, The Institute of Environmental and Human Health, Texas Tech University, Lubbock, Texas 79409, United States*

We demonstrate a novel technique for quantitative detection of carbon nanotubes (CNT) in biological samples by utilizing the thermal response of CNT under microwave irradiation. In particular, rapid heating of CNT due to microwave absorption is employed to quantify CNT uptake in agricultural samples with excellent sensitivity. We inject alfalfa (Medicago sativa) roots with a known quantity of CNT (single walled and multi walled) and expose the samples to a microwave field (30-50 W) to generate standard temperature-CNT concentration relationships; this detection method is then used to accurately determine CNT uptake by alfalfa plant roots grown in CNT-laden soil. The threshold for detectable CNT concentration is much lower than common analytical methods such as electron microscopy and Raman spectroscopy. Considering the lack of effective detection methods for CNT uptake in plants, our concept is not only unique but also practical, as it addresses a major problem in the field of nanomaterial characterization and nanotoxicology risk assessment.

COLL 406

Nanotopography and surface modification influence the behavior of cells on gallium nitride interfaces

***Albena Ivanisevic**, ivanisevic@ncsu.edu.MSE, NC State University, Raleigh, NC 27695, United States*

The chemical stability and electrical properties of gallium nitride have made it a promising material for the development of biocompatible electronics, a range of devices including biosensors as well as interfaces for probing and controlling cellular growth and signaling. To improve the interface formed between probe material and cell or biosystem, surface topography and chemistry can be designed to modify the ways in which the device interacts with its environment. PC12 cells are cultured on as-grown flat, unidirectionally polished, etched nanotextured, and nanowire GaN surfaces with and without a physisorbed peptide sequence that promotes cell adhesion. Raman spectroscopy identifies the chemical similarity of the surfaces, while scanning electron microscopy and atomic force microscopy confirm the topography and surface roughness for each substrate preparation. Cells demonstrate preferential adhesion to roughened surfaces over as-received, flat surfaces. Additionally, the morphology of that roughness influences cellular adhesion and the conformation of differentiation in neurotypic cells. Addition of the peptide sequence contributes further to cellular adhesion, with general increases in the number of adherent cells as well as changes in the cell morphologies observed on the different surfaces.

COLL 407

Role of fiber length on phagocytosis and inflammatory response

*Carahline M. Stark[1], **Leonid A. Turkevich**[2], LLT0@cdc.gov, Julie A. Champion[1].Â (1) Department of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0100, United StatesÂ (2) Department of Aerosol Research / CEMB / DART, NIOSH / CDC, Cincinnati, OH 45226, United States*

Asbestos fibers induce chronic lung inflammation and have been associated (WHO estimate) with 10^5 lung cancer deaths per year worldwide. In the lung, immune cells (macrophages) attempt to engulf inhaled foreign materials (like asbestos), secreting inflammatory molecules. The inability of macrophages to effectively remove asbestos leads to chronic inflammation and disease. Although the health effects of asbestos have been extensively investigated, this study examines the role of fiber length on phagocytosis and molecular inflammatory responses so as to characterize fiber toxicity at the cellular level. A major challenge is obtaining fibers of the same diameter, d, but differing in length, L. Glass fibers, with d ~1μm, were used as a model for asbestos. Samples with different measured length distributions were prepared: aggressive crushing for short fibers (L < 15 μm) and successive sedimentation for long fibers (L < 15 μm).

The interactions of MH-S murine alveolar macrophages with the fibers were analyzed by time-lapse video microscopy, to qualitatively describe attempted phagocytosis in real time, and by flow cytometry, to quantitatively measure attachment and internalization of fibers. Short fibers were observed (microscopy) to bind to macrophages, being internalized with little effort; macrophages literally wrestled with long fibers over many hours, usually with unsuccessful internalization; short fibers were twice as likely to be internalized as the long fibers. Production of pro-inflammatory molecules was measured following exposure of macrophages to a range of fiber doses. Tumor necrosis factor alpha (TNF- α), a potent, general inflammatory secreted cytokine, was measured by ELISA. Cyclooxygenase-2 (Cox-2), an enzyme in cells that produces radical intermediates and is upregulated in mesothelioma, was measured by Western blot.Both exhibited a dose-dependent increase that was greater for long fibers than for short fibers. These results corroborate the critical importance of fiber length in both physical and biochemical cell response and support epidemiological observations of higher toxicity for longer fibers.

COLL 408

Ordered molecular monolayers on single crystal TiO_2 surfaces

***Matthias Batzill**, mbatzill@usf.edu.Department of Physics, University of South Florida, Tampa, FL 33620, United States*

The adsorption and ordering of molecules at well-defined TiO_2 surfaces are investigated by a combination of scanning tunneling microscopy and density functional theory calculations. The interplay between molecule-substrate and intermolecular interaction can give rise to ordered overlayer structures of the molecules. The influence of surface structure on the adsorption of molecules is explored on the example of carboxylic acid adsorption on the rutile TiO2(110) versus TiO_2(011)-2x1. On the (110) surface a well-ordered molecular superstructure is formed due to a bridge-bidentate adsorption of a carboxylate. In contrast the surface reconstruction of the (011) surface strongly modifies the adsorption. A partial lifting of the surface reconstruction as a result of the strong molecule-substrate interaction results in an anisotropic adsorption forming quasi-one dimensional carboxylate clusters. In a second part of this talk we investigate the adsorption of a nitro-group containing molecule (2-4 dinitrotoluene). Unlike carboxylic acid that adsorbs through the dissociation of the acidic proton, we show that nitro-group containing molecules may adsorb molecularly intact. On the rutile (110) surface an

ordered monolayer structure may be observed for 2-4 dinitrotoluene for saturation coverage at room temperature.

COLL 409

Chemical self-assembly strategies for metal-organic surface structures

Wilfred T Tysoe, *wtt@uwm.edu, John Kestell, Michael Garvey.Chemistry and Biochemistry, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53211, United States*

A self-assembly reaction, in which extended structures grow parallel to a surface is found based on isocyanide-containing molecules, in particular, with 1,4-phenylene diisocyanide (PDI), which forms long, one-dimensional oligomeric chains when adsorbed on the Au(111) surface. It is found that the isocyanide functionality binds strongly enough to gold that it can extract gold atoms from low-coordination sites on a Au(111) surface to form extended, one-dimensional oligomeric Au-PDI structures. The π-conjugation is maintained throughout the oligomeric species and that they are reasonably mobile. The self-assembly pathway is explored using density functional theory calculations to estimate the energetics of the self-assembly reaction. It is found that a PDI-Au adatom complex is the precursor to oligomer formation and propagates by attaching to the end of a PDI-terminated chain. It is found that analogous chemistry can, in some cases, occur with thiol-functionalized analogs of PDI and two-dimensional metal organic framework structures can be synthesized using 1,3,5-triisocyanobenzene.

COLL 410

Formation process studies of flatly oriented porphyrin self-assembled layers on Au(111)

Toshihiro Kondo, *kondo.toshihiro@ocha.ac.jp, Nana Aoki, Tomoko Arisaka, Yurika Ishikawa.Department of Chemistry, Ochanomizu University, Bunkyo-ku, Tokyo 112-8610, Japan*

Porphyrin derivatives are well-known to have unique photochemical, electrochemical and catalytic properties and then have extensively used as a building block in construction of molecular devices. In order to construct molecular devices using porphyrin with higher efficiency, we should control porphyrin ring orientation, namely porphyrin ring should be adsorbed parallel to the substrate surface. Moreover, ordered multilayers of porphyrins can be constructed by alternating construction of ligand and porphyrin layers if the flatly adsorbed porphyrin monolayer is formed on the substrate surface as a first layer. In this report, a novel porphyrin derivative with 4 thiol groups as surface binding groups to gold, 5,10,15,20-tetrakis(m-mercapto-p-methoxyphenyl) porphyrin (TMMPP) was designed and synthesized, and self-assembly process of TMMPP on Au(111) single crystal surface was investigated by electrochemical and scanning tunneling microscopy (STM) measurements.

After annealing and quenching of Au(111) single crystal disk, TMMPP self-assemled monolayer (SAM) on Au(111) was prepared by dipping the Au(111) substrate into benzene solution containing 0.05 mM TMMPP for certain periods. Linear sweep voltammograms of the Au(111) electrodes modified with TMMPP SAM, which was prepared for several dipping periods, were measured in 0.1 M KOH solution. Ex situ STM measurement of each TMMPP SAM on Au(111) was performed in air at room temperature.

Based on the experimental results, we found that TMMPP molecule was flatly adsorbed in the initial stage of SAM formation process and flatly adsorbed TMMPP was arranged in order on the atomic arrangement of the underlying Au(111) surface at the final stage of TMMPP self-assembly.

COLL 411

Plasma chemistry and film growth in a complex organic systems

Matthew J Goeckner, *goeckner@utdallas.edu.Mathematical Sciences, University of Texas at Dallas, Richardson, TX 75083, United States*

In an idealized thin-film production system, one would be able to precisely control the resultant product. However, many thin-films produced via conventional chemical processes do not have some desired properties (e.g. adhesion, thickness, etc.). Often these properties can be obtained if one makes use of plasma processing. Unfortunately, limited knowledge of the complex chemistry in plasma systems often makes development of optimized deposition processes difficult. In this talk we will examine the major chemical processes that occur in plasma deposition of a few organic based thin-films.

COLL 412

In-situ studies of low reactivity surfaces: Defects and functionalization

Robert M Wallace, *rmwallace@utdallas.edu.Materials Science and Engineering, University of Texas at Dallas, Richardson, TX 75080, United States*

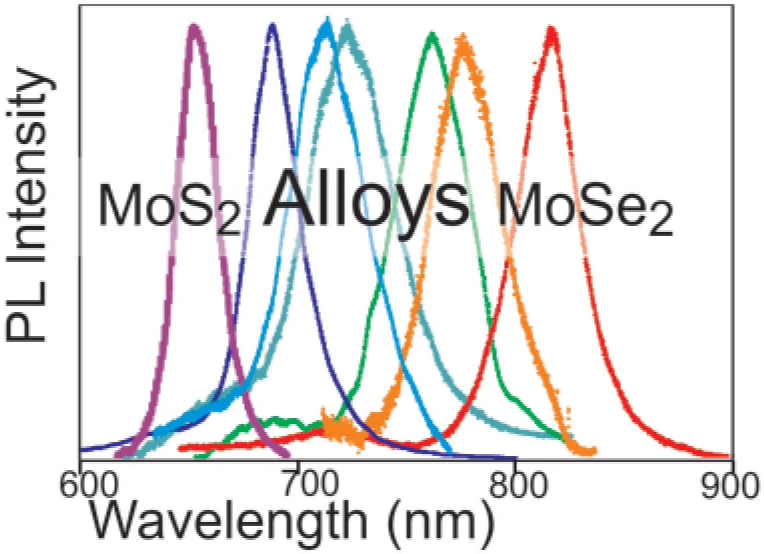
Electronic device technologies are evolving to emphasize the dominance and manipulation of surfaces and interfaces to obtain desirable properties. In this talk, we will present our recent examination of reactions on 2D materials including graphene and transistion metal dichacogenides using in-situ methods from an electronics materials perspective. In addition to the role of defects, we will describe the effects of residual contamination and intentional functionalization which impact the surface/interfacial chemistry for useful device properties.

COLL 413

Growth and post-growth modification of MoS_2, $MoSe_2$ and $MoS_{2(1-x)}Se_{2x}$ alloys

*John Mann[1], David Barroso[1], Ariana Nguyen[1], Dezheng Sun[2], Quan Ma[1], **Ludwig Bartels**[1], bartels@ucr.edu.Â (1) University of California, Riverside, CA 92521, United StatesÂ (2) Columbia University, New York, NY 10027, United States*

We have prepared monolayer films of molybdenum dichalcogenide alloys with composition varying continuously between MoS_2 and $MoSe_2$. The films are grown on a SiO_2 surface using organic sulfur/selenium precursors and a MoO_3 solid source. The composition of the films for different growth conditions is determined directly using photoelectron spectroscopy. All $MoS_{2(1-x)}Se_{2x}$ films exhibit a direct band gap and transition energies that can be tuned continuously between 1.87 eV (pure single-layer MoS_2) and 1.55 eV (pure single-layer $MoSe_2$) through control of the S/Se ratio.



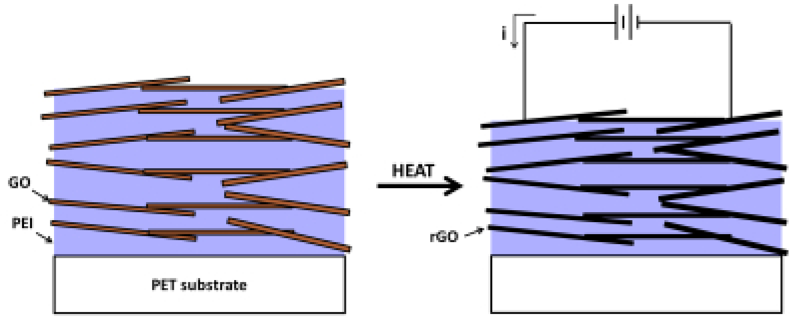
I will also talk about recent efforts in post-growth S/Se exchange in these films.

COLL 414

Thermally reduced graphene oxide-PEI multilayer thin films as electrically conductive gas barrier layer

***Bart Stevens**[1], bartstevens@tamu.edu, Alexander D Todd[2], Christopher W Bielawski[2], **Jaime C Grunlan**[1,3], jgrunlan@tamu.edu.Â (1) Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843-3123, United StatesÂ (2) Department of Chemistry, University of Texas at Austin, Austin, TX 78712, United StatesÂ (3) Department of Materials Science, Texas A&M University, College Station, TX 77843-3123, United States*

In many cases, electronics packaging requires electrical conductivity and barrier to oxygen, even under humid conditions. These two properties have simultaneously been realized through the use of surfactant-free aqueous layer-by-layer (LbL) processing, in the form of a polymer composite nanocoating. By layering graphene oxide (GO) with polyethyleneimine (PEI), a 'nano brick wall' structure has been created, imparting gas barrier properties to the film. Reducing the graphene oxide with a thermal treatment further produces high oxygen barrier in humid conditions and imparts low electrical sheet resistance. These thin films (less than 400 nm) are flexible relative to traditional conductive thin films (e.g. ITO), and processing occurs under ambient conditions with water as the only solvent.



COLL 415

Selective assembly of 1D nanostructures: From the directed placement of DNA-origami on surfaces, to the controlled formation of carbon nanotubes junctions

Matteo Palma[1]*, m.palma@qmul.ac.uk, Erika Penzo*[2]*, Risheng Wang*[2]*, James Hone*[3]*, Ming Zheng*[5]*, Colin Nuckolls*[4]*, Shalom J. Wind*[2]*.Â (1) School of Biological and Chemical Sciences, Queen Mary University of London, London, United KingdomÂ (2) Department of Applied Physics and Applied Mathematics, Columbia University, New York, United StatesÂ (3) Department of Mechanical Engineering, Columbia Univeristy, New York, United StatesÂ (4) Department of Chemistry, Columbia University, New York, United StatesÂ (5) Department of Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States*

One of the ultimate goals in nanotechnology is the ability to produce efficient optoelectronic devices based on individual functional molecules and nanostructures. Many challenges remain, and principal among these is the difficulty in fabricating functional devices at nanometer dimensions, due to the poor control over the assembly.

Here we present different approaches towards the controlled and ordered assembly of one-dimensional (1D) nanoobjects from solutions to surfaces. This is achieved via the combination of high resolution patterning with selective end-functional chemistry. In particular we have assembled 1D DNA nanostructures with high precision via hybridization in situ on properly lithographically patterned, and selectively functionalized, surfaces. Using electron-beam and nanoimprint lithography we fabricated sub-10nm metal dots arranged in multiple configurations. The DNA-origami employed functioned as a model-system for the bivalent self-assembly of nanorods on metal-nanodot pairs. By varying the length of the ssDNA linker, we were able to study the binding efficiency as a function of interaction strength. Using the same basic approach, we have begun studying the selective binding of carbon nanotubes to the nanodot anchors. Fixed-length SWNT segments, wrapped with ssDNA, were indeed attached to amine-functionalized nanodot anchors.

We further extended our studies to the controlled formation of carbon nanotube junctions via linker-induced assembly in aqueous solution. We will describe a facile and green strategy for the controlled formation of one dimensional and multi-terminal single walled carbon nanotube (SWCNT) junctions via directed chemical reactions. We found that different shaped linkers yield SWCNTs with higher order structures that go beyond simple linear arrays to ones that are multiterminal and circular. These unusual structures are formed from a self-assembly process in aqueous solutions that is controlled by the geometry, and the chemical nature, of the linker. The approach presented is of general applicability for the sustainable fabrication of solution-processable (CNT-based) nanoscale devices.

COLL 416

Layer-by-layer assembly and characterization of metal-organic coordinated thin films

*Monica L Ohnsorg, Christopher K Beaudoin, Alexandra S Benson, **Mary E Anderson**, meanderson@hope.edu.Chemistry, Hope College, Holland, MI 49423, United States*

Metal-organic coordination can be utilized to direct layer-by-layer (LBL) assembly of thin films. With sequential deposition of the organic and metal component on the surface, tailoring of film structure and composition is permitted. Controlled step-wise assembly defines the resulting film structure, presenting an opportunity to design the framework for specific applications. Toward this realization, this research focuses on understanding the fundamentals of film formation for two types of metal-organic coordinated thin films, multilayers (MLs) and frameworks (MOFs). The ML system studied was an assembly of α,ω-mercaptoalkanoic acids and Cu (II) ions and the MOF system was composed of benzene-1,3,4-tricarboxylic acid and Cu (II) ions (HKUST-1, $Cu_3(btc)_2$). Throughout the alternating solution-phase deposition, films were characterized using ellipsometry to measure film thickness and scanning probe microscopy (SPM) to map topographical morphology of film growth LBL. Using image analysis software, quantitative data regarding the growth of these thin films based on the images was procured (e.g. Particle Analysis and Percent Area Coverage). For both ML and MOF systems, ellipsometry shows that film thicknesses uniformly increase by 2 nm per layer deposited. However, SPM images of the foundational film layers reveal two distinct growth mechanisms, one that forms a semi-continuous conformal film with distinct features (ML) and one that

forms a rough surface of nucleating crystallites (MOF). Work is underway to determine how many layers are necessary for the MOFs to form a continuous film and to investigate if the growth mechanism transitions at that point. Further studies will investigate the effect of processing variables such as morphology of underlying substrate, chemical functionality of organic binding layer, and post-deposition annealing.

COLL 417

Vesicle and particle assembly driven by polymer-DNA recognition

***Dennis Bong**, bong.6@osu.edu.Department of Chemistry and Biochemistry, The Ohio State University, Columbus, Ohio 43210, United States*

We have recently reported the discovery of a new class of peptide nucleic acids that utilize non-native bifacial triamino triazine nucleobase recognition elements that we term bifacial peptide nucleic acid (bPNA). The synthetic triazine base may engage with two thymine or uracil bases simultaneously, resulting in the formation of heterotriplex structures when polythymidylate or polyuridylate strands are assembled a single bPNA strand. We have discovered that the L-peptide backbone may be replaced by polyacrylates appropriately functionalized with triazines while retaining selective nucleic acid folding function. These polyacrylates were prepared with low polydispersity using RAFT polymerization, which further yielded terminal thiol functional groups after cleavage of the trithiocarbonate chain transfer agent used in RAFT. Thiol alkylation was facile, permitting coupling to lipid vesicles and gold nanoparticles. The subsequent particles could be noncovalently derivatized in solution with polythymidine terminated DNA molecules that guide vesicle and particle assembly. We report herein biophysical and structural characterization of vesicle and particle assemblies.

COLL 418

Targeted membrane fusion using a pair of lipidated coiled coil peptides

***Alexander Kros**, a.kros@chem.leidenuniv.nl.Leiden Institute of chemistry, Leiden University, Leiden, - 2300RA, The Netherlands*

For many years, nature has been a source of inspiration for supramolecular chemistry. Here, scientists design relatively simple molecules which assemble into functional materials with well-defined properties, typically following a bottom up approach. Recent progress has resulted in molecular assemblies which are responsive to multiple stimuli and are therefore highly controlled, emulating nature ever more closely. A relatively new branch of development is the application of supramolecular constructs in an *in vitro* and *in vivo* environment, to directly mimic, study and influence biological processes in live cells. We are inspired by the fusion of biological membranes as it allows the delivery of molecules across lipid bilayers, barriers that are usually impervious to the molecules. In nature, SNARE-proteins mediate intracellular membrane fusion, in concert with other proteins.

Inspired by this SNARE protein complex, we showed that complementary coiled coil forming lipidated peptides embedded in liposomal membranes are able to induce rapid, controlled and targeted membrane fusion. Here we will discuss its scope and our current understanding of its mechanism of fusion.

COLL 419

Role of ligand presentation on the selective affinity of proteins to lipid membrane domains

Darryl Y. Sasaki[1], *dysasak@sandia.gov, Noor Momin*[3]*, Stacey Lee*[1]*, Carl C. Hayden*[2]*, Jeanne C. Stachowiak*[3]*, George D. Bachand*[4]*.Â (1) Department of Biotechnology and Bioengineering, Sandia National Laboratories, Livermore, CA 94551, United StatesÂ (2) Department of Combustion Chemistry, Sandia National Laboratories, Livermore, CA 94551, United StatesÂ (3) Department of Biomedical Engineering, University of Texas, Austin, Austin, TX 78712, United StatesÂ (4) Department of Nanosystems Systems/Analysis, Sandia National Laboratories, Albuquerque, NM 87185, United States*

Spatiotemporal control over protein assemblies in membranes is essential for modeling cellular processes, such as signaling, adhesion, and trafficking. How the confinement and organization of these proteins occur, however, is not fully understood as the interplay of protein-membrane interactions and phase partitioning are complex. Previously, we showed that proteins could be confined to specific lipid membrane domains through interfacial interaction with metal chelates (Cu-IDA, Ni-NTA) and his-tags on the proteins. Recently, we have found that ligand presentation strongly influences the location of bound proteins in heterogeneous membranes. For biotin-streptavidin complexes, where the ligand binding site is deep within the protein, the distance between the ligand and membrane surface can affect protein-membrane interactions and the phase to which the membrane-bound proteins reside. We studied a series of biotinylated lipids with different spacer lengths and tail structures that direct partitioning of the lipids into specific membrane phases (i.e., liquid ordered or liquid disordered). For the shortest spacer lengths, streptavidin binding was exclusively observed in the liquid disordered regions of the membrane regardless of tail structure. As the spacer length increased, however, the selectivity of the protein to specific domains was increasingly dictated by the lipid tail structure. These results provide further understanding of the selective functionalization of specific membrane domains to enable the assembly of complex molecular machinery.

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COLL 420

Quantum dots encapsulated within phospholipid membranes: Phase-dependent structure, photostability, and site-selective functionalization

*Weiwei Zheng, Yang Liu, Ana West, Erin Schuler, R. Brian Dyer, James Kindt, **Khalid Salaita**, k.salaita@emory.edu.Department of Chemistry, Emory University, Atlanta, Georgia 30322, United States*

Lipid vesicle encapsulation is an efficient approach to transfer quantum dots (QDs) into aqueous solutions, which is important for renewable energy applications and biological imaging. However, little is known about the molecular organization at the interface between a QD and lipid membrane. To address this issue, we investigated the properties of 3.0 nm CdSe QDs encapsulated within phospholipid membranes displaying a range of phase transition temperatures (Tm). Using photoluminescence, ICP-MS, optical microscopy, and ligand exchange studies, we found that the Tm of the membrane controls QD photostability and ligand accessibility. Atomistic molecular dynamics simulations support these observations and indicate that membranes are disordered near the particle surface. Using membrane disorder, we site specifically functionalize the QD surface to generate gold nanoparticle-QD assemblies programmed by Watson-Crick base-pairing.

COLL 421

Role for ROCK1-dependent contractility in proteolytic degradation by cancer cell invadopodia

***Aron Parekh**, aron.parekh@vanderbilt.edu.Department of Otolaryngology, Vanderbilt University Medical Center, Nashville, TN 37232, United States*

Cells sample and respond to extracellular matrix (ECM) stiffness with actomyosin-generated contractile forces in a process known as rigidity mechanosensing. In cancer, the rigidity of the tumor-associated ECM has been implicated in promoting invasive migration by cancer cells via mechanical signaling pathways. We have previously shown that cancer cell contractile forces are dependent on ECM rigidity and are predictive of ECM degradation by invadopodia, actin-rich subcellular protrusions which are thought to be essential for invasion and metastasis. Cellular contractility is regulated by myosin light chain kinase (MLCK) and rho-associated kinase (ROCK). Numerous studies have utilized common kinase inhibitors to show that MLCK and ROCK influence invasive migration similarly. However, recent work has shown that the isoforms ROCK1 and ROCK2 participate in some non-redundant signaling pathways that depend on cellular spatial localization. In addition, MLCK also displays preferential cellular localization which results in little effect on sustained force generation. In support of these differences, we present data utilizing siRNA against the two ROCK isoforms and MLCK that reveal diverse effects on actomyosin contractility and invadopodia activity. These results suggest that only a ROCKI-dependent mechanical signaling pathway may be involved in directly regulating both contractile forces and ECM degradation.

COLL 422

Transmembrane protein characterization and analysis of cellular mechano-sensing using polymer-tethered membrane architectures

*Corey Lin[1], Yifan Ge[1], Noor F Hussain[1], Daniel E Minner[2], Amanda P Siegel[2], **Christoph A Naumann**[1], canauman@iupui.edu.Â (1) Department of Chemistry and Chemical Biology, Indiana University-Purdue University Indianapolis, United StatesÂ (2) Integrated Nanosystems Development Institute, Indiana University-Purdue University Indianapolis, United States*

Physisorbed polymer-tethered lipid bilayers comprised of phospholipids and lipopolymers represent highly versatile supramolecular assemblies of adjustable dynamic and mechanical properties. At low lipopolymer concentrations, these membrane systems are well-suited for the investigation of transmembrane proteins in well-defined lipid compositions using sensitive biophysical detection techniques. Polymer-tethered membranes also allow the controlled adjustment of bilayer diffusivity and membrane elasticity. On the basis of this attractive feature, we developed two types of biomembrane-mimicking cell substrates of tunable viscoelasticity. The first type enables control of substrate viscoelasticity by variation of lipopolymer concentration in a single polymer-tethered lipid bilayer. Such cell substrates are particularly interesting because they can be built with an elastic (lipopolymer) gradient. The second type of cell substrate is based on a polymer-tethered lipid multi-bilayer. Here modification of substrate viscoelasticity is achieved by altering the number of bilayers in the stack. Experiments on different mechano-sensitive cell lines are presented, which demonstrate the functionality of both types of biomembrane-mimicking cell substrates.

COLL 423

Non-covalent functionalization, dispersion, and processing of colloidal graphene

*Dorsa Parviz, Sriya Das, Fahmida Irin, **Micah Green**, micah.green@ttu.edu.Department of Chemical Engineering, Texas Tech University, Lubbock, Texas 79409, United States*

This work focuses on the central concept of producing graphene from graphite without covalently functionalizing the graphene basal plane; such graphene may be stabilized, dispersed, and processed for use in a range of high-performance materials. In particular, our group has shown that both polyvinylpyrrolidone as well as pyrene derivatives can naturally absorb to the graphene surface, create repulsive (steric and electrostatic) forces, and prevent aggregation. This allows for graphene dispersion in a wide range of organic solvents and composite precursors without compromising graphene structure. Such dispersions are stable against aggregation even when subjected to extreme temperature changes, pH changes, and freeze drying. The graphene/stabilizer ratio obtained by this method is exceptionally high relative to conventional surfactants. The mechanism of stabilization by pyrene derivatives were

investigated as a function of the type and number of functional groups, counterions, and the electronic interaction between the functional groups and the basal plane.

Polymer nanocomposites formed from these dispersions include graphene-loaded epoxy and graphene-loaded polyvinyl alcohol films and nanofibers; these composites consistently show enhanced modulus, strength, and electrical conductivity. We also demonstrate novel results in the area of graphene aerogel templating to achieve an ultralow percolation threshold. These dispersions also show promise for applications to organic solar cells, conductive films, and inkjet-printed electronic devices.

COLL 424

Microwave induced funtionalization and purification of carbon nanotubes

***Zheqiong Wu**, zw52@njit.edu, Somenath Mitra.chemistry and environmental science, NJIT, newark, NJ 07102, United States*

The conventional approach to functionalization of raw carbon nanotubes (CNTs) is via some form of acid treatment, which typically leads to over-functionalization and unwanted oxidation products. A majority of the functionalization schemes use acid treatment as a first step to introduce covalently bonded carboxylic functional groups on CNTs, which then can be further functionalized to amine, ester, amide, polymeric, or other groups. Dilute base-washing has been shown to remove oxidation debris by converting the acidic groups to their dissolvable conjugate salts. In this work we present the effect of advanced purification such as base-washing for the purification of microwave induced carboxylated carbon nanotubes. The effect on solubility, colloidal stability and surface functionalities are presented.

COLL 425

Colloidal stability of functionalized graphene in aqueous sodium dodecyl sulfate solutions: From surfactant adsorption to dispersion behavior

***Andrew G. Hsieh**[1], aghsieh@princeton.edu, Christian Punckt[1,2], Sibel Korkut[1,2], Ilhan A. Aksay[1].Â (1) Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544, United StatesÂ (2) Vorbeck Princeton Research Center, Vorbeck Materials Corp., Monmouth Junction, NJ 08852, United States*

The adsorption of sodium dodecyl sulfate (SDS) onto functionalized graphene sheets (FGSs) in an aqueous system is measured at broad SDS and FGS concentration ranges by conductometric surfactant titration. We find that, for FGS with a carbon-to-oxygen ratio of ~18, monolayer adsorption of SDS on FGS reaches full surface coverage by ~12 µM SDS. Additionally, the critical surface aggregation concentration (csac) for surface micelle formation on FGS is measured to be ~1.5 mM SDS.

The colloidal stability of FGSs, ultrasonically dispersed in aqueous SDS solutions of different surfactant concentrations, is studied by optical microscopy and ultraviolet-visible light absorption. Below ~10 µM SDS, FGSs reaggregate within a few minutes, forming ramified structures in the absence of SDS and increasingly compact structures as the SDS concentration increased. Above ~10 µM, the rate of reaggregation decreased with increasing SDS concentration; above ~40 µM, the suspensions were stable for over a year. Thus, neither surface micelle formation nor dense monolayer coverage is required to obtain stable aqueous FGS dispersions.

We support our experimental results by calculating the van der Waals and electrostatic interaction energies between FGSs as a function of SDS concentration, showing that the experimentally observed transition from an unstable to a stable dispersion correlates with a transition from negative to positive interaction energies between FGSs in the aggregated state. Furthermore, our calculations support experimental evidence that the FGS aggregates tend to develop a compact structure over time.

COLL 426

Bombardment of free-standing graphene with nano-sized projectiles

Chao-Kai Liang[1], Michael J. Eller[2], ***Aaron B. Clubb**[1]*, *aaron.clubb@chem.tamu.edu, Stanislav V. Verkhoturov[1], Serge Della-Negra[2], Emile A. Schweikert[1].Â (1) Department of Chemistry, Texas A&M University, College Station, Texas 77843-3144, United StatesÂ (2) Universite Paris-Sud, CNRS/IN2P3, Institut de Physique Nucleaire d' Orsay, Orsay, Cedex F-91406, France*

We present the first experimental data from Au_{400}^{4+} projectiles impacting free-standing 1, 2, and 4 layer graphene at ~30 km/s. The bombardment was run at the level of single Au_{400}^{4+}impacts. Au_{400}^{4+}(~2 nm diameter) was produced with a liquid metal ion source, accelerated to 130 kV (520 keV), secondary ions were identified with dual time-of-flight mass spectrometers in front and back of the free-standing target. Secondary ion emission was recorded from each impact simultaneously in both reflection and transmission emission directions. Our observations show that the nano-size projectiles rupture the graphene and cause abundant secondary ion emission attributed to intense electronic excitation. The negative mass spectra in transmission show higher ion yields than those in reflection. Up to $C_{12}^{-}$was detected in transmission, while ion yields in reflection extended up to C_8^-. Surface contaminants (e.g. H_2O) were also measured. The key findings are: surprisingly large sputter yields and ionization efficiencies for carbon clusters which depend upon the ejection direction.

COLL 427

Strong and selective adsorption of lysozyme on graphene oxide

Shanghao Li, *s.li12@umiami.edu, Jerome Mulloor, Roger M. Leblanc.Department of Chemistry, University of Miami, Coral Gables, FL 33143-6875, United States*

Biosensing methods and devices using graphene or graphene oxide (GO) have recently been developed with specific detection from body fluid samples, such as saliva, milk, urine, and serum. Graphene and GO have also been shown to have promising applications in other biomedical researches, such as photothermal treatment of cancer, drug and gene delivery, and cellular imaging. All these applications in practice will have to contact with the body fluid. As lysozyme (1,4-β-N-acetylmuramidase) is an abundant protein in the body fluid, one important question is to address how GO interacts with lysozyme. In this study, GO has demonstrated huge quenching effect on fluorescence of lysozyme, but it only slightly quenches other proteins, such as serum albumins, insulin, and amyloid β 40. The nature of this strong interaction between GO and lysozyme is found to be electrostatic interaction from studies of fluorescence quenching, dynamic light scattering, zeta potential, and atomic force microscopy. This interaction is so strong that we are able to selectively load lysozyme on GO.

COLL 428

Thermal reduction method to improve the photoluminescence of carbon dots

Jilong Wang, *jilong.wang@ttu.edu, Jingjing Qiu.Department of Mechanical Engineering, Texas Tech University, Lubbock, Texas 79409, United States*

Carbon dots (CDs) have attracted great attention because of their excellent properties such as unique electronics and optical property, biocompatibility, and low toxicity. In this paper, blue luminescent CDs were prepared by thermal reduction CDs from citric acid. After thermal reduction, the increase of sp2 domains in tCDs and decrease of carboxyl group on the surface of tCDs can improve the photoluminescence of CDs. The quantum yield of the thermal-reduced CDs (tCDs) was increased 2 fold. This work may provide a “neat” and eco-friendly pathway to increase the QY of CDs.

COLL 429

Ultrasensitive SERS probe for label-free biosensing using hybrid graphene oxide

Paresh Ray, *paresh.c.ray@jsums.edu.Chemistry & Biochemistry, Jackson State University, Jackson, MS 39217, United States*

Development of highly sensitive biosensing technologies which has ability to shift medical diagnosis to the next level will have numerous applications, including the detection of DNA/RNA or antigen/antibody for the measurement of clinical parameters, pathogens and circulating tumor cells. Here we discuss our recent report on graphene oxide attached popcorn shape gold nanoparticle based hybrid SERS probe with ultra-sensitive label-free sensing of HIV DNA, bacteria and providing its chemical fingerprint. We demontrate that hybrid material can be used for label-free detection of HIV DNA in femto molar level. We also show that label-free SERS detection limit using hybrid material can be as low as 10 CFU/ mL for MRSA bacteria.

COLL 430

Quantitative insights into gel-based single-chirality carbon nanotube separation

Kevin Tvrdy[1]*, ktvrdy@uccs.edu, Rishabh Jain*[2]*, Rebecca Han*[2]*, Michael Strano*[2]*.Â (1) Department of Chemistry and Biochemistry, University of Colorado Colorado Springs, Colorado Springs, CO 80918, United StatesÂ (2) Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

Semiconducting single walled carbon nantoubes (SWNTs) exhibit chirality dependent absorption and emission line widths in the infrared region of the spectrum, properties which have been successfully exploited in both next generation solar cells and biosensing schemes. Because the process used to synthesize bulk quantities of SWNT relies on the growth and extrusion of a graphene-lattice atop and from a catalyst nanoparticle, the resulting specific SWNT molecular structure (or chirality) varies significantly within each batch due to catalyst size inhomogeneity. To better exploit the unique properties of SWNT, it is critically important to develop methodologies that can separate SWNT based on their chirality at the bulk scale. One such methodology involves the selective adsorption and desorption of semiconducting SWNT to and from amide-functionalized hydrogels, a process that has been shown to be chirality sensitive. A general scheme illustrating this process is shown in Figure 1.

[figure 1]

This work presents a quantitative model of the carbon nanotube to gel binding-site adsorption process that dictates both the separation order and relative concentration of each fraction of separated nanotubes. Quantitative insight, coupled with small methodological changes, allow for the generation of 10+ milliliter fractions containing 96%, 87%, 64% and 56% pure (6,5), (7,3), (7,6), and (7,5) chiralities, respectively. Further, this work provides quantitative rate constants which allow for the prediction of separation order, purity, and total SWNT content, for every separation fraction.

COLL 431

Hydrothermal synthesis of highly fluorescent self-passivated carbon dots

Mohammed J. Meziani*, meziani@nwmissouri.edu,* ***M. Abdul Mottaleb****, mmottal@nwmissouri.edu, Hyukjin Kwon, MinSeok Kim, Jeonguen Kim.Department of Natural Sciences and Center for Innovation and Entrepreneurship, Northwest Missouri State University, Maryville, Missouri 64468-6001, United States*

In recent years, fluorescent nanomaterials have drawn special attention over conventional fluorophores, offering great potentials for optical bioimaging, medical diagnosis, photocatalysis, and photovoltaic devices. Semiconductor quantum dots (QDs) especially those based on cadmium salts and related core-shell nanostructures have proven to have excellent performance, predictable fluorescence color variations,

and long term resistance to photobleaching. However, a serious disadvantage with these popular QDs is that they contain heavy metals, such as cadmium, whose significant toxicity and environmental hazard are well documented. In the search for alternative QD-like nanomaterials, carbon-based nanomaterials have emerged as the most promising due to their relatively high quantum yields, low cost, non-toxic nature, and excellent biocompatibility. Since the original report in 2006, carbon dots have been investigated by many research groups worldwide, with great advances made in their syntheses, mechanistic understandings, and evaluations for potential bio-applications. However, despite these advances many fundamental and technological issues with C-dots still await further investigation. For example, efficient and simple strategies for the fabrication of C-dots on a large scale and with better control of their dimensions, surface chemistry, and tunable emission profiles are still challenge in this field. Herein, we report a simple one step hydrothermal method for the synthesis of highly fluorescent self-passivated carbon dots by combining various carbon sources of carboxylic acids and amine molecules. The structural and optical properties were characterized using various techniques like UV-vis and fluorescence spectroscopy, Fourier Transform Infra-Red, elemental analysis, and SEM. This method is a convenient, environment friendly, inexpensive and efficient process for large-scale production. The as-prepared carbon dots exhibited excellent water solubility, good photostability, and a high quantum yield. The implication of the results to the mechanistic framework for photoluminescence emissions will be discussed.

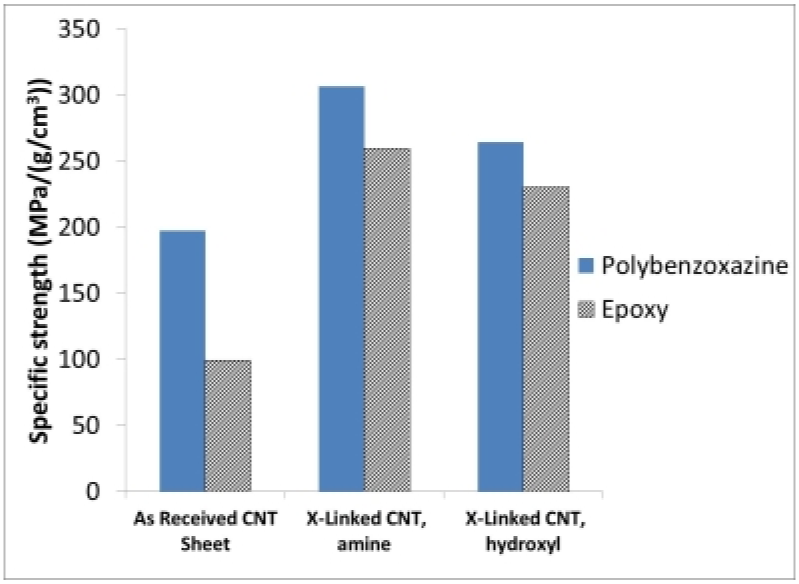
COLL 432

Improved composites using crosslinked, surface-modified carbon nanotube materials

***James S Baker**, jsb39@zips.uakron.edu, Tiffany S Williams, Sandi G Miller, Michael A Meador.Polymer Branch, NASA Glenn Research Center, Cleveland, Ohio 44135, United States*

Individual carbon nanotubes (CNT's) exhibit exceptional tensile strength and stiffness; however, these properties have not translated well to the macroscopic scale. Premature failure of bulk CNT materials under tensile loading occurs due to the relatively weak frictional forces between adjacent CNTs, leading to poor load transfer through the material. When used in polymer matrix composites (PMC's), the weak nanotube-matrix interaction leads to the CNTs providing less than optimal reinforcement.

Our group is examining the use of covalent crosslinking and surface modification as a means to improve the tensile properties of PMCs containing carbon nanotubes. We are working with sheet material comprised of un-aligned multi-walled carbon nanotubes (MWCNT) as a “drop-in” replacement for carbon fiber in the composites. We have examined a variety of post-processing methods for covalently crosslinking the CNTs to overcome the weak inter-nanotube shear interactions, resulting in improved tensile strength and modulus for the bulk sheet material. Residual functional groups from the crosslinking chemistry may have the added benefit of improving the nanotube-matrix interaction. Composites prepared using these crosslinked, surface-modified nanotube sheet materials exhibit superior tensile properties to composites using the as received CNT sheet material.



COLL 433

Complete model of carbon nanotube solar cell structure and chemistry

Darin O Bellisario[1]*, dob@mit.edu, Rishabh M Jain*[2]*, Zackary Ulissi*[2]*, Michael S Strano*[2]*.Â (1) Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02144, United StatesÂ (2) Department of Chemical Engineering, Massachusetts Institute of Technology, cambridge, MA 02139, United States*

With solution-process-ability, scale-able fabrication and purification, and cheap input materials, semiconducting single-walled carbon nanotube (SWNT) networks represent promising materials for solar cell (SC) applications. This promise has motivated a body of work not only developing solar cells but also exploring alignment/deposition methods and SWNT photovoltaic physics. Despite this interest, there is to date *no* quantitative model of SWNT solar cell operation analogous to bulk semiconductor p-n junction photovoltaics, allowing a rigorous understanding of the physical tradeoffs driving experimental observations and informing what research will enable technological progress. We present a framework and model, the first, for describing the steady state operation of an active SWNT layer in a solar cell, capable of accounting for arbitrary distributions of nanotube chiralities, lengths, orientations, defect types and levels, bundle fraction and size, density, dielectric environment, and electrode combination. We achieve this by treating individual SWNT properties as random variables, and describing the network by the dependent distributions of those properties, yielding coupled stochastic differential equations for light absorption, exciton transport, and free carrier transport. We have applied the model to arbitrarily aligned and isotropic networks of monochiral (6,5) SWNT. The resulting predictions of optimal SC geometry are both qualitatively and quantitatively consistent with to-date experimental devices, and motivate experimental investigations to improve them. In particular, it suggests prioritizing higher-density films, sensitivity to which explains the variation in observed EQE for existant devices, as well as vertical-alignment methods taking advantage of the high longitudinal diffusivity in SWNT. We also show that there is a strongly optimal film thickness that shifts with film density (and orientation of aligned films), reflecting an inherent tradeoff between light absorption (i.e. exciton generation) and diffusion to the electrodes.

COLL 434

X-ray reflectivity studies on the hydrophobic water gap

***Markus Mezger**, mezger@mpip-mainz.mpg.de.Max Planck Institute for Polymer Research, Mainz, GermanyDepartment of Physics, Johannes Gutenberg-University, Mainz, Germany*

The density deficit of water at hydrophobic interfaces, frequently called the hydrophobic gap, has been the subject of numerous experimental and theoretical studies. Recent experiments give values for the interfacial depletion that consistently correspond to less than a monolayer of water. However, its origin and the relation to the chemistry and molecular geometry of a particular hydrophobic coating or with macroscopic parameters such as the contact angle are still unclear. To elucidate how the underlying mechanisms affect the extent of the interfacial depletion we carried out a high-energy X-ray reflectivity study of water adjacent to a hydrocarbon and perfluorinated hydrophobic surface with a spatial resolution on the molecular scale.

References:

M. Mezger et al., *J. Am. Chem. Soc.* 132, 6735-6741 (2010).

M. Mezger et al., *Proc. Natl. Acad. Sci. USA* 103, 18401-18404 (2006).

COLL 435

Molecular insights into surfactant, nanoparticle, and polymer assembly at planar and spherical oil/water interfaces

***Geraldine L. Richmond**, richmond@uoregon.edu.Department of Chemistry, University of Oregon, Eugene, OR 97403-1253, United States*

From destroying HIV-1 and tuberculosis pathogens, to cleaning up oil spills and extinguishing fires, emulsions and emulsion stabilizing agents are pervasive in our lives. Yet it is remarkable how little we know about the molecular details of how these agents assemble and structure at water/hydrophobic liquid interfaces. The studies in our laboratory are aimed in exactly this direction: investigating the molecular factors that contribute to the assembly at an oil/water interface of surfactants, polymers and nanoparticles that are used as emulsion stabilizers in a variety of applications. This presentation will provide our most recent results where we combine vibrational sum frequency spectroscopy, surface tension and computational methods to examine the assembly of selected surfactants, polyelectrolytes and nanoparticles at planar and nanoemulsion oil/water surfaces.

COLL 436

Tailoring fluid transport properties by surfaces: From nanofluidics toward application in energy harvesting

***Lyderic Bocquet**, lbocquet@mit.edu.University of Lyon, Villeurbanne, FranceMassachusetts Institute of Technology, Cambridge, MA 02139, United States*

The dynamics of fluids at interfaces are extremely sensitive to their wetting properties. More than a decade of intense experimental and theoretical work has shown that the hydrophobic nature of surfaces tends to reduce solid-liquid friction. This is quantified by fluid-solid slippage, which is much larger for hydrophobic than for hydrophilic surfaces. Manifestation and consequences of this property have been thoroughly explored in the litterature. Beyond, it raises the question of tuning fluid transport via the molecular properties of the fluid solid interface.

I will discuss several results obtained in my group on the fluid transport at surfaces, as well as in nanoscale confinement. I will in particular discuss flow optimization in the hour-glass shape of aquaporins.
I will then focus on the study of transport inside a single Boron-Nitribe nanotube. Experiments show unprecedented energy conversion from salt concentration gradients. Applications in the field of osmotic energy harvesting will be discussed.

References:

« Giant osmotic energy conversion measured in a single transmembrane boron-nitride nanotube », A. Siria, P. Poncharal, A.-L. Biance, R. Fulcrand, X. Blase, S. Purcell, and L. Bocquet, Nature 494 455-458 (2013)

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COLL 437

Probing hydrophobic interfaces by direct force measurements and electrochemistry

***Georg Papastavrou**, georg.papastavrou@uni-bayreuth.de.Physical Chemistry II, University of Bayreuth, Bayreuth, Germany*

Direct force measurements based on AFM in combination with the colloidal probe technique provide a highly sensitive method to probe the diffuse layer of hydrophobic substrates. Here, such measurements have been performed on gold electrodes whose surface has been modified by self-assembled monolayers (SAMs). The gold electrodes are connected to a potentiostat and can be thus controlled in terms of their electrical potential. Thus, in addition to the functional groups terminating the SAM and the solution conditions (i.e. ionic strength and pH) also electrostatic interactions can be tuned by means of the externally applied potential. This approach does not only allow tuning diffuse layer properties and adhesion but it provides also a versatile approach to study ion adsorption phenomena by quantitatively evaluating the interaction force profiles. For hydronium and hydroxyl ions, we determined the adsorption constants based on a simple semi-quantitative model. Adsorption for these ions is much more pronounced for hydrophobic SAMs and the adsorption constant for hydroxyl ions is much larger than the one of hydronium. Finally, it is demonstrated that the potentiostatic control of the interaction forces allows also a new approach towards nano- and micromanipulation by AFM.

COLL 438

Hydrophobic interactions and aggregation in aqueous t-butyl alcohol solutions

***Dor Ben-Amotz**[1], bendor@purdue.edu, Blake M Rankin[1], Ben Widom[2].Â (1) Department of Chemistry, Purdue University, West Lafayette, IN 47907, United StatesÂ (2) Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853, United States*

Nature sometimes sends us contradictory messages: On one hand, we know that oil and water don't mix while, on the other hand, we know that clathrate hydrate mountains under the ocean are composed of water-separated hydrophobic groups. Here we present experimental, simulation, and theoretical results leading to the conclusion the hydrophobic interaction free energy between t-butyl alcohol (TBA) molecules in water is repulsive, in the sense that water-separated configurations are more stable than direct contact configurations. Moreover, we present evidence indicating that the first aggregates formed above a TBA concentration of 0.5 M consist of more than two TBA molecules, and yet remain highly hydrated. These conclusions are based on experiments that combine Raman spectroscopic measurements with a multivariate curve resolution (Raman-MCR) analysis to probe aggregation induced changes in both the TBA hydration-shell OH band and methyl group CH stretch band, measured as a function of both concentration and temperature. The experimental results are interpreted with the aid of molecular dynamics simulations and a lattice theory of TBA aggregation, built upon a random mixing reference system.

COLL 439

Forces between hydrophobic solids in water

***William Ducker**, wducker@vt.edu, Dean Mastropietro.Chemical Engineering, Virginia Tech, Blacksburg, VA 24060, United States*

The interaction between two hydrophobic surfaces separated by water is a difficult area of research that has been subject to continuous scrutiny for decades, motivated mainly by the importance in colloidal interactions. Water trapped in a thin film between two hydrophobic solids can be unstable compared to a vapor cavity. For particles, the energy is lower when the particles are in contact, rather than separated by a water film, causing a large adhesion between the particles. This talk describes experiments in which we attempt to determine the forces between solids coated intethered alkane surfaces when they are separated by a thin film of 1-10 nm of aqueous solution. The forces were measured using the Atomic Force Microscopy (AFM) colloid probe technique. We find that the force in degassed solution is very short ranged, less than about 5 nm in extent. The influence of temperature is small. The influence of salt is confounded by the expected variation in the double-layer force. The hydrophobic force between alkane chains is a weak force. It is weaker than the double-layer force except in concentrated salt solutions (>0.15 M KCl) where the double-layer force is heavily screened.

COLL 440

Understanding the forces at the surface of hair and skin and its modification by polymers

***Gustavo S. Luengo**, gluengo@rd.loreal.com.L'OREAL Research and Innovation, Aulnay sous Bois, France*

Keratin-based biological substrates like hair and skin are examples of natural hydrophobic surfaces. In both, the membranes of the living cells which generate these two evolved structures have formed a hydrophobic barrier against a more hydrophilic protein material. Most cosmetic formulations (shampoos, conditioners) used in hair care are based upon the subtle balance between the various interactions (hydrophobic, electrostatic) among cationic polyelectrolytes, surfactants and the hair surface itself that allows the conditioning agents to be adsorbed and restore or improve its functional properties.

While several experimental approaches allow the process of co-assembly of polyelectrolytes with oppositely charged surfactants, to be modelled or simulated, it still remains a challenging topic. Modelling bulk co-assembly and corresponding adsorption

on surfaces so far ignored the effect of the chain architecture of the polymers. This presentation will focus upon the effects of the chain architecture of polymers and surfactants on the co-operative adsorption of associative mixtures of these components onto both hydrophilic and hydrophobic surfaces. We adopt the self-consistent field theory of Scheutjens and Fleer and discuss adsorption scenarios originating either from pure electrostatic or other interactions between the segments of surfactants and/or polymers with the (charged) surfaces. We show that tuning the position of hydrophobic and hydrophilic fragments at the monomer level, e.g. through including short hydrophilic side chains attached to the hydrophobic backbone of the polymer or inserting short polyoxyethylene sequences may lead to tailored adhesive and tribological properties.

COLL 441

Non-coalescence of water droplets on oil-infused surfaces

Jonathan B Boreyko*, boreykojb@ornl.gov, C Patrick Collier.Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6493, United States*

Here, we show that water droplets exhibit non-coalescence in air when deposited on oil-infused surfaces. This surprising phenomenon is due to the oil meniscus that surrounds each water droplet; when the menisci of two or more neighboring droplets overlap, the droplets spontaneously zip together to minimize the system's free energy and an oil film is squeezed upward from the substrate to form a barrier between the colliding droplets (Figure 1). While droplet coalescence will eventually occur due to film drainage, the time required for film rupture is orders of magnitude larger compared to water droplets submerged in an oil bath, such that oils of moderate viscosity can sustain non-coalescing droplets for over 24 hours. The prolonged non-coalescence of water droplets on an oil-infused surface is due to the inherent asymmetry of droplet collision, where a large-area oil film is squeezed between the droplets from the bottom-up. This is in sharp contrast to water droplets submerged in oil, which exhibit a point-contact during collision resulting in a small-area oil film with a faster drainage time. These findings should enable the construction of air-stable droplet networks useful for drug screening, bio-sensing, and synthetic biology.

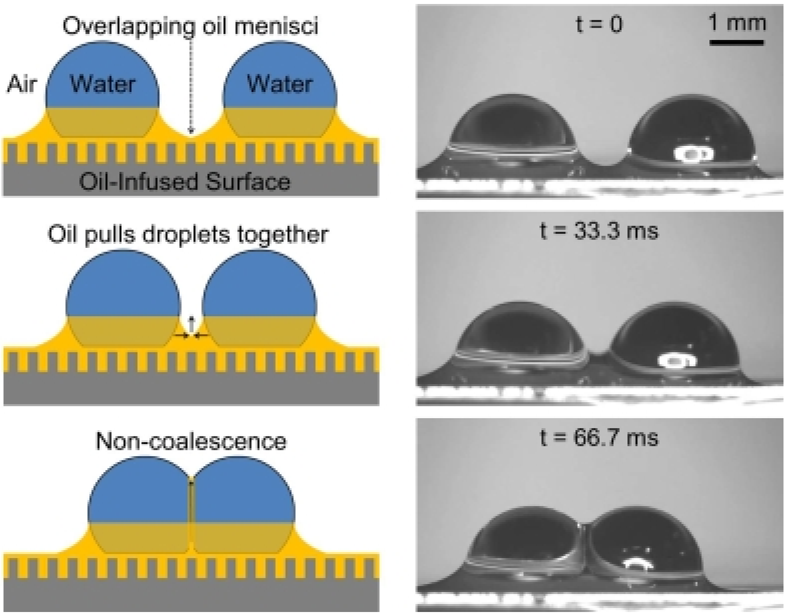

Figure 1: Water droplets on oil-infused surfaces exhibit non-coalescence.

COLL 442

Heterogeneous uptake and adsorption of gas-phase formic acid on oxide and clay particle surfaces: The role of adsorbed water in formic acid adsorption and the impact of formic acid adsorption on water uptake

Gayan R Rubasinghege, *grubasinghege@stcloudstate.edu, Vicki H Grassian.Department of Chemistry, University of Iowa, Iowa City, Iowa 52246, United States*

Organic acids in the atmosphere are ubiquitous and are often correlated with mineral dust aerosol. Heterogeneous chemistry and the uptake of organic acids on mineral dust particles can potentially alter the properties of the particle. In this study, heterogeneous uptake and reaction of formic acid, HCOOH, the most abundant carboxylic acid present in the atmosphere, on oxide and clays of the most abundant elements – Si and Al – present in the Earth's crustare investigated under dry and humid conditions. In particular, quantitative adsorption measurements using a Quartz Crystal Microbalance (QCM) coupled with spectroscopic studies using Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy are combined to allow for both quantification of the amount of uptake and identification of distinct adsorbed species formed on silica, alumina and kaolinite particle surfaces at 298 K. These oxides and clay particles show significant differences in the extent and speciation of adsorbed HCOOH due to inherent differences in surface –OH group reactivity. Relative humidity plays a key role in the formic acid reaction with mineral oxide surfaces. Higher relative humidity favors the total and irreversible uptake of formic acid on alumina surface.

Interestingly, this thin coating of adsorbed formate on the particle surface significantly enhances the hydrophobic nature of the surface, thereby decreasing the amount of water taken up by the surface as measured by QCM. Lower water content on mineral particle surface limits heterogeneous reactions, in particular with water soluble gases (e.g. NOx and SOx). Therefore, the processed aerosols in the presence of organic acids may behave differently in the atmospheric reactions that warrant further investigation.

COLL 443

Using the gold nanoparticles plasmonically enhanced elastic and inelastic light scattering in following molecular cell functions: Applications in nanomedicine

***Mostafa A El-Sayed**, melsayed@gatech.edu.Chemistry & Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400, United States*

We have developed simple plasmonic imaging techniques (T-PECIS) (1, 2) using the enhanced elastic and inelastic Plasmonic scattering properties of targetted Gold nanoparticles to study some important molecular cell properties of potential medical importance like drug efficacy , mecanism of cell death, dynamics of drug delivery, ...

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COLL 444

On the Eisenthal chi(3) method

***Franz Geiger**, geigerf@chem.northwestern.edu.chemistry, Northwestern U, evanston, IL 60208, United States*

The Eisenthal chi(3) method is discussed in the context of free energy relationships in the electrical double layer.

COLL 445

Ultrafast vibrational sum-frequency spectroscopy and dynamics of OH groups at mineral/aqueous interfaces

***Eric Borguet**, eborguet@temple.edu.Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122, United States*

The dephasing dynamics of a vibrational coherence can reveal the interactions of chemical functional groups with their environment. To investigate such processes at a surface, we employ free-induction decay sum-frequency generation (FID-SFG) to measure the time it takes for free OH stretch oscillators at the mineral/water interfaces to loose their collective coherence. By employing non-collinear optical parametric amplification (NOPA) technology and FID-SFG, we showed that the single free OH peak observed in non-linear vibrational SFG spectroscopy of an alumina/water (Al_2O_3/H_2O) interface actually corresponds to two distinct oscillators oriented opposite to each other. The total dephasing time, T_2, of the free OH stretch modes at the Al_2O_3/H_2O interface (pH~13, KOH) was measured with sub-40 fs temporal resolution. Our results revealed that the free OH oscillators associated with interfacial water dephase on the time-scale of ~90 fs, whereas the dephasing of interfacial alumina hydroxyls is an order of magnitude slower.

COLL 446

Characterization of protein structures at interfaces using chiral sum frequency generation spectroscopy

***Elsa C. Y. Yan**, elsa.yan@yale.edu.Chemistry, Yale University, New Haven, CT 06520, United States*

Characterization of protein secondary structures using vibrational spectroscopy is challenging because of strong vibrational backgrounds from water and spectral overlapping of proteins' vibrational bands. Our recent studies have shown that chiral sum frequency generation (SFG) spectroscopy can be used to address these challenges. We found that cSFG spectra of the amide I and N-H stretch of protein backbones provide highly characteristic vibrational signatures to distinguish parallel beta-sheets, anti-parallel beta-sheets, alpha-helices, 3-10 helices, and disordered structures at interfaces. Because chiral SFG spectra are muted to achiral solvent, chiral SFG can be used to characterize chiral secondary structures at interfaces without water background. Using cSFG, we studied the aggregation of human islet amyloid polypeptide (hIAPP), which is associated with type II diabetes. We observed *in situ* and in real time the misfolding of hIAPP from disordered structures to alpha-helices and then beta-sheets at a lipid/water interface and measured the orientation of the early beta-sheet aggregates at the interface. The results provide insight into the pathogenic mechanism for type II diabetes. The studies also demonstrate the capability of chiral SFG in probing self-assembling process of chiral native and synthetic biopolymers at interfaces in situ and in real time, useful in solving fundamental and engineering problems in biological and biomedical sciences.

COLL 447

Molecular interactions at nanoparticle surfaces and biological membranes probed by second harmonic light scattering

***Hai-Lung Dai**, hldai@temple.edu.Department of Chemistry, Temple University, Philadelphia, PA 19122, United States*

Second harmonic light scattering from colloidal particles has been developed into a powerful and versatile technique for characterizing surfaces of colloidal objects ranging from nanoparticles to biological cells since the first demonstration of the detection of second harmonic generation from molecules adsorbed on micron size polystyrene particles by Eisenthal and coworkers (Chem. Phys. Lett. 259 (1996), 15-20). In this presentation, several topics on which insight has been gained from SHLS studies are discussed:

1) Reactions of thiols at the noble metal nanoparticle surface, which are often used to modify particle properties, are found to be an activated process. Through detecting SHLS from the Ag particle surface, the activation energy for the adsorption, which may be attributed to the transition state in the bonding reaction, of the thiol is determined.

2) Interactions of hydrophobic ions at the surface of charged or neutral polystyrene beads immersed in salted solutions are probed using SHLS. It is found that in situations where charge-charge forces dominate surface-molecule interactions, salt ionic strength but not ionic specificity affects the adsorption of the molecular ion. In contrast, when hydrophobic interactions dominate, ion specificity counts more. This observation has implications for understanding the Hoffmeister Series for proteins in salted solutions.

3) Molecular transport at the membrane of living biological cells has been examined in real-time by SHLS. Studies of adsorption/transport of hydrophobic ions at the membrane of various cells have revealed the effects of both membrane and molecular structures on molecular transport across cell membranes.

COLL 448

Protein-binding interactions on membranes measured using the new technique of second harmonic correlation spectroscopy

*Krystal L. Sly, **John C Conboy**, conboy@chem.utah.edu.Department of Chemistry, University of Utah, Salt Lake City, Uta 84112, United States*

The use of second harmonic correlation spectroscopy (SHCS) to measure the adsorption and desorption kinetics of proteins to membrane immobilized ligands will be discussed. By measuring the fluctuations of the measured second harmonic (SH) signal, the binding kinetics and thermodynamics of several model protein-ligand binding events on a model membrane surface have ben retrieved through autocorrelation of the measured SH signal. A comparison of the SHCS method with other steady-state equilibrium and kinetic measurements will also be discussed. SHCS has several advantages over existing methods, including a reduction in the amount of analyte required for analysis and faster acquisition times as compared to traditional binding isotherm studies. Additionally, the surface specificity and label-free nature of SHCS

eliminate some of the challenges seen in fluorescence correlation spectroscopy. The simplicity and efficiency of SHCS makes it a new and valuable technique to directly and precisely ascertain the binding kinetics of molecules at a surface without a label.

COLL 449

Static and dynamic evolution of polarity along a silica film polarity gradient, as probed by single molecule microscopy

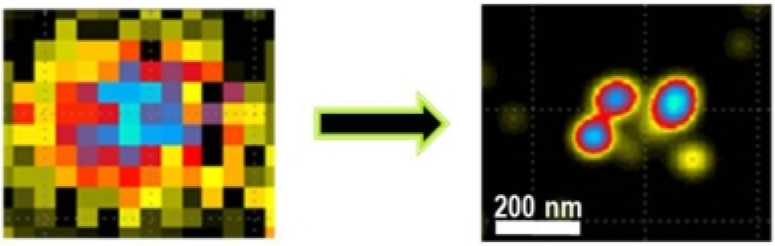
Dipak Giri[1]*, giri@ksu.edu, Chelsea N Hanks*[1]*, Maryanne M Collinson*[2]*, Daniel A Higgins*[1]*.Â (1) Department of Chemistry, Kansas State University, Manhattan, KS 66506, United StatesÂ (2) Department of Chemistry, Virginia Commonwealth University, Richmond, Virginia 23284, United States*

Organosilane-based polarity gradients were prepared by infusion-withdrawal dip-coating and characterized by two-color single molecule microscopy (SMM). Gradients were formed by dipping a cover glass in a sol of time varying composition. The sol was initially derived from phenyltrimethoxysilane (PTMOS); a tetramethoxysilane (TMOS) sol was gradually infused into the deposition reservoir, while the mixed sol was withdrawn. Sessile drop water contact angle data revealed a continuous increase in wettability along the gradient. Raman mapping of the same film depicted a gradual decrease in the phenyl C-H stretching band at 3059 cm^{-1}. These data demonstrated the formation of an unidirectional polarity gradient from nonpolar (high PTMOS end) to polar (low PTMOS end). The nanoscale polarity properties of the film were probed by two-color SMM, using the polarity sensitive Nile Red dye. SMM videos obtained along the gradient were divided into two bands: one centered at 640nm, the other at 590nm and simultaneously detected by a CCD camera. The fluorescent spot intensities were employed to determine the emission ratio for each molecule as a function of position and time. The results were used to estimate the local dielectric constant. Spatial and temporal variations in the polarity data revealed evidence of micrometer-sized (and smaller) polar and nonpolar domains due to phase separation. Ensemble averaged single molecule results verified the presence of a polarity gradient. A better understanding of gradient properties on nanometer length scales will lead to improved applications in high throughput screening and in stationary phase gradient chemical separations.

COLL 450

Unified super-resolution experiments and stochastic theory provide mechanistic insight into protein ion-exchange adsorptive separations

***Christy Landes**, cflandes@rice.edu.Department of Chemistry, Rice University, Houston, TX 77005, United States*



We present the direct super-resolution mapping and kinetic characterization of functional sites on ion-exchange ligands based on agarose, a support matrix routinely used in protein chromatography. Chromatographic protein separations, immunoassay, and biosensing all typically involve the adsorption of proteins to surfaces decorated with charged, hydrophobic, or affinity ligands. Despite increasingly widespread use throughout the pharmaceutical industry, mechanistic detail about the interactions of proteins with individual chromatographic adsorbent sites is only available via inference from ensemble measurements such as binding isotherms, calorimetry, and chromatography. By quantifying the interactions of single proteins with individual charged ligands, we demonstrate that functional adsorbent sites can be mapped with a resolution of 30 nm, that clusters of charges are necessary to create detectable adsorption sites, and that even chemically identical ligands create adsorption sites of varying kinetic properties that depend on steric availability at the interface. Additionally, we relate experimental results to the stochastic theory of chromatography. Simulated elution profiles calculated from the molecular-scale data suggest that for ion-exchange systems, separation efficiencies could be improved by as much as a factor of five by deliberately exploiting clustered interactions that currently dominate the separations process only accidentally.

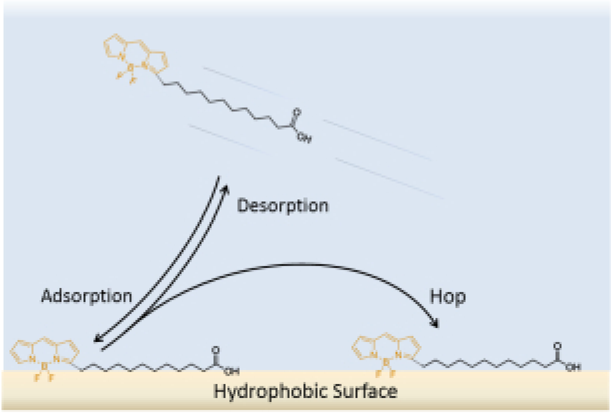
COLL 451

Connecting adsorption, desorption, and diffusion at a solid-liquid interface

Joshua N Mabry, *joshua.mabry@colorado.edu, Michael J Skaug, Daniel K Schwartz.Department of Chemical and Biological Engineering, University of Colorado, Boulder, CO 80303, United States*

Total internal reflection fluorescence microscopy (TIRF) is a powerful technique for observing the dynamics of single proteins, polymers and amphiphiles on solid surfaces. The rates of desorption and surface diffusion can be separately described in exquisite detail by empirically fitting the full distributions of observed rates. This reductionist approach to single-molecule data has been widely practiced by our research group and others and is a hallmark of single-molecule methods.

We propose to take a unified approach to interpreting dynamic phenomena that have traditionally been considered independent of each other. For example, in the regime where surface transport is dominated by “intermittent hopping,” we find that the rates of desorption and surface diffusion are highly correlated. A direct comparison between the statistical properties of molecular trajectories and those observed in kinetic Monte Carlo simulations leads to new insights into the nature of the three-dimensional molecular trajectories that we and others have long observed in two-dimensions using TIRF.



COLL 452

Fluorescence imaging of single-molecule retention trajectories within individual reversed-phase chromatographic particles

Justin T. Cooper, Eric M. Peterson, ***Joel M. Harris****, harrisj@chem.utah.edu.Department of Chemistry, University of Utah, Salt Lake City, UT 84112-0850, United States*

Reversed-phase liquid chromatography (RPLC) has become an indispensable separations tool in numerous application areas that require isolation and identification of compounds in mixtures, including quality control in synthesis, pharmaceutical standards, and environmental analysis. For resolving complex samples, improving the efficiency of the separation process requires an understanding of the dynamics of interfacial transport that is responsible for molecular retention in chemically-modified porous silica stationary phases. In the present work, single-molecule fluorescence imaging is used to follow the transport of individual molecules within RPLC particles. This technique allows direct measurement of intraparticle molecular residence times, intraparticle diffusion rates, and the spatial distribution of molecules within the particle. Based on the localization uncertainty and measured diffusion rates, statistical criteria were developed to resolve the frame-to-frame behavior of molecules into moving and stuck events that reveal a range of interactions with the stationary phase surface. The measured diffusion coefficient of moving molecules was used in a Monte-Carlo simulation of a random-walk model within the cylindrical geometry of the particle diameter and microscope depth-of-field. The simulated molecular transport was in good agreement with the experimental data for the residence times and spatial distribution moving molecules, indicating that the molecular motions in the porous particle are well described by a homogeneous random-walk. The observation of stuck molecule events, however, provides direct evidence of the heterogeneity of molecular interactions with the chromatographic media, where the stationary molecules held fixed by strong adsorption would be major contribution to peak tailing in chromatographic elution. When compared with trajectories with no strong-adsorption events, trajectories that included stuck events exhibited 10-times longer residence times. While these trajectories only make up 12% of the molecular visits, they more than double the average residence time of all molecules within the particle and contribute significant dispersion to the histograms of molecular residence times.

COLL 453

Monte Carlo simulation for smFRET with multistate transitions

Jixin Chen, *jixin.chen@rice.edu, Christy F. Landes.Department of Chemistry, Rice University, PO Box 1892, MS-60, Houston, TX 77025, United States*

The Monte Carlo method is used to simulate time trajectories for single-molecule Förster resonance energy transfer (smFRET) experiments. Single molecule FRET has been widely used to study many biological processes, where the variation of FRET values represents the dynamics of the system. For a system that has multiple transition states and a network of transition routes, such as protein and nucleotide folding/unfolding, it is difficult to obtain the rate constants from complicated time trajectories. We used simulated data to check the algorithm that calculates rate constants. Experimental conditions such as total sampling time, signal to noise ratio (SNR), bin time, and camera blur were tuned to understand their effects on the errors of the calculation. We conclude that Monte Carlo simulation is useful in designing smFRET experiments and analyzing complicated smFRET data.

COLL 454

Mechanisms of surface-mediated DNA hybridization

Jon Monserud, *jmonseru@gmail.com, Daniel K Schwartz.Chemical Engineering, Universityof Colorado, Boulder, Boulder, Colorado 80303, United States*

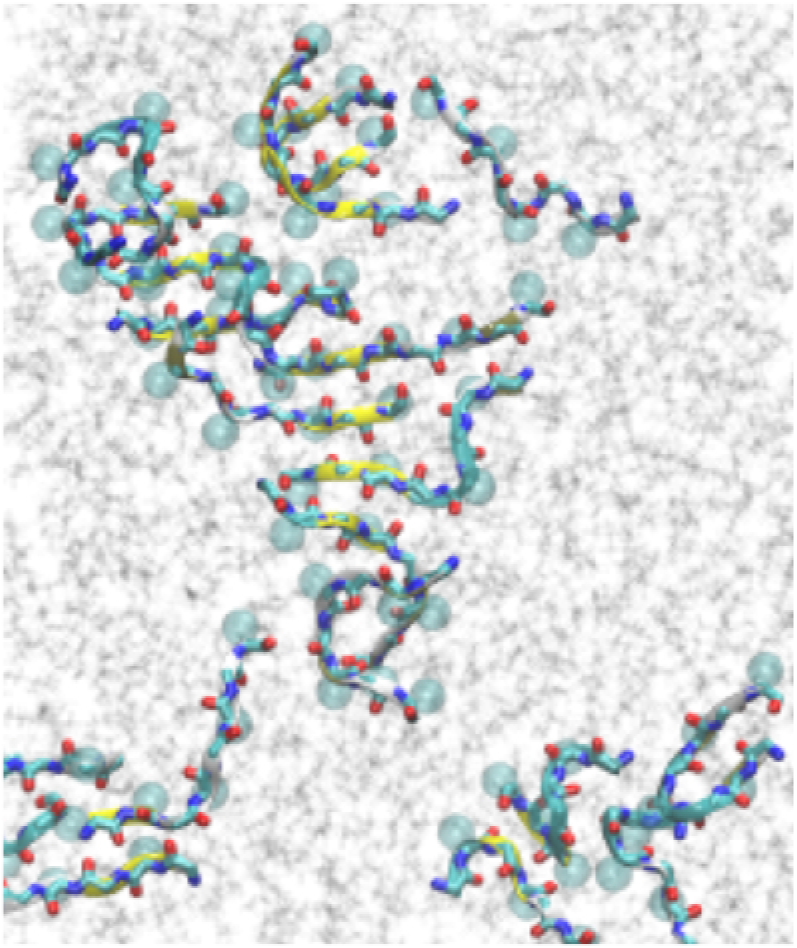
Single-molecule total internal reflection fluorescence microscopy was used to observe the dynamic behavior of ssDNA oligonucleotides on modified silica surfaces. High throughput molecular tracking was used to determine >75,000 molecular trajectories. Nonspecific interactions occurred where the oligonucleotides interacted with a surface lacking the oligonucleotide's complement strand covalently bound to the surface. These interactions were monitored using total internal reflection fluorescence microscopy

(TIRF) and labeled probe oligonucleotides in solution. Specific oligonucleotide interactions occurred when target molecules in solution hybridized to probe molecules attached to the surface. These interactions were monitored using two-chennel TIRF and labeled probe and target oligonucleotides, where the labels were a resonance energy transfer (RET) pair. The use of RET provided a signal when a target molecule transitioned to a hybridized state. Using the molecular trajectories acquired through RET TIRF experiments, the rate constants of molecules transitioning between hybridized and melted states, as well as the fraction of molecules in a specific state that transition to each potential state, were determined.

COLL 455

Molecular simulation studies of peptide self-aggregation at membrane-water interfaces

Régis Pomès, *pomes@sickkids.ca.Molecular Structure and Function, Hospital for Sick Children, Toronto, Ontario M5G 0A4, CanadaDepartment of Biochemistry, University of Toronto, Toronto, Ontario, Canada*



The capacity to form β-sheet structure and to self-organize into amyloid fibrils, which contain extended β-sheets, is a property shared by many peptides and proteins. The formation of amyloid, a slow nucleated process in water, is catalyzed by lipid bilayers and reverse micelles, and by the hydrophobic surfaces of hexane granules, nonpolar nanoparticles, and nonpolar droplets. In addition, the air-water interface has also been shown to promote the self-assembly of peptides into β-sheets. Together, this evidence suggests that the catalysis of amyloid formation is a generic property of water-hydrophobic interfaces. Importantly, severe neurodegenerative pathologies such as Alzheimer's and Parkinson's diseases are thought to involve the interaction of amyloidogenic protein oligomers with neuronal membranes. However, although the effect of surfaces on amyloid formation is well-known and the link between membranes and the toxicity of amyloid diseases is well-appreciated, the molecular basis of these phenomena is presently unclear. To understand the experimentally-observed catalysis of amyloid formation by lipid membranes and water-hydrophobic interfaces, we use large-scale molecular dynamic simulations in atomic detail to examine the effect of interfaces on the self-assembly of β-sheet-forming peptides. I will present several recent and ongoing studies of peptide adsorption and aggregation at an octane-water interface and in hydrated lipid bilayers.

COLL 456

Development of interfacial force field capabilities in LAMMPS to facilitate the accurate simulation of interfacial behavior

Robert A Latour[1], *latourr@clemson.edu, Jeremy A Yancey*[2], *Christian D Lorenz*[3]*.Â (1) Department of Bioengineering, Clemson University, Clemson, SC 29634, United StatesÂ (2) Department of Bioengineering, Clemson University, Clemson, SC 29634, United StatesÂ (3) Department of Physics, King's College, London, United Kingdom*

The molecular environment at the interface between two phases of a biphasic system can be distinctly different from the environment within the bulk region of each phase. This situation causes two major difficulties for the simulation of interfacial behavior using empirical force field methods. First, there is no basis to expect that nonbonded force field parameters (i.e., partial charges, Lennard-Jones well-depths and atomic radii) that were established to represent the intra-phase behavior for a biphasic system will adequately represent interactions between the two phases at the interface. Secondly, if the nonbonded parameters of one of the phases are modified to correct for identified errors in the representation of interfacial behavior, then these changes will cause unknown errors in the simulation of the intra-phase behavior for which that parameter set was initially tuned. In order to provide a solution to both of these problems, we have developed new modules for the LAMMPS molecular simulation program to enable each individual phase of a biphasic system to be controlled by its own force field while enabling nonbonded interactions between the two phases to be independently represented by a separate full set of interfacial force field parameters. This development provides the ability to then separately adjust molecular behavior at the interface to

match targeted interfacial characteristics while preserving the ability to adequately represent intra-phase behavior for each phase. This approach should be applicable for the simulation of any biphasic system to facilitate the accurate representation of interfacial behavior. As an important part of this effort, we have also developed LAMMPS modules to implement the CMAP correction for the CHARMM22 protein force field to facilitate the simulation of protein-surface interactions. This research was supported by a Marie Curie International Incoming Fellowship within the 7th European Community Framework Programme.

COLL 457

On the role of cell entry mechanism in cytotoxicity

Francesco Stellacci, *francesco.stellacci@epfl.ch.Institute of Materials, Ecole Polytechnique FÃ©dÃ©rale de Lausanne, Switzerland*

Recently we have found that ambiphilic gold nanoparticles coated with a mixture of octane thiol and mercaptoundecanesulfonic acid are able to penetrate cell membranes in an energy independent mechanism. In this talk I will show recent results that relate the entry mechanism to the toxity of the partilcle. This collaborative work was performed with the group of Pompa at IIT in Lecce, Italy. The results will be shown to be valid for a good range of nanoparticles.

COLL 458

Single-molecule resolution of interfacial protein dynamics

Daniel K Schwartz, *daniel.schwartz@colorado.edu.Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, CO 80309, United States*

Interactions between proteins and surfaces lead to complex and highly-varied interfacial behavior, where heterogeneity may arise from spatial variation of the surface/interface itself or from molecular configurations (i.e. conformation, orientation, aggregation state, etc.). These phenomena influence subsequent cell-surface interactions through both specific and non-specific effects. The direct observation of adsorption, interfacial diffusion, and desorption of individual fluorescently-labeled protein molecules permits the characterization of heterogeneous interfacial behavior in ways that are inaccessible to traditional ensemble-averaged methods. Moreover, spectral information can be used to simultaneously track molecular configuration (aggregation or folding state). Single-molecule tracking experiments have traditionally been limited by small sample sizes (e.g. a few hundred molecules), leading to poor statistical significance and a lack of sensitivity to rare populations. However, new advances in high-throughput tracking methods now enable hundreds of thousands of molecules to be followed in a given experiment. This approach has recently been used to characterize heterogeneous molecule-surface interactions including: multiple modes of desorption and diffusion associated with both internal and external molecular configuration, surface-mediated conformational changes, non-specific intermolecular associations, spatially dependent interactions, and others.

COLL 459

Interactions of cells with zwitterionic-modified nanoparticles

***Shaoyi Jiang**, sjiang@u.washington.edu.Department of Chemical Engineering, University of Washington, Seattle, Washington 98195, United States*

In this talk, I will overview our efforts to modify nanoparticles (NPs) with zwittterionic materials, enabling their stability in complex media and selective interactions with cells. NPs studied include silica, iron oxide, gold, quantum dots and nanogels. Due to their unique surface chemistries, a variety of surface adhesive groups are necessary, including thiol, silane or DOPA. Due to their unique applications, polymer coatings based on poly(carboxybetaine) (PCB) or thin coatings with only one carboxybetaine (CB) group are used. It should be emphasized that PCB or CB is functionalizable via routine NHS/EDC chemistry for ligand immobilization. These NPs are fully characterized for their particle sizes, surface charges, and long-term stability in undiluted blood serum, and phosphate-buffered saline (PBS) and 10% NaCl solutions. Macrophage cell uptake studies were performed. Quantitative analysis was performed to evaluate these NPs conjugated with a targeting RGD peptide for human umbilical vein endothelial cell (HUVEC) uptake.

COLL 460

Gold nanoparticle vesicles as a drug delivery carrier enabling rapid drug release upon light irradiation

***Kenichi Niikura**[1], kniikura@poly.es.hokudai.ac.jp, Naoki Iyo[2], Yasutaka Matsuo[1], Hideyuki Mitomo[1], Kuniharu Ijiro[1].Â (1) Research Institute for Electronic Science, Hokkaido University, sapporo, Hokkaido 001-0021, JapanÂ (2) Graduate School of Chemical Science and Engineering, Hokkaido University, sapporo, Hokkaido 001-0021, Japan*

We report that the synthesis of water-dispersible gold nanoparticle vesicles (AuNVs) by cross-linking each gold nanoparticle with thiol-terminated PEG and the AuNVs can work as a drug delivery carrier enabling light-triggered release. Rhodamine dyes were encapsulated within the cross-linked vesicles by heating to 62.5 °C. The cross-linked AuNVs released encapsulated dyes upon short-term laser irradiation by again opening the nanogaps between each nanoparticle in the vesicle. On the contrary, when heating the solution, the release speed of encapsulated dyes was much lower (more than 2 h) than that triggered by laser irradiation, indicating that cross-linked AuNVs are highly responsive to light. The drug-encapsulated vesicles were internalized into cells released anticancer drugs upon laser irradiation in cells. These results indicate that cross-linked

AuNVs, sub-100 nm in size, could be a new type of light-responsive drug delivery carrier applicable to the biomedical field.

[Reference] Niikura *et al. ACS Appl. Mater. Interfaces*, **2013** , 5, 3900.

COLL 461

Surprising in vivo instability of near-IR absorbing hollow Au-Ag nanoshells

***Naomi J. Halas**, halas@rice.edu.Rice University, Houston, Texas 77005-1892, United StatesPhilipps UniversitÃ¤t Marburg, Germany*

Photothermal ablation based on resonant illumination of near-IR absorbing noble metal nanoparticles that have accumulated in tumors is a highly promising cancer therapy, currently in multiple clinical trials. A crucial aspect of this therapy is the nanoparticle size for optimal tumor uptake. A class of nanoparticles known as hollow Au (or Au-Ag) nanoshells (HGNS) is appealing because NIR resonances are achievable in this system with diameters less than 100 nm. In this study, we report a surprising finding that *in vivo* hollow Au-Ag nanoshells (HGNS) are unstable, fragmenting with the Au and the remnants of the sacrificial Ag core accumulating differently in various organs. We synthesized 43, 62, and 82 nm diameter HGNS through a galvanic replacement reaction, with nanoparticles of all sizes showing virtually identical near-infrared resonances at ~800 nm. A theoretical model indicated that alloying, residual Ag in the nanoparticle core, nanoparticle porosity, and surface defects all contribute to the presence of the plasmon resonance at the observed wavelength. While PEG functionalization resulted in stable nanoparticles under laser irradiation, an anomalous, strongly element-specific biodistribution observed in tumor-bearing mice suggests that an avid fragmentation of all three sizes of nanoparticles occurred *in vivo*. Stability studies across a wide range of pH environments and in serum confirmed HGNS fragmentation. These results demonstrate the importance of tracking both materials of a galvanic replacement nanoparticle in biodistribution studies and of performing thorough nanoparticle stability studies prior to any intended *in vivo* trial application.

COLL 462

Controlled delivery of quantum dots to specific cellular locations: Implications for highly functional nanosystems for biological imaging and sensing

***James Delehanty**[1], james.delehanty@nrl.navy.mil, Kelly Gemmill[1], Kimihiro Susumu[1], Juan Blanco-Canosa[2], Philip Dawson[2], Alan Huston[1], Igor Medintz[1].Â (1) US Naval Research Laboratory, United StatesÂ (2) The Scripps Research Institute, United States*

One of the chief goals of our laboratory is the interfacing of inorganic nanomaterials with biological moieties to realize functional nanosystems with enhanced capabilities for cellular labeling, imaging and sensing. To that end, we have developed a suite of peptidyl motifs and bioconjugation chemistries that mediate the controlled delivery of

semiconductor quantum dots (QDs) and other nanoparticle materials to discrete cellular locations with fine control. This talk will highlight several of these systems and the implications for their use in the imaging and sensing of physiological processes in living cells will be discussed.

COLL 463

Spectroscopic and analytical characterization of luminescent nanoparticles and multiplexing applications

Ute Resch-Genger[1]*, ute.resch@bam.de, Martin Kaiser*[1]*, Christian Würth*[1]*, Thomas Behnke*[1]*, Katrin Hoffmann*[1]*, Marko Moser*[1]*, Soheil Hatami*[1]*, Ralf Schneider*[1]*, Susanne Leubner*[2]*, Nikolai Gaponik*[2]*, Alexander Eychmüller*[2]*.Â (1) Analytical Chemistry, BAM, Berlin, Germany D12489, GermanyÂ (2) Technical University Dresden, Dresden, Germany 01062, Germany*

Luminescent particles ranging from quantum dots and upconversion phosphors to dye-doped polymeric beads play an ever important role in the life sciences as fluorescent reporters in the case of nm-sized materials and as μm-sized carriers in bead-based assays [1]. The development of rational design strategies for new nanomaterials and the evaluation of material performance require spectroscopic tools for the determination of signal-relevant optical properties like the fluorescence quantum yield [2-4] and analytical tools for the quantification of the number of surface groups and ligands [5-7]. Here, we present examples for the optical and analytical characterization of different types of nanomaterials and their use in new multiplexed detection schemes [9].

COLL 464

Real time detection and diagnostics using plasmonic particles

***Ramon Alvarez-Puebla**, ramon.alvarez@urv.cat.ICREA, Tarragona, Spain*

The ideal strategy for the clinical diagnosis and detection of biological agents (biodetection) must allow simultaneously investigating a large number of parameters, which is known as “high-throughput screening”, such that a quick conclusion can be reached concerning the health conditions of a specific patient or environment. Here we present alternatives based in nanophotonics, in general, and in SERS in particular to achieve accurate real time monitoring of virus, bacteria and unicellular eukaryotic cells.

COLL 465

Orientation-specific attachment of polymeric microtubes on cell surfaces

Jonathan B Gilbert[1]*, gilbert@mit.edu, Janice S O'Brien*[2]*, Harini S Suresh*[2]*, Robert E Cohen*[1]*, Michael F Rubner*[2]*.Â (1) Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United StatesÂ (2) Department of*

Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

The interaction of living cells with micro or nanoparticles has become more important as particles are increasingly used for drug delivery and other biomedical applications. Shape, surface chemistry and size characteristics can be designed to increase drug delivery efficiency by controlling the targeting of synthetic particles. In particular, it has been found that the local shape of an anisotropic particle in contact with the cell determines the internalization rate of the particle. This insight drives the desire to design anisotropic particles that orient themselves on the cell surface to either promote or resist internalization. Inspired by the use of chemically non-uniform Janus particles to control the local orientation of synthetic particles in colloid systems, we designed a tube-shaped, chemically non-uniform microparticle with the capability to control its orientation on cell surfaces.

Anisotropic microtubes were designed to present cell-adhesive ligands on the ends of the tubes and a cell-resistant surface on the sides. In this work the cell-adhesive region incorporated hyaluronic acid to interact with the CD44 receptors on B-cells and a highly swollen polyelectrolyte multilayer to resist adhesion. We show that by altering the presentation of polymer on the end versus the side we can alter the proportion of cells connecting to the end of tubes versus the side of tubes. This simple method to make anisotropic and chemically non-uniform particles is generalizable and could incorporate a variety of materials. Recent literature also has shown that the conjugation of material to the cell surface is useful for cell-mediated drug delivery and by controlling the orientation of the material on the cell surface we can design the cellular response to the synthetic materials. This advancement opens the possibility to design new cell-biomaterial hybrids for a variety of biomedical applications.

Work Published: Gilbert ,O'Brien, Suresh, Cohen, Rubner **(2013)** *Advanced Materials* (epub)

COLL 466

Mucoadhesive nanocarriers for potential bladder cancer therapy

Koon Gee Neoh[1]*, chenkg@nus.edu.sg, Shengjie Lu*[1]*, Quan Zhang*[1]*, En-Tang Kang*[1]*, Edmund Chiong*[2]*.Â (1) Department of Chemical & Biomolecular Engineering, National University of Singapore, Singapore, SingaporeÂ (2) Department of Surgery, National University of Singapore, Singapore, Singapore*

Bladder cancer is one of the most commonly diagnosed malignancies and has the ninth highest incidence rate worldwide. The great majority of cases are superficial or non-muscle-invasive carcinomas, where the tumor is confined in the urothelial lining. Intravesical chemotherapy following resection of the bladder tumors has been advocated as a means to destroy residual microscopic tumor cells and to prevent re-implantation. However, the major limitation of this treatment is the rapid and almost complete washout of the drugs from the bladder on first voiding of urine. Our work focuses on the development of mucoadhesive and sustained drug delivery systems, which can prolong the dwell-time of the drug and increase its uptake into bladder tissue to increase the efficacy of the treatment. Two types of mucoadhesive drug delivery systems have been developed, for a hydrophobic drug and a hydrophilic drug, respectively: (i) cationized serum albumin loaded with docetaxel and (ii) thiol-functionalized mesoporous silica nanoparticles loaded with doxorubicin. *Ex vivo* evaluation confirmed that both systems interact strongly with pig bladder wall. *In vitro* assays also confirmed that these nanoparticles are endocytosed by bladder cancer cells resulting in cytotoxic effects on these cells.

COLL 467

Self-organization, structure, and electronic properties of organic molecular films

***Miquel B Salmeron**, mbsalmeron@lbl.gov.Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States*

Understanding structure and the electronic and chemical properties of self-assembled organic layers is key to the development of new technologies, including solar cells, chemical sensors, and batteries. We studied oligothiophene molecules with carboxilic acid head groups to produce crystalline monolayer films by Langmuir-Blodgett techniques on Si wafers. Atomic force microscopy with conducting tips was used to characterize the films and to determine correlations between molecular structure, friction and electrical transport. D5TBA, a molecule containing 5 thiophene rings, was found to form two-dimensional films, one molecule thick, which were additionally examined by TEM to determine its crystalline structure. With AFM we found that the electrical conductivity of the film is anisotropic, with preferential transport along paths of highest overlap between the pi-system of the thiophene subunits along different crystallographic directions.

COLL 468

High-fidelity self-assembly of crystalline organic thin films by π–π stacking from a metal surface

***Daniel Skomski**[1], dskomski@indiana.edu, Christopher D. Tempas[1], Junyong Jo[1], Dongwhan Lee[2], Steven L. Tait[1].Â (1) Department of Chemistry, Indiana University - Bloomington, Bloomington, IN 47405, United StatesÂ (2) Department of Chemistry, Seoul National University, Seoul, Gwanak-gu 151-742, Republic of Korea*

Two of the most well-exploited intermolecular interactions in synthetic supramolecular chemistry are hydrogen bonding and aromatic stacking. In surface-assisted self-assembly, hydrogen bonding has been used extensively in the fabrication of ordered monolayer surface architectures. In contrast, aromatic stacking has been less explored as a route to direct crystallization and orientation of thin films, despite its importance in

the assembly of many biological structures and organic crystals. In this contribution, we present the growth of atomically flat, crystalline organic thin films from a metallic surface with high-fidelity through π-π stacking, enabled by the electrostatic complementarity between donor and acceptor subunits. The self-assembly process is maintained over > 20 molecular layers and enables effective charge transport through the ordered molecular stacks, as confirmed by scanning tunneling microscopy (STM) as well as atomic force microscopy (AFM) and X-Ray photoelectron spectroscopy (XPS) studies. The strategies presented towards highly ordered, intimate co-facial stacking of extended π-conjugation could lead to useful applications in molecularly constructed electronic materials and devices.

COLL 469

Polarization effects in organic nanostructures

Axel Enders*, a.enders@me.com.Department of Physics and Astronomy, University of Nebraska - Lincoln, Lincoln, NE 68588, United States*

Organic materials have several distinctive advantages over inorganic materials such as semiconductors and complex oxides. The often show similar electronic properties, such as a band gap, but in addition can be designed chemically to exhibit useful additional physical properties, such as a magnetic moment or an electric dipole. There are no such strict requirements with regards to structural ordering as there are for complex oxide, which simplifies considerably the fabrication process and reduces fabrication costs. Even better: novel, flexible and bendable, perhaps even printable materials seem feasible with organics! However, before organics can be exploited in various applications, and in order for them to evolve into viable alternatives for the currently widely studied complex oxides, the fundamental correlation between chemical design, self-assembly and physical properties has to be established through basic research.

In this talk I will give a brief review over recent experiments on interface- and hybrid-effects in 2D surface-supported organic nanostructures and how such effects can be exploited manipulate their electronic properties. On the example of strongly dipolar benzoquinonemonoimine zwitterion molecules I will discuss the formation of 2D structures where the molecular electric dipoles are spontaneously aligned parallel, thus forming a 2D electret. This spontaneous alignment is not observed in the bulk phase of the same molecules and is actually electrostatically not favored, but made possible by the particular arrangement of hydrogen bonds in the 2D sheet. In a second example I will show how organic ferroelectric nanostructures are stabilized through surface interactions. What is unique here is that the smallest polarized units are dimers of molecules, croconic acid in this case. What is important is that the polarization is based on the hydrogen bonds the molecules form with each other, and that the switching is enabled through surface interactions.

Such fundamentally important observations may pave the road towards organic materials with switchable, even programmable, physical and chemical properties, and even organic dipolar logic structures.

COLL 470

Interfacial molecular dipoles and their effect on 2D molecular self-assembly

***Giovanni Costantini**, g.costantini@warwick.ac.uk.Department of Chemistry, University of Warwick, Coventry, United Kingdom*

A crucial step in the fabrication of organic photovoltaic or electronic devices is represented by the growth of the first few molecular layers. In fact, these determine the structure of the molecular film and the energy level alignment at the interface between the organic layer and the conductive substrate.

In this talk, we will explore the formation of model metal-organic junctions by analysing the interplay between molecule-substrate charge transfer and supramolecular self-assembly. By using ad-hoc designed molecules with specific ionisation energies and electron affinities and by varying the work function of the substrate, we will show that it is possible to finely tune the resulting molecular assembly. In particular, we will demonstrate a novel growth mode characterised by anomalous coarsening and show that it derives from a competition between the omnipresent short-range attractive van der Waals interactions and long-range repulsive forces due to charge-transfer induced molecular dipoles. Moreover, we will analyse the behaviour of codeposited acceptor and donor molecular units, showing that the resulting complex assemblies are a consequence of the interactions between oppositely oriented molecular interfacial dipoles.

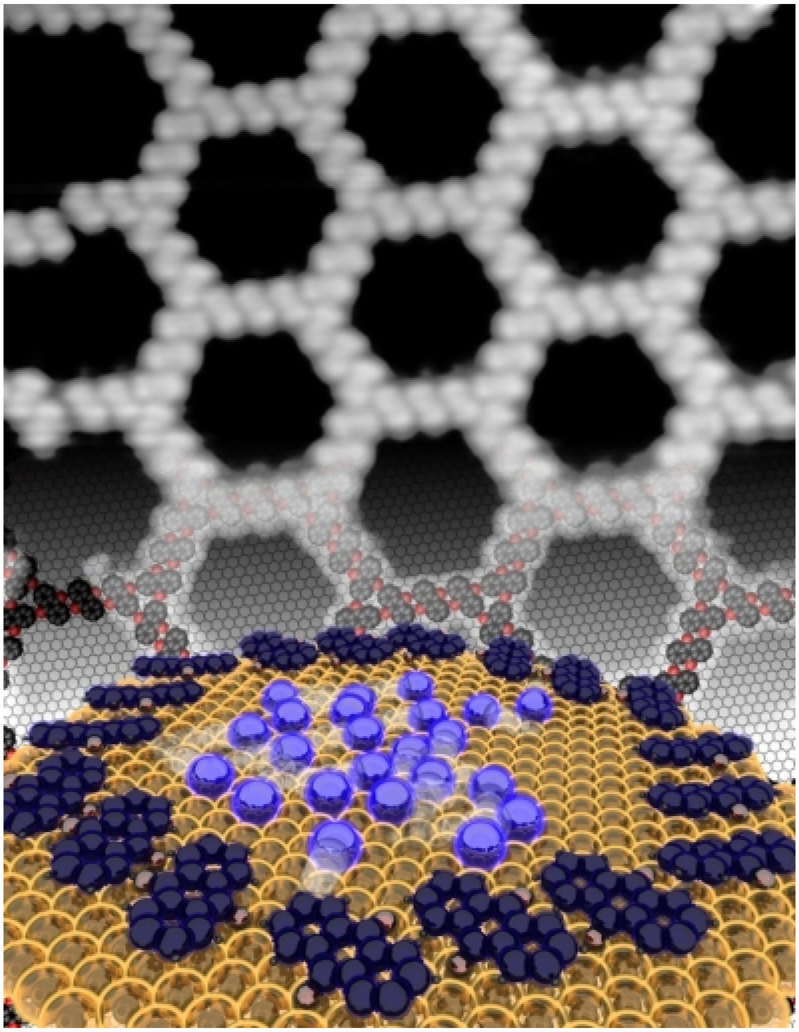
While allowing to rationalise also previously reported experimental findings by identifying the precise conditions that molecule and substrate must meet in order for these novel growth modes to occur, our work further shows that specific molecular linkage patterns can reveal the occurrence of charge transfer. This provides a novel means for obtaining crucial information on the electronic properties of metal-organic interfaces. Due to the fundamental nature of the processes at play, we anticipate that our results could be generalised to a large class of metal-organic systems.

COLL 471

Surface state-directed self-assembly of well-ordered supramolecular networks

***Ludwig Bartels**, bartels@ucr.edu.University of California, Riverside, CA 92521, United States*

Since the seminal construction of quantum corrals in the Eigler group two decades ago, such structures have been used to elucidate many properties of surfaces states ranging from their dispersion to quantum mirages. Yet work with quantum corrals is painstakingly difficult, because the corrals need to be assembled one atom at a time at atomic precision. In this presentation, I show that the confinement of electrons inside a corral-like structure can be the driving force behind the self-assembly of a surface overlayer that provides a regular pattern of extended pores.



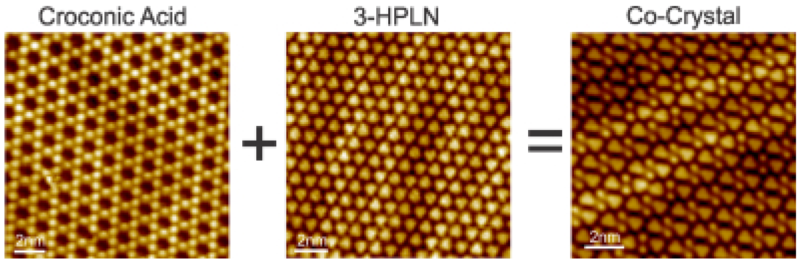
I will explore the adsorption and diffusion of CO inside the pores, which reveal the pores electronic structure and the effects confinement can have on molecular motion such as accelerated diffusivity, permanence of dislocation lines, etc.

COLL 472

Self-assembly and co-crystallization of ferroelectric organics on noble metal surfaces

Donna A Kunkel[1], *donna.ann.kunkel@gmail.com, James Hooper*[2], *Scott Simpson*[2], *Sumit Beniwal*[1], *Paulo Costa*[1], *Eva Zurek*[2], *Axel Enders*[1]*.Â (1) Department of Physics & Astronomy, University of Nebraska, Lincoln, NE 68588, United StatesÂ (2) Department of Chemistry, State University of New York, Buffalo, NY 14260, United States*

Proton-transfer type ferroelectricity was recently discovered for certain organic crystals. For some compounds, such as croconic acid, the transfer mechanism occurs within two-dimensional sheets the molecules form within the bulk crystal, which implies this phenomenon is also possible for a surface supported two-dimensional assembly. With that motivation, we present scanning tunneling microscopy (STM) studies on the two dimensional growth of two such compounds, with focus on croconic acid and 3-hydroxyphenalenone (3-HPLN), on the <111> facets of Au, Ag, and Cu substrates. The self-assembled structures of both compounds differ markedly from the bulk crystals, and the surface plays a strong role in controlling the self-assembly. First principle density functional theory calculations further explore the structure, electric polarization, and proton transfer mechanism of these structures. Remarkably, for networks of croconic acid on Ag, the surface enables proton transfer. Additionally, we present STM studies of hydrogen bonded co-crystals of croconic acid and 3-HPLN on Au(111). We will describe the observed polymorphic co-crystals as a function of the stoichiometry of the constituents. Combining organics into hydrogen bonded co-crystals creates innumerable possibilities for novel engineered materials.



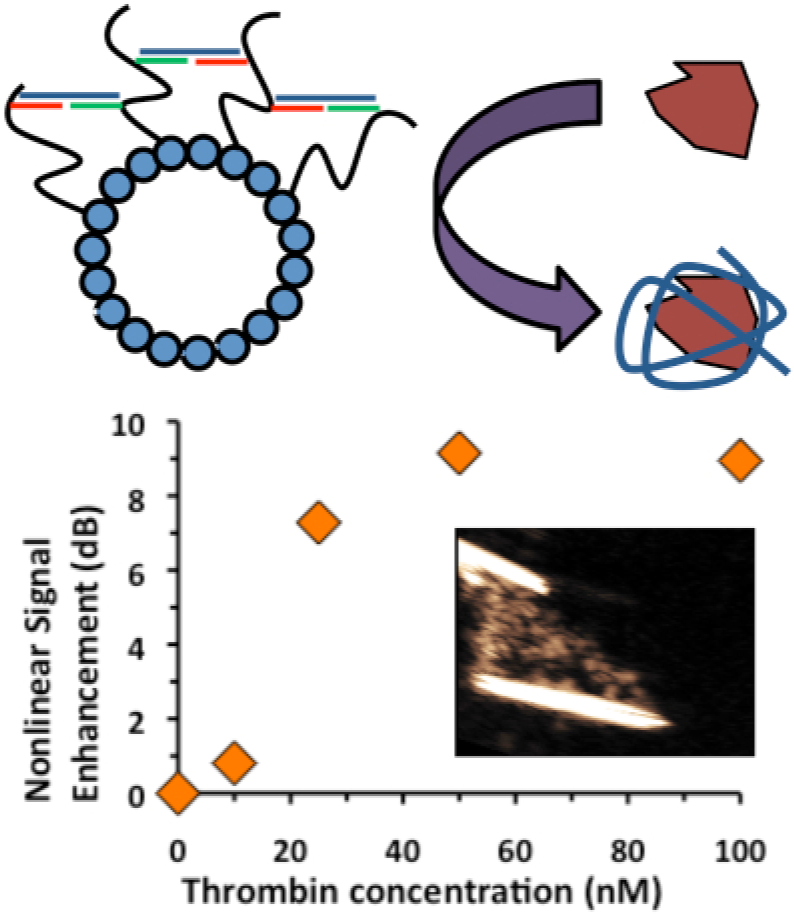
COLL 473

Self-assembly of DNA oligonucleotides on microbubble surfaces: Enabling in vivo chemical sensing with ultrasound contrast agents

Matthew A. Nakatsuka[1], *Christopher V. Barback*[3], *Kirsten R. Fitch*[1], *Sadik C. Esener*[2], *Robert F. Mattrey*[3], *Jennfer N. Cha*[1,2], ***Andrew P. Goodwin***[1], *andrew.goodwin@colorado.edu.Â (1) Department of Chemical and Biological Engineering, University of Colorado, Boulder, Boulder, Colorado 80303, United StatesÂ (2) Department of Nanoengineering, University of California, San Diego, La Jolla, CA 92093, United StatesÂ (3) Department of Radiology, University of California, San Diego, San Diego, CA 92121, United States*

The use of microbubbles as ultrasound contrast agents is one of the primary ways to diagnose intravascular diseases such as Deep Venous Thrombosis. However, current

microbubble imaging strategies for DVT require a clot to be sufficiently large as to affect the flow of bubbles around it. In this talk we will present our efforts to sense for chemical gradients in the body using ultrasound by imparting chemical responsiveness to the surface of microbubbles. Using the self-assembly of DNA oligonucleotides on the microbubble-medium interface, the microbubbles were designed to sense for thrombin as a biomarker for blood clotting. Microbubbles were encapsulated with a phospholipid-polymer containing oligonucleotides crosslinked by a DNA sequence containing sequences with affinity for thrombin. The presence of thrombin displaced the DNA crosslinks, reducing the stiffness of the shell and allowing the microbubble to emit selectively-detectable nonlinear echoes in response to ultrasound. In addition, it was found that longer poly(ethylene glycol)-lipid conjugates could be incorporated into the microbubbles to impart greater stability to circulation without affecting the chemical responsiveness of the microbubbles themselves. This talk will focus on the design of the microbubbles and their validation in static and flow in vitro models and an in vivo rabbit vascular injury model. In particular, the microbubbles were able to sense elevated thrombin levels in less than 30 seconds and should represent a viable methodology for the design of stimulus-responsive colloids in future research directions.



COLL 474

Electrochemical STM investigation of hydrogen bonded self-assembled structure at aqueous solutions/electrode interfaces

Shinobu Uemura[1]*, shinoue@eng.kagawa-u.ac.jp, Yusuke Nakamura*[2]*, Masashi Aono*[2]*, Masashi Kunitake*[2]*.Â (1) Department of Advanced Materials Science, Kagawa University, Takamatsu, Kagawa, JapanÂ (2) Graduate School of Science and Technology, Kumamoto University, Kumamoto, Japan*

Investigation of 2D self-assembled porous networks composed of organic molecules has been a key issue in nanoscience and nanotechnology. For construction of the 2D porous networks, building blocks with highly symmetrical features and functional groups for multiple intermolecular interactions with neighbour molecules are required because of thermodynamically unstability of such networks with low surface density. Among various building blocks, melamine is often used in supramolecular chemistry, because of its symmetrical shape with three functional groups for hydrogen bonding at the apexes. In this presentation, we report the investigation of 2D self-assembly of melamine and melem, which is a similar molecular shape to melamine, at the aqueous solution/Au(111) interfaces by electrochemical (EC) STM.

Under the bicomponent solutions of melamine and melem, several bicomponent self-assembled honeycomb networks were found at the interfaces. These structures were formed due to side-by-side hydrogen bonds. Depending on the mixture ratio and the solution concentration, different mono- and bicomponent networks were constructed.

In the similar way to the monocomponent networks in the previous study, the electrochemical studies of the self-assembled structures was carried out. The “order-order-order” transition between three different self-assembled structures was also occurred under the potential control. The mono melem honeycomb, binary honeycomb and finally mono melamine honeycomb structures were appeared from negative (-0.6 V vs. SCE) to positive potential (0 V). This appearing order agrees with the order of the surface density of the observed structures.

COLL 475

Natural clay nanotubes as a novel enzyme immobilization support

Joshua Tully[1]*, jtu006@latech.edu, Rawil Fakhrullin*[2]*, Yuri Lvov*[1]*.Â (1) Institute for Micromanufacturing, Louisiana Tech University, Ruston, Lousiana 71272, United StatesÂ (2) Department of Microbiology, Kazan Federal University, Kazan, Republic of Tartarstan 420008, Russian Federation*

Physical adsorption of proteins on to inorganic supports such as zeolites and silica is a well-documented phenomenon. We utilized enzyme immobilization in halloysite nanotubes by loading anionic proteins inside of halloysite's 15nm lumen. This can be accomplish efficiently because: 1) The diameter of the lumen is large enough to accommodate proteins of 2-5nm diameter and the hydrophilic chemical character of

said lumen. 2) Since the interior of the tube is positively charged and the exterior is negatively charged, one can prevent adsorption of protein on the outer surface of the tube by controlling the pH relative to the proteins pI. We have demonstrated loading of various proteins, with a net negative charge in water, such as glucose oxidase, pepsin, urease, and lipase. We were able to load the proteins into the nanotubes from concentrated aqueous solutions and achieve 5-8 wt % loading efficiency, dry them for long term storage while preserving moisture inside of the tubes, then utilize the sample for release kinetic studies or enzymatic activity assays. Approximately 25% of the loaded protein was released within five to six hours after being place into solution, while the other half seem resistant leaving the lumen of halloysite. Halloysite nanotubes are non-toxic and biocompatible and if loaded with biologically active materials then one can imagine the many potential uses of these functionalized nanocontainers.

COLL 476

Spray-assembled composite polyelectrolyte-clay thin films as selective layers in RO membranes

Jason R. Kovacs*, jkovacs@mit.edu, Paula T. Hammond.Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

Efficient water desalination is vital to sustaining the quality of life for populations living without access to sufficient freshwater resources as well as treating the wastewater produced from industrial activities before reuse or being discharged to the environment. In this work, we utilize the flexibility of the layer-by-layer (LbL) assembly process to create composite thin films comprised of cross-linkable polyelectrolytes and silicate clay nanoparticles to serve as a substitute for the polyamide selective layer in commercially-available reverse osmosis (RO) membranes. The spray layer-by-layer (spray-LbL) assembly process enables the deposition of large, asymmetric thin films with intercalated clay platelets orders of magnitude faster than possible through traditional dip-LbL processing. The composite thin films were deposited on polyethersulfone nanofiltration (NF) membranes, with composition and physical properties fine-tuned by manipulating the assembly conditions such as spray time and pH of the film components, the number of layers deposited, and the time and temperature of the post-deposition heat treatment. Films were characterized with ATR-FTIR and TGA to determine the efficacy of the cross-linking treatment as well as the clay content. Using mathematical modeling on data collected from a dead-end permeation cell, permeability coefficients for water and salt through selective layers of varying film composition were calculated. At operating pressures up to 300 psi (20.7 bar) and both brackish and seawater desalination conditions, the water permeability coefficient calculated for these composite thin films was found to be an order of magnitude greater than what was observed for a commercially-available polyamide selective layer. Over the same range of operating pressures, the composite thin films rejected up to 93.3% of aqueous NaCl. These experimental results confirm the viability of using composite polyelectrolyte-clay thin films as an alternative selective layer.

COLL 477

High capacity methane hydrates based on bio-promoters

*Weixing Wang[1], Haoran Chen[2], Zhan Huang[1], Zhuyan Tan[1], Caixing Chen[1], **Luyi Sun**[2], luyi.sun@uconn.edu.Â (1) Ministry of Education Key Laboratory of Enhanced Heat Transfer & Energy Conservation, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, Guangdong 510640, ChinaÂ (2) Department of Chemical & Biomolecular Engineering, University of Connecticut, Storrs, CT 06269, United States*

Gas hydrates, or gas clathrates, are non-stoichiometric, crystalline inclusion compounds composed of a hydrogen-bonded water lattice which traps small molecules within polyhedral cavities. Recently, gas hydrates have drawn significant interests in the potential applications in the separation, capture, storage, and transportation of a wide range of gases, including methane, carbon dioxide, and hydrogen. However, there is a key issue to be addressed: slow formation rate of gas hydrate, which is approximately inversely proportional to the thickness of the hydrate zone, and low capacity. Herein, we report, to the best of our knowledge, for the first time regarding using lignosulfonates (LSs), a promoter derived from biomass, for the formation of high capacity methane hydrates. LSs, which are byproducts of pulp and paper industry, can be used as effective promoters for the formation of methane hydrate in terms of both formation rate and storage capacity (up to 167 v/v under standard temperature and pressure). The lignosulfonates promoted system also exhibited excellent recyclability.

COLL 478

High performance crumpled graphene-TiO_2 photocatalysts for water treatment technologies

***Yi Jiang**, jiang.y@wustl.edu, Wei-Ning Wang, Pratim Biswas, John D Fortner.Department of Energy, Environmental, and Chemical Engineering, Washington University in St. Louis, St. Louis, MO 63130, United States*

Water treatment using advanced photocatalysts, particularly TiO_2, has garnered considerable research attention and has been successfully demonstrated in a number of applications. Recent material advances with combined TiO_2-carbon nanomaterial based photocatalysts, such as graphene, have demonstrated superior physical and chemical properties compared to traditional analogues. However, flat graphene (or reduced graphene oxide, rGO)-TiO_2 nanocomposites restack due to strong π-π attraction which inevitably leads to significant decay of photocatalytic performance. In this work, aggregation resistant crumpled graphene-TiO_2 nanocomposite has been synthesized via a facile aerosol route and demonstrated as superior aqueous photocatalyst. The as-synthesized quasi-spherical, core-shell nanostructured composites, with controllable size and functionality, have demonstrated enhanced photocatalytic activity compared to bare TiO_2 due to increased lifetime of photo-induced holes and electrons. Reactive oxygen species, such O_2-·, H_2O_2, and OH·, have been identified by employing various radical scavenging experiments. In addition, cross-linked crumpled graphene-TiO_2 nanocomposite layer (with tunable pore size), deposited atop polyethersulfone (PES) support membrane, readily rejects and photo-degrades model aqueous pollutants. This study highlights the application potential for crumpled graphene-based nanocomposites in water treatment technologies, both as a high performance photocatalyst and assembling components of the reactive membrane.

COLL 479

Effective oil dispersible clay-based dispersant systems for oil-in-seawater emulsions

***Jiannan Dong**[1], jiannan.dong@utexas.edu, Andrew J. Worthen[1], Yunshen Chen[1], Lynn M. Foster[1,2], Jonathan A. Bollinger[1], Thomas M. Truskett[1], Steven L. Bryant[3], Christopher W. Bielawski[2], Keith P. Johnston[1].Â (1) Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712, United StatesÂ (2) Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX 78712, United StatesÂ (3) Department of Petroleum and Geosystems Engineering, The University of Texas at Austin, Austin, TX 78712, United States*

For the natural remediation process of oceanic oil spills, it is essential to disperse oil slicks into small and stable oil droplets with dispersants. Introducing micro- or nanoparticles such as natural clays to dispersant systems could minimize the amount of surfactant required for emulsion stability. We developed an oil-dispersible system of Montmorillonite clay and an ethoxylated amine surfactant for effective formation and stabilization of dodecane-in-synthetic seawater emulsions. This system allowed the direct delivery of the clay-based dispersant from the oil phase, which is desirable for oil spill treatment. Before emulsification, clay particles remained in the oil phase due to surface modification through adsorption of surfactant, which was determined by interfacial tension and contact angle measurements. The emulsions were characterized by laser diffraction to measure droplet size distributions, optical photography to quantify phase separation, and optical microscopy to observe droplet morphologies. The effects of total concentration of surfactant and clay, ratio of surfactant to clay, and water volume fraction on emulsion properties were investigated. With a fixed ratio of surfactant to clay, increasing total concentration reduced droplet size and enhanced creaming stability. For o/w emulsions prepared at a fixed total concentration, the average droplet size decreased with increasing water volume fraction. With increasing surfactant to clay ratio, emulsion type inverted from o/w to o/w. The emulsions near the inversion point were found to be least stable.

COLL 480

Functionalized environmentally-benign nanoparticles as substitute for nanosilver antimicrobials

Alexander P. Richter[1]*, aprichte@ncsu.edu, Vesselin N. Paunov*[2]*, Simeon D. Stoyanov*[3]*, Orlin D. Velev*[1]*.Â (1) Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, United StatesÂ (2) Department of Chemistry, University of Hull, Hull, United KingdomÂ (3) Laboratory of Physical Chemistry and Colloid Science, University of Wageningen, Wageningen, The Netherlands*

The introduction of antimicrobial silver nanoparticles (AgNPs) in industrial applications has been a concern to the U.S. Environmental Protection Agency (US EPA) due to potential environmental dangers of the persistent nanoparticles. We will present a new class of nature-inspired environmentally-benign nanoparticles (EbNPs) with antimicrobial functionality, which have a degradable core and can serve as highly efficient microbicidal substitutes of the AgNPs. The EbNPs are made of biodegradable lignin biopolymers, e.g. Indulin AT (IAT) and High Purity Lignin (HP-L), and are infused with optimal amount of silver in the form of adsorbed Ag+ ions. The release of the active Ag+ ions takes place during the targeted adsorption of the surface-modified particles onto bacterial membranes. We show that Ag+ ion functionalized EbNPs exhibit higher antimicrobial activity towards Gram-negative human pathogens *Escherichia coli* and *Pseudomonas aeruginosa* in direct comparison with silver nanoparticles and silver nitrate solution, and that the particles are effective against quaternary ammonium resistant *Ralstonia* species. The enhanced antimicrobial action is due to highly-biocidal Ag+ ions released from the EbNP system at the cell. We will report on the fabrication of these particles with simple, inexpensive, and non-toxic processes, by applying an environmentally friendly water-based acid precipitation method, and by employing a solvent exchange precipitation method at room temperature. Dynamic Light Scattering is employed to determine the EbNP size distributions as a function of the operating parameters such as pH drop magnitude, initial modified lignin loading in stock solution, and choice of solvent. We obtained EbNPs with diameters ranging from 40 to 200 nm and with pH stability ranging from pH 4.0 to 9.0. Comprehensive bioactivity studies on various eukaryotic cells in collaboration with the US EPA are being performed to evaluate the biotoxicity and the environmental impact of these EbNPs.

COLL 481

Application of membrane-filters modified with carbon-based nanomaterials for water treatment

Debora F Rodrigues*, dfrigirodrigues@uh.edu.Department of Civil and Environmental Engineering, University of Houston, Houston, TX 77204, United States*

Conventional chemical disinfectants such as chlorine, chloramines and ozone have been used extensively by water treatment plants for effective removal of pathogenic microorganisms. However, due to their tendencies to form harmful disinfection byproducts, alternative methods are highly desirable. Given the antimicrobial properties of several nanomaterials and due to their unique properties (i.e. high aspect ratio, ability to disperse with other materials, and relatively easy preparation), in this project we have

modified conventional microfilters with five nanomaterials, namely: carbon-nanotubes (CNTs), graphene oxide (GO), polyvinyl carbazole (PVK), PVK-GO, and PVK-CNT. The surface modified-membranes were examined via surface sensitive techniques such as X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), and Atomic Force Microscopy (AFM). The antimicrobial properties of the modified filter membranes were tested against suspensions containing pure cultures of *Escherichia coli* and *Bacillus subtilis.* Filtrates were plated for quantification of colony forming units and to determine microbial removal from the water. Viability tests were also performed on the membranes by live-dead staining and fluorescence microscopy. Preliminary results with *E. coli* and *B. subtilis* showed that the modified membranes with CNTs, GO, PVK, PVK-GO, and PVK-CNT were effective for bacterial removal and inactivation as compared to unmodified filters. These results suggest that nanomaterial-modified filters can be very effective for water disinfection.

COLL 482

Nanocomposite adsorbents for environmental remediation

Zhanhu Guo[1]*, zhanhu.guo@lamar.edu, Cuixia Xu*[1]*, Bin Qiu*[1,2]*, Dezhi Sun*[2]*, Suying Wei*[1,3]*.Â (1) Department of Chemical Engineering, Lamar University, Beaumont, TX 77710, United StatesÂ (2) College of Environmental Science and Engineering, Beijing Forestry University, Beijing, Beijing 100083, ChinaÂ (3) Department of Chemistry and Biochemistry, Lamar University, Beaumont, TX 77710, United States*

In this talk, the toxic Cr(VI) removal from polluted water by different nanocomposites adsorbents including graphene decorated with magnetic nanoparticles, iron oxide nanoparticles coated with polyaniline, carbon fabric coated with magnetic nanoparticles, etc will be comparatively reported. The effects of initial Cr(VI) concentration, adsorbent dose and pH value on the Cr(VI) removal will be covered. The Cr(VI) removal kinetics in the different pH solutions will be determined. The Cr(VI) removal mechanisms will be investigated by Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), energy-filter TEM (EFTEM) and temperature dependent resistivity.

COLL 483

Designing enhanced 1D electrocatalysts for the oxygen reduction reaction: Probing size- and composition-dependent electrocatalytic behavior in noble metal nanowires

Stanislaus S. Wong*, stanislaus.wong@stonybrook.edu.Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY 11794-3400, United StatesCondensed Matter Physics and Materials Sciences Department, Brookhaven National Laboratory, Upton, NY 11973, United States*

Despite increasing interest in the use of one dimensional (1D) noble metal nanostructures for the oxygen reduction reaction, there has been a surprising lack of effort expended in thoroughly and rationally examining the influence of various physicochemical properties of 1D electrocatalysts with respect to their intrinsic catalytic performance. In this talk, we address this important issue by investigating and summarizing recent theoretical and experimental progress aimed at precisely deducing the nature of the complex interplay amongst size, chemical composition, and electrocatalytic performance in high-quality elemental and bimetallic 1D noble metal nanowire systems. In terms of these structural parameters, significant enhancements in both activity and durability of up to an order of magnitude in the case of functionalized Pt~$Pd_{1-x}Au_x$ nanowires, for example, can be achieved by rationally tuning both wire size and composition. The fundamental insights acquired are then utilized to discuss future and potentially radically new directions towards the continuous improvement and optimization of 1D catalysts.

COLL 484

Electroless deposition of copper nanowires on micropatterned organic substrates

Ashley A. Ellsworth[1]*, axe120730@utdallas.edu, Amy V. Walker*[1,2]*.Â (1) Department of Chemistry, The University of Texas at Dallas, Dallas, TX 75080, United StatesÂ (2) Department of Materials Science and Engineering, The University of Texas at Dallas, Dallas, TX 75080, United States*

Electroless nanowire deposition on micropatterned substrates (ENDOM) is a promising technique for the *in situ* growth and simultaneous nanoscale placement on substrates. We have studied the reaction pathways involved in the deposition of copper nanowires on patterned –OH/-CH_3 terminated alkanethiolate self-assembled monolayers (SAMs). The nanowires nucleate at the interfaces of the –OH and –CH_3 terminated SAM areas as nanoparticles which later coalesce to form a polycrystalline nanowire. Since the nanowire is formed via electroless deposition, the nanowire dimensions can be controlled by varying reaction conditions such as bath pH, temperature, reagent concentrations, and deposition time. We demonstrate that Cu ENDOM can be performed over a wide range of reaction conditions leading to nanowires with dimensions ranging from 50-300 nm in height, ~300-1500 nm in width. These nanowires are ultralong (centimeters) and can be grown in arbitrary shapes such as going around a right angle bend or a circle.

COLL 485

Janus-like deposits on TiO_2 nanowires by the combined action of bipolar-electrochemistry and light

Paolo Ugo[1]*, ugo@unive.it, Michael Ongaro*[1]*, Alexander Kuhn*[2]*.Â (1) Department of Molecular Sciences and Nanosystems, University Ca' Foscari of Venice, Venice, ItalyÂ (2) ISM, UMR 5255, ENSCBP, UniversitÃ© de Bordeaux, Pessac, France*

In bipolar electrochemistry (BPE), faradaic reactions are driven on conducting particles not directly connected to an electrical power source, but immersed in a dielectric (solution) polarized by an applied electric field. Examples of use of BPE for controlling asymmetrical depositions on metal particles have been widely reported, while, few or no study dealt with BPE deposition on semiconductor nanoparticles. In a BPE experiment on a semiconductor in the dark, the holes concentration at the anodic side is so low that the oxidation occurs at a negligible rate so hindering also the associated cathodic process. The situation changes when BPE is performed under UV-light irradiation, so that the electrons are promoted to the conduction band, triggering the occurrence of oxidation and reduction reactions at the two opposite sides of the particle. In this work, these principles are used to control deposition processes onto the tips of TiO_2 nanowires (TiO_2-NWs). We demonstrate here that, when BPE is performed in the dark on TiO_2-NWs in Au(III) solutions, no gold deposit is formed. When the NWs suspension is irradiated with UV light in the absence of an electric field, small metallic deposits, randomly located all over the particles are formed. Finally, when both UV light and electric field are applied, a metallic deposits is formed, but in a precise position of the NW, that is at its cathodic tip. These results indicate that the application of the external electric field allows one to drive locally the action of the light thus achieving the localized asymmetrical modification of the TiO_2-NWs. The technique is applied to drive the deposition of different metals and/or conducting polymers at one or at the two opposite tips of TiO_2-NWs. Relevant results and prospects are presented and discussed.

COLL 486

Dealloyed porous NiCu for hydrogen evolution reaction catalysis

*Kyla R. Koboski[1], Evan F. Nelsen[1,2], **Jennifer R. Hampton**[1], hampton@hope.edu.Â (1) Department of Physics, Hope College, Holland, Michigan 49423, United StatesÂ (2) Department of Physics and Astronomy, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, United States*

Porous metals are of interest for their high surface area and potential for enhanced catalytic behavior. Electrodeposited NiCu thin films with a range of compositions were electrochemically dealloyed to selectively remove the Cu component. The structure, composition, and reactivity of these samples were characterized both before and after the dealloying step using scanning electron microscopy, energy-dispersive x-ray spectroscopy, and electrochemical measurements. The hydrogen evolution reaction was measured on the dealloyed porous Ni samples and compared to similar measurements on the as-deposited samples. The dealloyed samples were generally more reactive than their as-deposited counterparts at low overpotentials, and less reactive than the as-deposited samples at high overpotentials. Nanostructured materials fabricated by this electrochemical dealloying procedure are a promising area of catalysis research.

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COLL 487

Bioinspired conversion of carbon dioxide to methanol

Krishnan Rajeshwar, *rajeshwar@uta.edu.Department of Chemistry & Biochemistry, University of Texas at Arlington, Arlington, TX 76019, United States*

In this talk, the synergies between electro- and photocatalysis will be underlined wit the dioxygen reduction and hydrocarbon oxidation as representative examples. The importance of conjugate processes occurring at the counterelectrode will be emphasized in both cases. Approaches based on the use of electrodes and photoelectrodes as well as those based on the use of colloidal suspensions will be compared and contrasted. Ideas on how we can learn from the intricate self-assembled architectures that Nature has evolved over millions of years, will be discussed with specific examples

Finally the talk will turn toward the very recent work in the author's laboratory on the solar photoelectrosynthesis of methanol from CO_2. This process was driven on hybrid CuO/Cu_2O semiconductor nanorod arrays for the first time at potentials ~800 mV below the thermodynamic threshold value and at Faradaic efficiencies of ~95%. The CuO/Cu_2O nanorod arrays were prepared on Cu substrates by a two-step approach consisting of the initial thermal growth of CuO nanorods followed by controlled electrodeposition of p-type Cu_2O crystallites on their walls. No co-catalysts (such as pyridine, imidazole or metal cyclam complexes) were used contrasting with earlier studies on this topic using p-type semiconductor photocathodes. The roles of the core/shell nanorod electrode geometry and the copper oxide composition were established by varying the time of electrodeposition of the Cu_2O phase on top of the CuO nanorod core.

COLL 488

Functionalizing oxide-free silicon surfaces and nanoparticles for nanoelectronic and energy applications

Yves J Chabal[1], *chabal@utdallas.edu, William J.I. De Benedetti*[1], *Abraham Vega*[1], *Wilfredo Cabrera*[1], *Yingzhen Lu*[1], *Peter Thissen*[2], *Tatiana Peixoto*[1], *Lihong Liu*[1], *Anton Malko*[3]*.Â (1) Department of Materials Science and Engineering, Unversity of Texas at Dallas, Richardson, Texas 75080, United StatesÂ (2) Institute of Functional Interfaces, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, GermanyÂ (3) Department of Physics, University of Texas at Dallas, Richardson, Texas 75080, United States*

A growing number of applications requires direct functionalization of oxide-free silicon surfaces, despite the superior electrical characteristics of the Si/Si-oxide interface. There have however been few studies to characterize the nature of functionalized Si surfaces and their dependence on chemical and atomic structures. This work focuses on developing a fundamental understanding of direct wet-chemical and vapor-phase functionalization of fully H-terminated and partially hydroxylated Si surfaces, using model systems such as flat nanopatterned Si(111) surfaces[1], stepped Si(111) surfaces, and even atomically flat Si(100) surfaces.[2] Electrical measurements indicate that the quality of the molecular layer/Si interfaces (through Si-C bonds) of atomically flat surfaces can be as good as that of thermally oxidized Si(111) surfaces, opening the door for electronic applications. Simple hydrosilylation is shown to be a powerful means to graft nanoparticles close to the electronic substrate, thus supporting a novel method for enhancing the efficiency of Si-based photovoltaic cells, based on non-radiative and radiative energy transfer into Si nanomembranes.[3] Furthermore, direct attachment of acid groups (through Si-O-X bonds) provides a means to incorporate dopant (P, As) into Si, necessary for applications requiring shallow doping. Finally, control and functionalization of oxide-free Si surfaces is important for fabricating single-electron systems on Si, characterized by a Coulomb staircase behavior.[4]

[work supported by NSF-CHE-1300180]

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COLL 489

Incorporating molecular monolayers in standard Si device fabrication

***Ayelet Vilan**, ayelet.vilan@weizmann.ac.il, David Cahen.Department of Materials and interfaces, Weizmann Institute of Science, Rehovot, Israel*

Molecular charge transport is of interest for functionalization and miniaturization of electronic devices. Use of molecular monolayers offers a more applicative route and better reproducibility than work with single molecules. We show that Si-molecular monolayer / Pb junctions (Figure 1) overcome two major obstacles facing monolayer devices.

The first is diffusion of metal atoms through a molecular monolayer, assembled on a substrate electrode. We suggest that the affinity between the deposited metal and the underlying substrate drives diffusion and creation of shorts. Thus a judicious match of non-interacting top and bottom electrodes, such as Pb and Si reduces formation of short-circuiting defects below a detectable electrical effect, even for thermally-evaporated Pb.[1]

The second is poor reproducibility of measured molecular transport. We show that a) strong covalent bonding, b) strict elimination of surface oxidation, and c) minimal surface corrugation to limit chemically active "hot-spots",[2] all contribute to achieving remarkable reproducibility in current – voltage response of Si-molecular monolayer / Pb junctions.

We used our cumulative experience for producing stand-alone, 10 μm wide junctions, within a thick SiO_2 layer. These junctions could be cycled thousands of times and cooled down to < 100K without altering their performance.

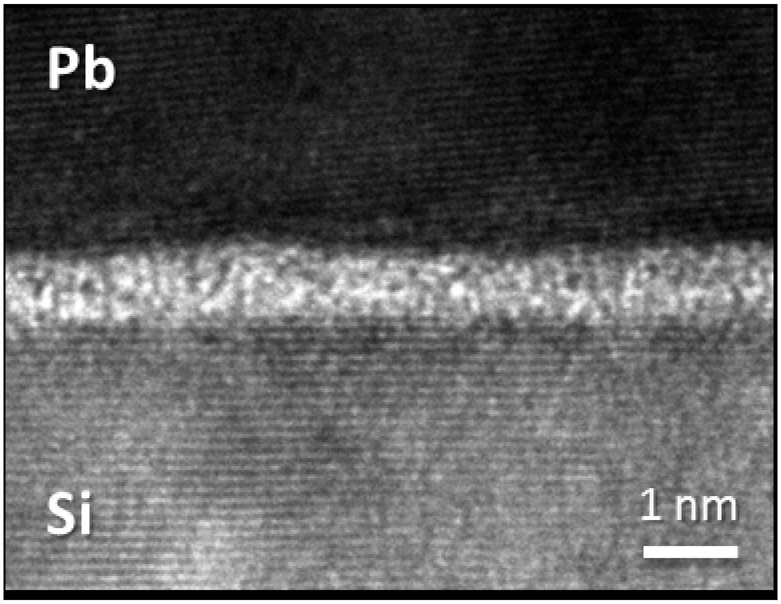

Figure 1: Cross section TEM of a Si(111)/Br-styrene/Pb junction.

1. Lovrinčić, Vilan, et al., *JPCL* (2013), **4** , 426;

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COLL 490

Chemical love at surfaces: Optimization toward the one and only

Han Zuilhof, *han.zuilhof@wur.nl.Organic Chemistry, Wageningen University, Wageningen, The Netherlands*

The modification of inorganic surfaces with (bio-)organic moieties provides the possibility to give entirely new functions to supposedly well-known substrates. The presentation will illustrate this based on a few principles also relevant to love: long-term stability,[1] specific recognition,[2] and optimal presentation.[3] Along the way highly detailed surface characterizations, smooth 'add and just stir' metal-free organic click reactions, and easy-to-use theory will pass to show what is behind the cartoons.

For example, functionalized Si and ITO surfaces can be prepared by the photochemical grafting with 1-alkenes (see Figure 1). By taking suitably substituted alkene substrates, a tailor-made organic functionalization of the surface can be obtained in one step!

The presentation will outline mechanistic features of the grafting reactions. In addition, it will point to current developments in this field regarding the potential for biofunctionalization of substrates with complex bio-organic and biological architectures, and finish off with a series of biological applications, including the use of oriented antibodies.

[figure 1]

Figure 1. Functionalization of ITO: Formation of covalently linked organic monolayers onto Indium Tin Oxide surfaces.

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COLL 491

Dewetting based directed assembly of nanostructure with and without self-assembled monolayer patterns

***Saleem Ghaffar Rao**[1], saleemg@kfupm.edu.sa, Lutfan Sinatra[2], Yuanfang Hou[2], Osman Bakr[2].Â (1) Physics, King Fahd University of Petroleum and Minerals, Dhahran, --- Please Select --- 31261, Saudi ArabiaÂ (2) Division of Physical Sciences and Engineering, and Photvoltaics Engineering Center,, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia*

Nanostructures (NSs) have been in focus of interest in the past few decades due to their unique electronic, magnetic, optical, and catalytic properties, which lead to novel applications. The ability to arrange NS into ordered 2D or 3D micro/nano structures is of utmost importance in developing new devices and applications of these nano-structures. Controlled spatial placement of nanostructures (NS) at micro/nano scale has attracted much attention due to their applications in NS based device fabrication. Different processes like, chemical interaction based to solvent driven patterned

assembly of NS have been reported. Here we will present patterned assembly of different NSs at micron scale controlling the dewetting of surfaces with and without self-assembled monolayer (SAM) patterns. SAMs with terminal end of $–CH_3$ were used to create wet-able and non-wet-able patterned regions on gold/silicon surfaces. After dipping the SAM patterned surface in the NS solution we observed NS assembly according to SAM molecular patterns in wet-able regions during solvent drying process. Whereas dewetting of bare substrate (without any SAM patterns) dipped in NS solution also results in line patterned assembly of NS. Although both processes can be used for patterned assembly of NSs however, with SAM we can control the frequency and shape of pattered regions. Using both processes different NSs (like nanodiamond, silver nano-cubes, Co NP etc.) patterned assembly will be discussed.

COLL 492

On-demand self-assembly of supported membranes using sacrificial, anhydrobiotic sugar coats

Thomas E. Wilkop[1]*, twilkop42@gmail.com, Jeremy Sanborn*[3]*, Ann E. Oliver*[1]*, Joshua M. Hanson*[2]*, Atul N. Parikh*[1]*.Â (1) Department of Biomedical Engineering, University of California Davis, Davis, CA 95616, United StatesÂ (2) Biophysics Graduate Group, University of California Davis, Davis, CA 95616, United StatesÂ (3) Applied Science Graduate Group, University of California Davis, Davis, CA 95616, United States*

Borrowing principles of anhydrobiosis, we have developed a technique for self-assembling proteolipid supported membranes on demand – simply by adding water. Intact lipid- and proteolipid vesicles dispersed in aqueous solution of anhydrobiotic trehalose are vitrified on arbitrary substrates producing glassy coats encapsulating biomolecules. These carbohydrate coats arrest molecular mobilities and preserve native conformations and aggregative states of the embedded biomolecules, thereby enabling long-term storage. Subsequent rehydration, even after an extended period of time (e.g., weeks), devitrifies sugar – releasing the cargo and unmasking the substrate surface – thus triggering substrate-mediated vesicle fusion in real-time producing supported membranes. Using this method, arrays of membranes, including those functionalized with membrane proteins, can be readily produced in situ by spatially addressing vitrification using common patterning tools – useful for multiplexed or stochastic sensing and assaying of target interactions with the fluid and functional membrane surface. Further vesicle fusion on demand allows it to initiate and monitor interactions between reactants (e.g., surface lipids and/or embedded cargo), that are either maintained in separate vesicle populations in the vitrified state or delivered on site during devitrification and bilayer formation.

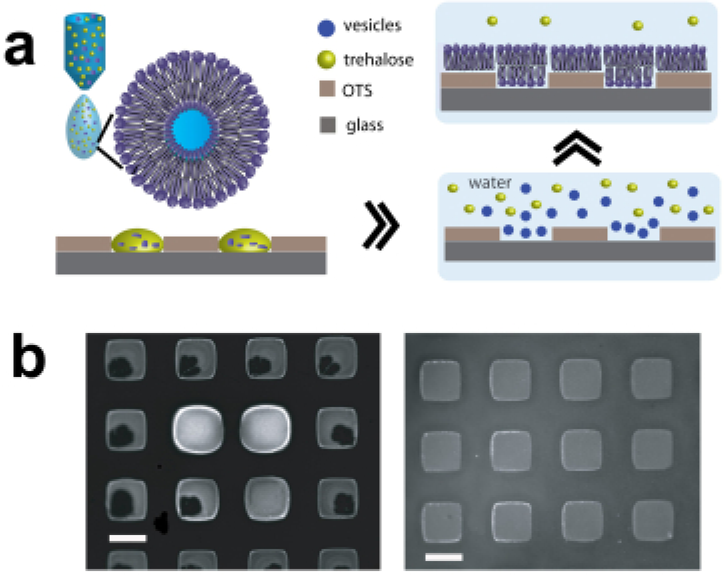


Figure 1. (a) Schematic of the method. Vesicle-encapsulating pre-vitrified trehalose coat, upon hydration releases the cargo, which recognize the unmasked substrate forming supported membranes. (b) Representative epifluorescence micrographs of a pattern of POPC vesicle-embedding arrays of trehalose coats in their vitrified (left) and devitrified (right) states. Scale bar 100 µm.

COLL 493

Generation and maintenance of plasma membrane transbilayer phospholipid asymmetry in health and disease: Role of flippases, floppases, and scramblases

David L. Daleke, *daleked@indiana.edu.Medical Sciences / Department of Biochemistry and Molecular Biology, Indiana University School of Medicine, Bloomington, Indiana 47405, United States*

A characteristic feature of all cell plasma membranes is the asymmetric transbilayer distribution of phospholipids. The choline-containing phospholipids, phosphatidylcholine and sphingomyelin are enriched in the outer monolayer, while the aminophospholipids, particularly phosphatidylserine (PS), are enriched on the cytoplasmic surface. The dissipation of this gradient and exposure of PS on the surface of the cell induces the recognition and destruction of the cell by macrophages and, in blood cells, the activation of plasma clotting factors. The action of several lipid-specific transporters, included an inwardly-directed, aminophospholipid-specific, ATPase or “flippase,” outwardly-directed "floppases," and a bi-directlional, non-specific "scramblase", play important roles in the generation, maintenance and regulated dissipation of plasma membrane phospholipid asymmetry. The goal of our studies is to identify and characterize these lipid

transporters, using substrate specificity and biochemical properties as criteria. We have purified and characterized two candidate flippases: a PS-stimulated ATPase from human erythrocytes and a P_4-ATPase (ATP8A1) heterologously expressed in insect cells. These enzymes share an exquisite structural specificity for PS that is distinct from other PS-binding proteins and support the hypothesis that they are PS-selective flippases.

In separate experiments, we have addressed the role of plasma membrane asymmetry in the cardiovascular complications associated with diabetes. Erythrocytes from poorly controlled diabetics express PS on the cell surface, which stimulates blood clotting factors and may promote unwanted thromboses. Using a combination of *in vitro* hyperglycemia, animal models of diabetes, and erythrocytes from human diabetics, we have determined that hyperglycemia induces oxidative damage of the erythrocyte membrane, increases passive phospholipid flip-flop, increases PS externalization, and stimulates blood clotting factors, all of which are suppressible with antioxidants. These studies indicate that lipid transporters are critical for the maintenance of plasma membrane phospholipid asymmetry and that they may be potential therapeutic targets for the treatment or prevention of cardiovascular disease in diabetes.

COLL 494

Interaction of metal ions with phospholipid head groups

***Paul Cremer**, psc11@psu.edu.Chemistry, Penn State, University Park, PA 16802, United States*

The head groups of phospholipids contain various positively and negatively charged chemical moieties. This includes the negatively charged phosphate and carboxylate groups as well as the positively charged amine and choline groups. These groups can interact with ions in solution such as Cu^{2+} in a variety of different ways. We have been able to show that Cu^{2+} binds especially tightly to phosphatidylserine (PS) and does so through both its amine and carboxylate groups. Specifically, we have found that the amino group becomes deprotonated upon metal ion binding and that the Cu^{2+} ions can interact with two PS lipids to for square planar complex. The equilibrium dissociation constant of this complex is dependent on the concentration of PS lipids in the membrane as well as the pH of the bulk solution. A variety of different techniques such as fluorescence microscopy and vibrational sum frequency generation (SFG) spectroscopy are used to explore the complex. Kinetic measurements are made as well.

COLL 495

Primitive osmoregulation in giant lipid vesicles

*Kamila Oglecka[1], Rachel S Kraut[1], Bo Liedberg[1], **Atul N Parikh**[1,2], anparikh@ucdavis.edu.Â (1) Materials Science & Engineering, Nanyang Technological*

University, Singapore, SingaporeÂ (2) BME, CHMS, University of California, Davis, Davis, CA 95616, United States

Giant unilamellar vesicles (GUVs), the simplest cell-like structures, are closed, semi-permeable flexible shells (4-6 nm thick, 5-100 µm dia.), isolating femto- to pico-liter quantities of aqueous core from the surrounding bulk. Although water equilibrates across vesicular walls (10^{-2}-10^{-3} cm^3 $cm^{-2}s^{-1}$), passive permeation of solutes is strongly hindered. Moreover, because of their large volume compressibility (~10^9-10^{10} Nm^{-2}) and area expansion (102-103 mNm-1) moduli, coupled with low bending rigidities (10^{-19} Nm), vesicular shells bend readily but resist volume compression and tolerate only a limited area expansion (~5%). Consequently, GUVs experiencing solute concentration gradients exhibit significant shape transformations, deforming in hypertonic media and swelling in hypotonic ones.

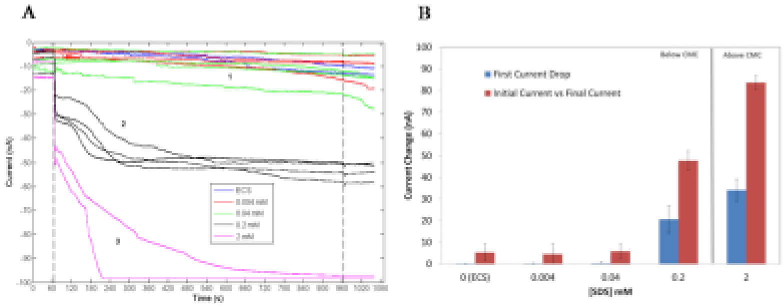
This talk presents unexpected experimental observations in which osmotic relaxation across vesicular boundary induces dramatic alteration in lipid-lipid phase separation. Specifically, the swelling of osomolyte-loaded vesicles produces an unusual oscillatory dynamics at the vesicular boundary in which the osmotic dissipation producing previously known periodic oscillations in size becomes coupled with membrane's internal compositional degrees of freedom producing unusual damped oscillations in vesicle texture between microscopically phase-separated states and a uniform one. Analyzing this behaviour in terms of well-known biophysical processes of membrane tension, poration, and solute leakage, We find that this unusual oscillatory phase separation emerges as a consequence of a well-orchestrated synergy during swell-burst cycles: Swelling, which is caused by the influx of water, raises membrane tension, promoting the appearance of microscopic domains when vesicles are swollen. Bursting, which facilitates solute leakage through membrane poration, relaxes the membrane tension, breaking up large domains into a homogeneous state in unswollen vesicles. This autonomous self-regulatory response – in which an external osmotic perturbation is dissipated by a co-ordinated and cyclical sequence of physical mechanisms allowing vesicles to sense (by domain formation) and regulate (by solute efflux) their local environment in a negative feedback loop – appears to recapitulate a kind of primitive quasi-homeostatic regulation in a material system produced from common components, namely, water, osmolytes, and lipids of broad importance in biology.

COLL 496

Disruption of the cell plasma membrane by detergent and polymers as measured by whole cell patch clamp and fluorescence

Mark Banaszak Holl[1,2], *mbanasza@umich.edu, Sriram Vaidyanathan*[2], *Bradford Orr*[3]*.Â (1) Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055, United StatesÂ (2) Department of Biomedical Engineering, University of Michigan, Ann Arbor, MI 48109-1055, United StatesÂ (3) Department of Physics, University of Michigan, Ann Arbor, MI 48109-1055, United States*

Detergents and polymers are used for solubilizing membrane proteins, drug delivery, and potentially for treating bacterial, fungal and viral infections; however, their ability to solubilize and/or create pores in cell membranes raises concerns about their cytotoxicity. We have used the IonFlux 16^{TM}, an ensemble whole cell patch planar clamp system, to directly monitor changes in plasma membrane permeability of HEK 293A cells exposed to the detergents sodium dodecyl sulfate (SDS), cetyl trimethylammonium bromide (CTAB), and fluorescent octadecyl rhodamine B (ORB). We have also examined the interactions with poly(amidoamine) dendrimers and poly(ethyleneimine). The time dependent evolution of detergent-induced plasma membrane permeability was quantified and cell morphology post detergent or polymer exposure was examined using fluorescence microscopy. An example is shown for SDS exposure in Figure 1. All detergents studied increased the plasma membrane conductivity of cells within a second after exposure and detergents below critical micelle concentration (CMC) increased membrane conductivity even when cells were physically intact. SDS solubilized cells for concentrations of 2 mM (2x CMC) whereas CTAB induced substantial membrane permeability but did not solubilize the cell membrane, even at concentrations 1.4 mM or 200x CMC.

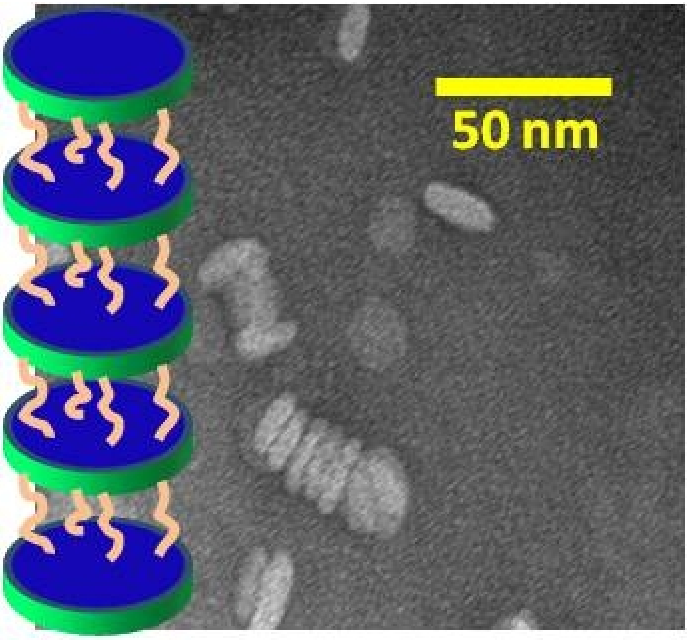


COLL 497

Controlling “stringed” lipid nano-aggregates

Mu-Ping Nieh[1], *mu-ping.nieh@ims.uconn.edu, Ying Liu*[2], *Michael Rottier*[2]*.Â (1) Institute of Materials Science, Chemical and Biomolecular Engineering, University of Connecticut, Storrs, Connecticut 06269, United StatesÂ (2) Chemical and Biomolecular Engineering, University of Connecticut, Storrs, Connecticut 06269, United States*

Uniform-sized lipid nano-aggregates (e.g., nanodiscs and vesicles) are made through either spontaneous formation or mechanical manufacturing. We are able to string them with triblock copolymer based on the principles of hydrophilic-hydrophobic interaction. This allows us to build up supramolecular hierarchical structures. I will present a few examples of the “stringed” lipid-based nanoaggregates and the parameters that control the morphology, aggregation kinetics and aggregation numbers such as charge density, polymer and lipid concentrations.



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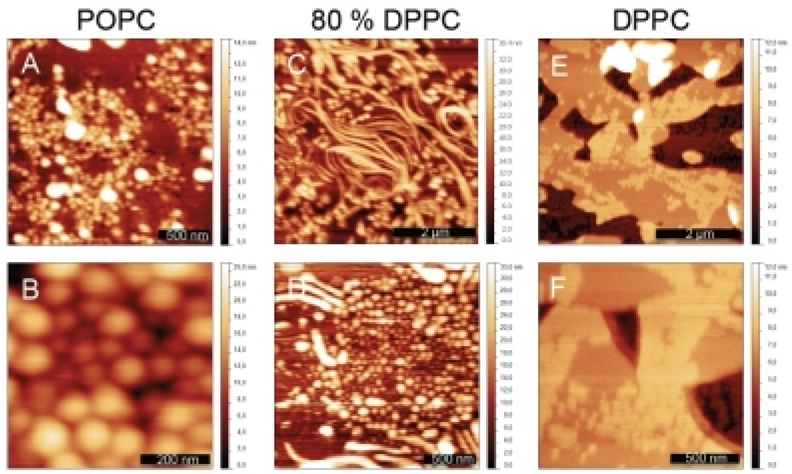
COLL 498

Nanoparticles at model cellular membranes

***Marite Cardenas**, cardenas@nano.ku.dk, Tania Lind, Vivien Jagalski.University of Copenhagen, Copenhagen, Select a State 2100, Denmark*

The worldwide increasing problem with bacteria growing resistant to common antibiotics urgently imposes the requirement for novel approaches that are less susceptible to induce resistance. Although effective, the specific mechanism of action of commercial antibiotics in combination with drug overuse increases the risk of resistance caused by mutations and transfer of resistance genes between bacteria. For the development of non-specific type of antibacterial drugs, appropriate cell mimicking surfaces are necessary to further advance the understanding of what are the drug properties needed to attain high antimicrobial activity and low cytotoxicity.Here we will present different strategies taken in our lab aimed at *constructing model cell mimetic surfac*es under controlled in situ conditions, which allow investigating processes occurring at the cell surface. We have done several model cell membrane systems and explored the effect of lipid composition on the physical properties of the membranes. *We show that lipid composition is determinant on the mechanism of interactions between nanodrugs with the cell membrane are of interest.*



We have chosen a particular interesting type of nanodrugs, peptide based dendrimers, since they present specificity towards certain type of bacteria and low cytotoxicity. These drugs act in a passive manner and thus we explore whether these differences can be explained by the differing lipid compositions in cellular membranes: for instance bacterial cells are known to contain a larger extent of phosphatidylglycerol lipids, which give them a higher surface charge density than red blood cells for instance. We have also developed methodology to perform AFM in liquid under flow, which allows to extract kinetics information on the structural changes induced by out dendrimer. In this lecture I will briefly present the challenges we face and some of the strategies undertaken to answer these issues.

COLL 499

Sulfur binding energy shifts in ZnS and CdS nanowires made from 1-adamantanethiol

Luis C Fernandez-Torres, *lfernandez-torres@stu.edu, Santana Thomas, Lateasha Saunders, Leslie Robinson, Carley Di Stasio.School of Science, Technology, and Engineering Management, Saint Thomas University, Miami Gardens, FL 33054, United States*

A novel synthetic route using adamantanethiol achieved zinc sulfide and cadmium sulfide nanowires with interesting properties at significantly more benign chemical conditions. The process utilizes water and/or ethanol as the main solvents, and 1-adamantanethiol as a novel sulfur source and growth modifier. The key step in the controlled reduction of these nanostructures is the temperature-controlled hydrolysis of the mild base hexamethylenetetramine (HMTA). Nanowires of ZnS and CdS were produced using 1-adamantanethiol. These nanostructures have been characterized with scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). XPS spectra of cadmium sulfide (and zinc sulfide) using adamantanethiol as sulfur source revealed a dramatic binding energy shift of the sulfur 2s peak. This shift is

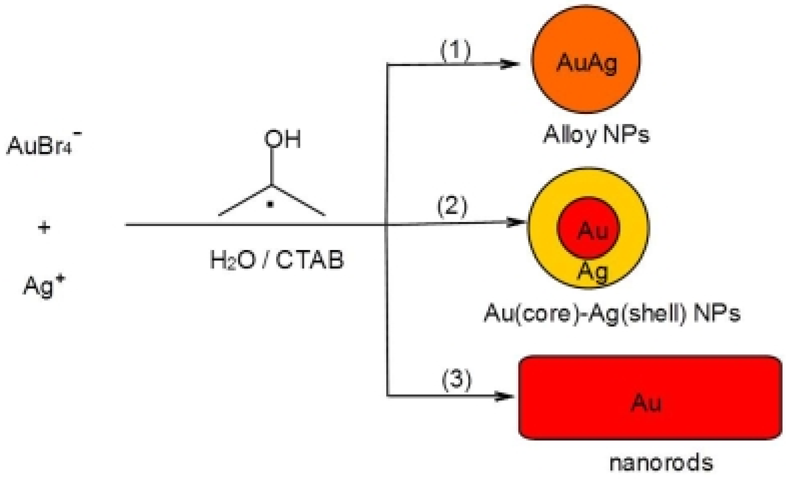
explained in terms of the bonding environment associated with sulfur atoms in the nanowire structure.

COLL 500

Facile synthesis of metal nanoparticles and quantum dots using ketyl radicals

Carlos M. Gonzalez[1]*, cmg178@txstate.edu, Tania Betancourt*[1]*, Willian Brittain*[1]*, Gavin F. Kirton*[1,2]*.Â (1) Department of Chemistry and Biochemistry, Texas State University, San Marcos, Texas 78666, United StatesÂ (2) Department of Chemistry, Rocky Mountain College, Billings, Montana 59102, United States*

Ketyl radicals offer a simple, versatile and environmentally friendly route to the extensive production of both metal nanoparticles (NPs, *e.g.* Au, Ag, AuAg, Cu, Pt, Pd, Co) and quantum dots (QDs, *e.g.* ZnO, CuO, CeO_2, MoO_3, WO_3). Through a single-step process, adjustment of reaction conditions allows the production of a variety of nanoparticle morphology and topology. For instance, aqueous solutions containing Ag(I) and Au(III) ionic species allow the production of either AuAg alloy or Au(core)-Ag(shells) NPs by simply varying the availability of reducing ketyl radicals. In parallel, by adjusting the concentration of surfactants (stabilizing ligands and nanoreactor precursors) specific nanoparticle topologies can be favored (*e.g*. core-shell vs. rod-shaped nanoparticles). For reactive metals, the reduction process in aqueous media produces metal-oxides QDs, *e.g.* ZnO, CeO_2. The synthetic route to nanomaterials under discussion offers substantial advantages over established methodologies, *i.e.* i) mild reaction conditions and short reaction times, ii) low cost, iii) versatility, iv) compatible with both aqueous and organic media. In spite of this, the method has been scarcely investigated. In this contribution, the advantages of this methodology will be discussed and relevant examples (innovative results) will be presented (*e.g.* Au, Ag, Cu, AuAg bimetallic NPs, and ZnO, CeO_2 QDs).



Preparation of AuAg nanoparticles with different architecture and composition

COLL 501

Relative binding affinity of L-type ligands for chloride-terminated CdSe nanocrystals

Nicholas C Anderson[1], *nca2116@columbia.edu, Aya K Buckley*[2], *Jonathan S Owen*[1]*.Â (1) Department of Chemistry, Columbia University, New York, NY 10027, United StatesÂ (2) Department of Chemistry, University of California, Berkeley, Berkeley, California 94720, United States*

Ligand exchange chemistry of metal chalcogenide nanocrystals is essential for functionalizing these materials for a variety of applications, ranging from photovoltaics to biological imaging. Many studies report qualitative changes in photoluminescence as evidence for the exchange of native, L-type ligands (such as tri-*n*-octylphosphine oxide) for functional Lewis bases (pyridine, primary amines, thiols). However very seldom is ligand exchange monitored directly or *in situ*, and often these results are convoluted by side reactions that occur between excess metal ions or organic X-type ligands at the nanocrystal surface. We report a series of L-type ligand exchanges using tri-*n*-butylphosphine-bound, chloride-terminated CdSe nanocrystals with several ligand classes, including aromatic, cyclic, and non-cyclic sulfides, ethers, and amines; primary, secondary, and tertiary amines and phosphines; tertiary phosphine chalcogenides; primary thiols, alcohols, isocyanides, and isothiocyanides; and N-heterocylic carbenes. Using ^{31}P NMR spectroscopy, we establish a relative binding affinity for these ligands which reflects electronic considerations but is dominated primarily by steric interactions.

This information should provide insight for rational ligand design for future applications involving metal chalcogenide nanocrystals.

COLL 502

Comparison of how dithiocarbamate ligands affect the band gap energies of colloidal CdSe nanospheres and nanobelts

***Andrea M Munro**, munroam@plu.edu.Department of Chemistry, Pacific Lutheran University, Tacoma, WA 98447, United States*

Colloidal CdSe nanocrystals are being investigated for use in transistor, light-emitting diodes, and photovoltaic solar cells. Much of the interest arises from their novel optical and electronic properties, such as their size-tunable band gap. They are also promising materials, because they can be processed from solution. The solubility of a colloidal nanocrystal is determined by its surface chemistry. Researchers have found that exchanging the native surface ligands (present from synthesis) with shorter, conjugated molecules can increase the efficiency of nanocrystal-based devices, leading multiple groups to investigate nanocrystal-ligand interactions.

Recently, Weiss et al. reported that exchanging the native ligands with dithiocarbamate molecules causes a red-shift in the absorbance spectra of CdS, CdSe, and PbS nanocrystals. The authors concluded that there is sufficient resonance between the HOMO energy level of the nanocrystal and ligand to allow for delocalization of the "hole" into the ligand shell, causing the band gap energy shift. They speculated that this class of molecules might improve charge transport in nanocrystal-based photovoltaics.

We investigate the effects of dithiocarbamate ligands on the absorbance spectra of colloidal CdSe nanospheres and nanobelts. We confirm that the addition of dithiocarbamate ligands to nanosphere samples causes the absorbance spectra of the nanospheres to red-shift as reported by Weiss et al. However, the addition of dithiocarbamate ligands to CdSe nanobelt samples **does not** correlate with a change in the band gap of the nanobelts. To date, most studies of nanocrystal-ligand interactions have focused on nanospheres, although elongated nanocrystal shapes are becoming more common in nanocrystal-based devices. We examine the different effects of dithiocarbamate ligands on these two colloidal nanocrystal shapes in terms of the HOMO & LUMO energies of each nanocrystal shape and addressing differences in ligand binding affinity to each nanocrystal shape.

COLL 503

Photo-assisted electrochemical corrosion of bulk powders: A novel method to fabricate β-SiC quantum dots

***Munuve Mwania**[1], munuve.mwania@mavs.uta.edu, Csaba Janaky[2], Peter Kroll[1].Â (1) Department of Chemistry and Biochemistry, The University of Texas at Arlington,*

Arlington, Texas 76019-0065, United StatesÂ (2) Department of Physical Chemistry and Materials Science, University of Szeged, Szeged, Hungary

Silicon carbide (SiC) quantum dots (QDs) are eminent candidates for various exciting applications ranging from bioimaging and energy conversion, to optics. In this talk, we describe a new top-down method for producing SiC QDs (< 10 nm) from bulk powders (> 50 nm) and slurries. Photo-assisted electrochemical etching is employed to obtain the quantum-sized clusters. We show that the process (hence, the amount of QDs synthesized as well as their size) can be controlled via regulating time and temperature as confirmed by both high-resolution transmission electron microscopy and photoluminescence studies. The presented method may serve as a new avenue to prepare size-controlled nanoparticles of different semiconductor materials.

COLL 504

Self-assembly of magnetic quantum dot nanocomposites via micellar electrospray

Matthew Souva[1], Gauri Nabar[1], Barbara Wyslouzil[1,2], ***Jessica O Winter**[1,3]*, *winter.63@osu.edu.Â (1) William G. Lowrie Department of Chemical and Biomolecular Engineering, The Ohio State University, Columbus, OH 43210, United StatesÂ (2) Department of Chemistry, The Ohio State University, Columbus, OH 43210, United StatesÂ (3) Department of Biomedical Engineering, The Ohio State University, Columbus, OH 43210, United States*

As researchers are increasingly successful at synthesizing single function nanoparticles, such as gold, quantum dot, and iron oxide materials; focus has shifted to the manufacture of multifunctional nanocomposites comprised of two or more constituent materials. Here, we describe a self-assembly-based approach to incorporate inorganic nanoparticles into nanocomposites using block co-polymers. This approach is based in part on the interfacial instability method in which thermodynamically-driven self-assembly of block co-polymer micelles is used to encapsulate hydrophobic cargos into the micelle core, but is combined with electrospray to yield a novel, semi-continuous manufacturing process for industrial scale production of these materials.

Micellar electrospray was used to synthesize particles comprised of superparamagnetic iron oxide nanoparticles, semiconductor quantum dots, and their combination using two types of amphiphiles to yield particles spanning 10-100 nm in diameter. Particle size was confirmed using dynamic light scattering, transmission electron microscopy, and single particle Brownian motion tracking and particles displayed very narrow size distribution (~5%). By varying process parameters, yield could be increased 30-fold by weight over that achieved using the batch method. Further, a rudimentary phase diagram was assembled indicating viable concentration/temperature combinations for micelle production. The relationship between constituent nanoparticle size, shape, and loading and final micelle morphology will be presented; however, this technique was capable of encapsulating spherical, rod, and tetrapod-shaped nanoparticles and can be

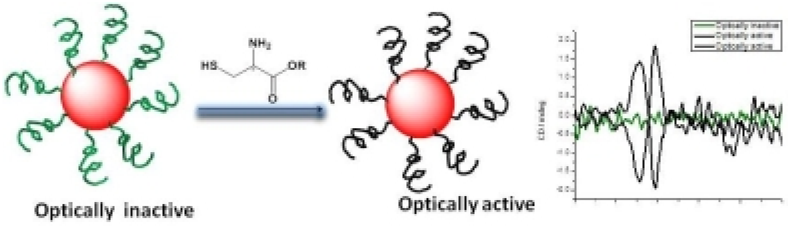
used to yield spherical or worm-like micelles. These particles represent a new class of micelles, in which the loaded cargo can contribute to the final size and shape of the micelle formed because of its large steric properties. Micellar encapsulation thus provides a robust platform to the synthesis of nanocomposites comprised of hydrophobic constituents with the potential for vastly increased throughput.

COLL 505

Inducing chiroptical properties in CdSe quantum dots using chiral organic capping ligands

***URICE N TOHGHA**, utohgha@uwyo.edu, MILAN BALAZ.University of Wyoming, Laramie, WY 82071, United States*

The appealing size-dependent electronic structure of semiconductor quantum dots (QDs) makes them very attractive for LEDs, photovoltaic devices, optical nanomaterials and biological sensors. Chiral optically active QDs have recently emerged as new attractive nanomaterials.[1] We will present an induction of chiroptical properties in colloidal achiral QDs using chiral organic capping ligands. QDs capped with D- and L-cysteines exhibit mirror-image circular dichroism and circularly polarized luminescence spectra.[2] Cysteine-capped QDs display strong size-dependent CD anisotropy comparable with previously reported data on chiral QDs.[3] We have employed ^{13}C magic angle spinning solid state NMR, FTIR and DFT calculation to shed light on a possible origin of induced chiroptical activity.



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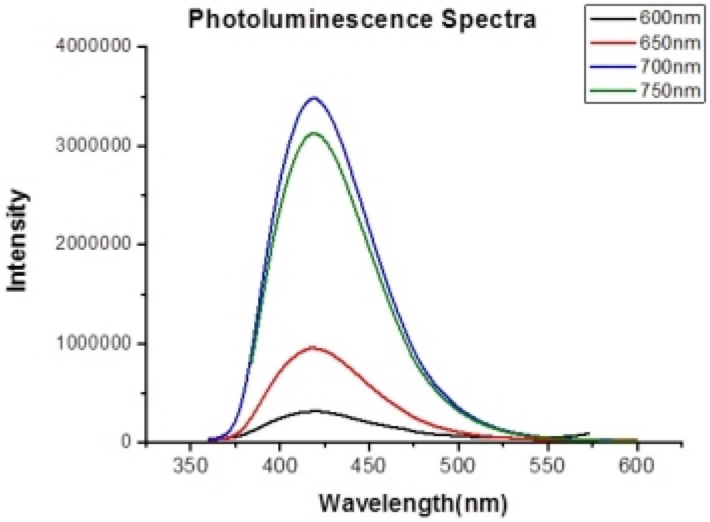
COLL 506

Well-order semiconductive nanodiamond array and its electrochemical property

***Siheng Su**, siheng.su@ttu.edu, Jenny Qiu.Mechanical Engineering, Texas Tech university, LUBBOCK, Texas 79409, United States*

Semiconductive nanodiamond is usually obtained by doping foreign elements (nitrogen, boron, etc.) into diamond cores. The doping method requires high power facilities, such as high energy photon/neutron/electron beams, chemical vapor deposition (CVD). These costly equipment limit the application of nanodiamond. In this study, heat annealing is used as an effective alternative method to synthesized semiconductive nanodiamond. 6nm detonation nanodiamond mixing with non-explosive chemical melamine was heated to 500ºC under nitrogen gas environment for 2hrs in a furnace. Characterization showed that nitrogen was added into the nanodiamond. The resultant products demonstrates the emittance of blue fluorescence under UV-vis excitation. The up conversion phenomenon was further observed under 600-750nm excitation



. This kind of fluorescent nitrogen-detonation nanodiamond (NDND) has lower band gap to make it becomes semiconductive which broadens applications of nanodiamond such as LED device fabrication. Simultaneously, 1-D semiconductive nanodiamond array will provide some orientation effect to make it a more promising material in electrical/electrochemical field. Therefore, the NDND is used as raw material to produce well-order nanodiamond array by a template-based electrophoretic deposition (EPD) method. And the electrochemical property of the array is firstly explored in 1mM potassium ferricyanide ($Fe(CN)_6^{3-}$) in this study.

COLL 507

Modular functional polydentate ADMET ligands for nanocrystal surface modification

***Elham Tavasoli**, elhamt@iastate.edu, Javier Vela.Chemistry, Iowa State University, Ames, Iowa 50010, United States*

We investigate a new approach to quantum dot surface modification by using a multifunctional polydentate capping ligands. We use ADMET to randomly oligomerize two dienes: One containing azide functionality as an active group capable of clicking with acetylene terminated molecule of interest, and one containing carboxylic acid surface coordinating head groups as a binding diene. Varying the azide-to-acid diene ratio allows us to control the relative degree of ligand functionality and nanocrystal surface binding ability. Varying the total dienes-to-Ru catalyst ratio allows us to control the extent of ADMET, which enables us to achieve an accurate control over polydentate ligand size. Our synthesized polymeric ligand is able to wrap around a wide range of nanocrystal compositions. 1D NMR and advanced 2D NMR techniques such as DOSY, as well as IR and size and zeta-potential measurements via Dynamic Light Scattering (DLS) show the type and extent of interaction associated between synthesized polymeric ligand and different types of nanocrystals surface. Extensive DLS studies demonstrate that the resulting acid/azide-containing polydentate ligands can be readily coated onto polyethylene glycol capped thick-shelled CdSe/CdS quantum dots and associate with nanocrystal surface native ligands, possibly through hydrogen bonding. However, multiple pendant azide functional groups can be subjected to click onto the gold nanoparticles bearing acetylene functionality. TEM images and EDS line scans confirm formation of such CdSe/CdS-Gold heteroassemblies in the presence of as synthesized polymer containing pre-selected number of azide and acid functional groups.

COLL 508

Large scale screening of organic molecules for strong QD coupling

***Victor Amin**, vamin@u.northwestern.edu, Emily A Weiss.Department of Chemistry, Northwestern University, Evanston, IL 60208-3113, United States*

Ligands that couple strongly to quantum dot (QD) electronic states can reduce or eliminate barriers to electron transport created by highly insulating native ligands. We have previously reported on one such strong coupling ligand, phenyldithiocarbamate (PTC), which selectively delocalizes the excitonic hole in CdSe, CdS, and PbS by mixing strongly with QD valence band electronic states. Here, we describe a computational pipeline for screening organic molecules for strong coupling with CdSe semiconductor nanocrystals. By conducting large scale screening on commercially available substances, we generate a flexible toolbox of organic molecules that can be used to design effective inorganic-organic hybrid devices.

COLL 509

Thiols as ligands and sulfur sources: Capping ligands that are more than skin deep

*Michael Turo, **Janet E Macdonald**, janet.macdonald@vanderbilt.edu.Department of Chemistry, Vanderbilt University, Nashville, TN 37235, United States*

There have been many recent reports using thiol ligands as a sulfur source for semiconductor nanoparticle synthesis to give high quality products. Thiol regents yield particles of Cu_2S and $CuInS_2$ that are single crystalline and monodisperse; shells of ZnS and CdS on CdSe prepared in this manner have exceptional fluorescence yields and reduced blinking. We show evidence here that in these syntheses the final capping thiols are incorporated into the particle in high coordination number sites which greatly affects the surface chemistry and electronic structure of the particles.

Strongly “crystal-bound” thiols are resistant to ligand exchange and surface modification, limiting the further application of these particles. To circumvent this challenge, dodecyl-3-mercaptopropanoate, a molecule possessing both a thiol and an ester, was used as the sulfur source for the synthesis of Cu_2S, $CuInS_2$, and a ZnS shell around CdSe. A post-synthesis base hydrolysis cleaves the ester, leaving a carboxylate and rendering the particles water-soluble. In the CdSe@ZnS system, when compared to surface-bound thiols, crystal-bound thiols demonstrated increased electronic coupling to the nanoparticle core, allowing for increased efficiencies of photoinduced charge transfer to solution species.

COLL 510

Water, proteins, and assembly at hydrophobic interfaces: A new molecular perspective

***Shekhar Garde**, gardes@rpi.edu.Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, United States*

Organization of water molecules near solutes, proteins, and interfaces leads to water-mediated interactions between them, which play an important role in many self-assembly processes in aqueous solution. What are the key features of water structure, and how to characterize them has, however, been a matter of controversy. Using molecular simulations and theory, we have developed a new perspective that identifies water density fluctuations as a key signature of nanoscale hydrophobicity of proteins and complex interfaces. This new perspective shows how hydration-dehydration phenomena may have been integrated into function of certain proteins. The distinct behavior of water density fluctuations at interfaces also affects water-mediated interactions and assembly in interfacial environments. Our results suggest that soft aqueous interfaces may serve as an excellent platform for assembly of biomolecules into quasi-two-dimensional structures.

COLL 511

Water in hydrophobic confinement

Amish Patel, *pamish@seas.upenn.edu.Department of Chemical & Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA 19104, United States*

Water near hydrophobic surfaces sits at the edge of a dewetting transition and is sensitive to perturbations. Such a perturbation is most readily provided by the presence of another hydrophobic surface nearby. In this presentation, I will discuss the thermodynamics and kinetics of wetting-dewetting transitions that result when water exists in such a hydrophobically confined region. Implications on biomolecular assembly as well as the design of superhydrophobic surfaces will also be discussed.

COLL 512

Wetting of hydrophobic and nanostructured surfaces

Alenka Luzar, *aluzar@vcu.edu.Department of Chemistry, Virginia Commonwealth University, Richmond, VA 23284-2006, United States*

The talk will highlight some of our recent progress on nanowetting of surfaces with topological and chemical heterogeneities using molecular modeling. Examples will include electrowetting and pressure induced transitions on superhydrophobic surfaces to achieve reversible switching between contrasting Cassie and Wenzel states; metastable nanodroplets on nanopatterned surfaces; design of new hydrophobic materials.

COLL 513

Hydrogen bond imbalances and charge transfer effects at aqueous interfaces

Steve W Rick, *srick@uno.edu.Department of Chemistry, University of New Orleans, New Orleans, LA 70148, United States*

A hydrophobic or vapor interface can induce hydrogen bond imbalances, creating alternating layers of water molecules with either fewer hydrogen bonds donated or accepted. This imbalance creates a shifting of electron density among the water molecules near the interface, resulting in charged layers. Solute molecules of various types (ionic, hydrophilic and hydrophobic) in the bulk region can change the hydrogen bond structure at the interface in different ways. Results from molecular simulations with newly developed models that include charge transfer effects will be presented for these interfacial systems. The implications of the charged water molecules at the interface to properties such as the surface tension, surface potential and zeta potential will be discussed.

COLL 514

Superhydrophobic micro- and nanofluidics

Olga I. Vinogradova, *oivinograd@yahoo.com.Laboratory of Physical Chemistry of Modified Surfaces, A.N.Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russian FederationDWI – Leibniz Institute for Interactive Materials, RWTH Aachen, Aachen, GermanyDepartment of Physics, M.V.Lomonosov Moscow State University, Moscow, Russian Federation*

Research on superhydrophobic materials has mostly focused on their extreme non-wettability, and implications of superhydrophobicity for transport phenomena, remain largely unexplored. Here I discuss how superhydrophobic surfaces induce novel hydrodynamic properties, such as giant effective slip, superfluidity, mixing, and low hydrodynamic drag, and how these impact electro-kinetic phenomena.

COLL 515

Effect of proximal charge groups on hydrophobic interaction

Kai Huang[1], *huangk05@gmail.com, Derek Ma*[2], *Nicholas Abbott*[2], *Izabela Szlufarska*[1,3]*.Â (1) Materials Science Program, University of Wisconsin-Madison, Madison, WI 53706, United StatesÂ (2) Department of Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, WI 53706, United StatesÂ (3) Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, WI 53706, United States*

Hydrophobic interactions play an important role in protein folding and nanoscale self-assembly. We performed molecular dynamics (MD) simulations to investigate how hydrophobic interactions depend on the presence of proximal charge groups. Specifically, we simulate interactions between a model amphiphilic molecule functionalized with charged groups and a neutral hydrophobic surface. We consider both anions and cations and we test the hypothesis that charged ions may be used to control hydrophobic interaction in this case. The major difference from earlier studies is that the charged ions are not able to diffuse in the liquid because here they are tethered to the backbone of the molecule. Calculations of free energies show that indeed proximal charge groups can modulate the depth of the energy well that corresponds to the strength of hydrophobic interaction, even when these groups are 1 nm away from the hydrophobic interface. Our analysis excludes the possibilities that the observed phenomenon is due either to the interaction of proximal charges with ions segregated to the hydrophobic surface or due to the rotation of the molecule. Our results imply that specific ion effect is not limited to the first hydration shell and that chaotropes can modulate the hydrophobic interaction without segregation to hydrophobic sites. We performed simulations for a range of proximal charges and found our conclusions to be general.

COLL 516

Effects of chain architecture on the co-assembly of polymers and surfactants in bulk and at interfaces

Soumi Banerjee[1]*, soumi.banerjee@wur.nl, Colette Cazeneuve*[2]*, Nawel Baghdadli*[2]*, Stephanie Ringeissen*[2]*, Frans A. M. Leermakers*[1]*, Gustavo S Luengo*[2]*.Â (1) Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Wageningen, Gelderland 6701 DK, The NetherlandsÂ (2) Recherche and Innovation, L'OrÃ©al, 1 avenue Eugene Scueller, Aulnay sous Bois 93600, France*

Cosmetic formulations for hair are mixtures of cationic polyelectrolytes and anionic surfactants. Adsorption of either the pure polyelectrolyte or the polyelectrolyte-surfactant associative mixture on the hydrophobic keratin surface restores or improves the tribological properties of hair. Modelling of such multicomponent mixtures is a challenging topic. This talk will focus on the effects of the chain architecture of polymers and surfactants on the co-operative adsorption of these component on both hydrophilic and hydrophobic surfaces using self-consistent field theory of Scheutjens and Fleer. We discuss adsorption scenarios originating either from pure electrostatics or other interactions between the segments of surfactants and/or polymers with the surfaces. We show that by tuning the position of hydrophobic and hydrophilic fragments on the monomer level, e.g. by inclusion of short hydrophilic side chains attached to the hydrophobic backbone of the polymer or insertion of short polyoxyethylene sequences the adhesive and tribological properties can be tailored.

COLL 517

Molecular structure and fluctuations at the intrinsic hydrophobic interface

Adam P. Willard*, awillard@mit.edu.Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States*

For liquid water in the vicinity of a hydrophobic interface details of the molecular structure differ from that of the bulk. The orientational and energetic changes associated with adapting the hydrogen bonding network to the locally anisotropic environment are nearly completely contained within a single molecular diameter of the instantaneous liquid phase boundary. Using molecular simulation we can identify these changes, characterize their fluctuations and evaluate their dependence on surface chemistry.

COLL 518

Selective adsorption of ions to aqueous interfaces and its effects on evaporation rates

Richard Saykally*, saykally@berkeley.edu.DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, Berkeley, CA 94720, United StatesCHEMICAL SCIENCES DIVISION, LAWRENCE BERKELEY NATIONAL LABORATORY, BERKELEY, CA 94720, United States*

By exploiting the strong charge-transfer-to-solvent (CTTS) resonances of selected anions in aqueous electrolytes, their interfacial adsorption properties are measured by UV-SHG spectroscopy. Temperature and concentration dependences are determined, with the goal of establishing a complete molecular description of selective ion adsorption. A study of thiocyanate reveals that its strong adsorption is driven by hydration forces and impeded by a novel entropy effect. A study of nitrite indicates adsorption as an ion pair with sodium. Evaporation rates are measured by combining liquid microjet technology and Raman thermometry. The relationship between surface propensities of ions and evaporation rates is investigated. A detailed molecular mechanism for both selective ion adsorption and aqueous evaporation is explored.

COLL 519

Surface nonlinear vibrational spectroscopy for complex molecular interface

***Hong-fei Wang**, hongfei.wang@pnnl.gov.Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington 99352, United States*

Molecular interface is intrinsically heterogeneous. Structure and interaction at interfaces are dynamic and complex. Interface selective sum-frequency generation vibrational spectroscopy (SFG-VS) has been a unique and powerful tool to study the structure and interaction at molecular interfaces. However, its application to complex interfaces has been limited by the lack of resolution and understanding of spectral or dynamical details. Here I would like to discuss recent experimental and theoretical progresses on sub-wavenumber resolution SFG-VS that can probe nearly intrinsic spectral line shape and details in coherent dynamics. Such developments provide new opportunities for applications of SFG in elucidating detailed structural inhomogeneity and dynamic interactions of complex molecular interfaces, including colloidal, environmental, material, and biological interfaces.

COLL 520

Ions, lipids, and water at the air-aqueous interface, probing organization and electric fields with sum frequency and Brewster angle imaging

***Heather Allen**, allen.697@osu.edu.Chemistry, Ohio State, United States*

Motivated by atmospheric aerosol chemistry of marine and urban regions, and biophysical applications related to lung lining and biomembranes, monovalent and divalent cations and anions were investigated using phase resolved sum frequency generation (SFG) spectroscopy to understand the surface propensity and availability for reaction at water surfaces. Ion valency, polarizability, size, shape, and identity of the counterion are critical factors in considering ion organization and subsequent changes in interfacial electric field at the air water interface. Phospholipids and fatty acids were also studied using both SFG and Brewster angle microscopy (BAM). Head group

differences, especially with regard to hydrogen bonding capability and extent, are discerning factors for surface organization and shape distinction at the water surface.

COLL 521

Theoretical study of the photo-induced excited state electron transfer at the water/N,N-dimethylaniline interface

***Ilan Benjamin**, ilan@ucsc.edu.Chemistry and Biochemistry, University of California, Santa Cruz, Santa Cruz, CA 95064, United States*

The photoinduced electron transfer (ET) reaction between coumarin 314 (C314) and *N,N*-dimethylaniline (DMA) at the water/DMA interface is investigated by molecular dynamics simulations. The solvent free energy curves for the ET reaction between excited C314 and DMA molecules are calculated and compared with those calculated for a simple point charge model of the solute. It is found that the reorganization free energy is very small when the full molecular description of the solute is taken into account. An estimate of the ET rate constant is in reasonable agreement with experiment. The rotational dynamics and the solvation dynamics of C314 at the liquid/liquid interface are also calculated and are in reasonable agreement with available experimental data.The calculations suggest that the polarity of the surface “reported” by the solute, as reflected by solvation dynamics and the reorganization free energy, is strongly solute-dependent.

COLL 522

Structure and dynamics at chemically functionalized surfaces

***Alexander V. Benderskii**, alex.benderskii@usc.edu.Department of Chemistry, University of Southern California, Los Angeles, CA 90089, United States*

This talk will review applications of the surface-selective vibrational sum frequency generation (SFG) spectroscopy to study molecular structure, orientation, conformation, and rotational dynamics at chemically functionalized surfaces. Examples will include alkane-thiol self-assembled monolayers (SAMs) functionalized with azobenzene moieties that can undergo switching by photoisomerization, and methyl-terminated silicon surfaces. Polarization-selected SFG allows us to measure orientation of the functional groups and follow it in real time, thus reporting on the rotational and photoisomerization dynamics. Steric hindrance of photoisomerization is observed in azobenzene SAMs when azobenzene moieties are close-packed. Hindered propeller-like rotation of the methyl groups at room temperature is observed on methyl-terminated silicon (111) surfaces.

COLL 523

Inspirational nanocrystals

***Catherine J. Murphy**, murphycj@illinois.edu.Department of Chemistry, University of illinois at Urbana-Champaign, Urbana, IL 61801, United States*

From the days of his postdoc with Louis Brus, Paul Alivisatos has been on the cutting edge of nanocrystal research. In this talk I will discuss how Paul's science has influenced the work of many others, including my own, about the growth, shape, and properties of inorganic nanocrystals.

COLL 524

Apportionment of MOF functionalities at the nanoscale

***Omar M. Yaghi**, yaghi@berkeley.edu.Department of Chemistry, University of California, Berkeley, Berkeley, California 94720, United StatesMaterials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States*

We determined the heterogeneous spatial apportionment of functional groups in a series of metal-organic frameworks containing BDC (1,4-benzenedicarboxylate) linkers with different functional groups. Our analysis discern between random, alternating, and various cluster forms of functional group apportionments. This is a first step in designing sequences of functionalities within ordered structures.

COLL 525

Nanomaterials design for energy and water

***Yi Cui**, yicui@stanford.edu.Materials Science and Engineering, Stanford University, Stanford, CA 94305, United States*

The development of nanotechnology in the past two decades has generated great capability of controlling materials at the nanometer scale and has enabled exciting opportunities to design materials with desirable photonic, electronic, ionic and mechanical properties, which are important for energy and environment technologies. In this talk, I will show how we design rationally nanostructured materials to address critical problems for these applications. Examples include: 1) High capacity nanostructured Si anodes and S cathodes. 2) Grid-scale energy storage based on Prussian blue open framework structures and newly invented semi-flow polysulfide batteries. 3) 3D nanoelectrodes for microbial fuel cells and microbial batteries. 4) High efficiency water filter for pathogen disinfection.

COLL 526

Nucleic acid-modified nanostructures as programmable atom equivalents: Forging a new “Table of Elements”

Chad Mirkin[1]*, chadnano@northwestern.edu, Robert J Macfarlane*[1]*, Evelyn Auyeung*[1]*, Monica Olvera de la Cruz*[2]*.Â (1) Department of Chemistry and International Institute for Nanotechnology, Northwestern University, Evanston, IL 60208, United StatesÂ (2) Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, United States*

The crystallographic parameters of atomic and ionic solids are fixed by the size and coordination number of their elemental building blocks, thus restricting the types of structures that can be formed. We have demonstrated that these limitations can be overcome using spherical nucleic acids (SNAs) as “artificial atoms” in nanoparticle superlattice assemblies. These three-dimensional conjugates consist of densely functionalized, highly oriented nucleic acids covalently attached to the surface of inorganic nanoparticles. The strength and length of the programmable DNA “bonds” between these structures can be adjusted by varying DNA sequence and length, and the properties of the “atoms” can be adjusted by varying nanoparticle size, shape, and composition. We have developed design rules for this assembly process, analogous to Pauling's Rules for ionic solids but ultimately more powerful. These rules can be used as a guide for the rational construction of functional nanoparticle-based materials for plasmonic, photonic, and catalytic applications

COLL 527

Shape-controlled synthesis and stability of metallic nanoparticles and their enhanced properties

Mostafa El-Sayed*, mostafa.elsayed@chemistry.gatech.edu.Department of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332, United States*

I will talk about two topics. In one, I shall discuss an aspect of the synthesis on the nanoscale that has confirmed theoretical prediction of the process of crystallization from solution that was discussed long ago. In the second topic, I will present some applications of plasmonic nanoparticles in molecular cell biology and medicine

COLL 528

Deciphering the biological entity of quantum dots in cells by ex-situ physical methods: Did you consider asymmetrical flow field-flow fractionation?

Francoise M Winnik[1,2]*, francoise.winnik@umontreal.ca, Alexandre Moquin*[1]*, Kevin D Neibert*[3]*, Dusica Maysinger*[3]*.Â (1) Faculty of Pharmacy and Dept of chemistry, universite de Montreal, Montreal, QC H3C3J7, CanadaÂ (2) National institute for materials science, WPI international center for materials nano architectonics, Tsukuba, Ibaraki 305-0044, JapanÂ (3) Department of pharmacology and therapeutics, McGill University, MOntreal, QC H3G1Y6, Canada*

The *in-vitro* or *in-vivo* fate of nanoparticles is determined primarily by their size and surface chemistry in the biological environment, two properties that remain difficult to determine experimentally. In this work, we determined the size of PEGylated quantum dots (QDs) and QDs bearing short ligands dispersed in biological media of increasing complexity, using asymmetrical flow field-flow fractionation (AF4) with UV-Visible absorbance, dynamic light scattering and static light scattering detection. AF4 analyses, carried out over a 1-hr incubation of QDs in biological media, gave a precise description of the time-dependent status of QD aggregation, as a function of the medium and of their initial structure in water. In parallel, we determined the preferred mode(s) of entry of the same QDs in N9 microglia cells using confocal fluorescence imaging of live cells pre-treated with pharmacological inhibitors that block specific modes of cellular entry. We observed an excellent correlation between the aggregation status of QDs in cellular media derived from AF4 analyses and their preferred mode of cellular uptake. Furthermore, we report, for the first time, that QDs are transported within the N9 microglial protrusions from their tip towards the soma. Since N9 microglia are the main cells in the central nervous system that respond strongly to nanoparticles, this study provides important new insights into the mode of entry of particles

COLL 529

Colloidal assembly of surfactant/oligomer complexes: Self-assembly, photophysics, and antimicrobial activity

***David G Whitten**, whitten@unm.edu, Eric H Hill, Harry C Pappas, Dominic Sanchez, Deborah G Evans.Department of Chemical and Nuclear Engineering and Center for Biomedical Engineering, University of New Mexico, Albuquerque, New Mexico 87131, United States*

This talk will focus on the interactions of charged oligomers of the two structural types shown below with oppositely charged surfactants below and above the critical micelle concentration. The presentation will cover both experimental studies and molecular dynamics simulations.

In our studies we have found that remarkably different behavior occurs when surfactant is added to an oppositely charged oligomer of the two different series. Oligomers having the charged groups only at the opposite ends of the molecule first undergo a blue shift of the absorption (compared to monomeric oligomer in solution) with a tail to the red. A concurrent decrease and broadening of the fluorescence occurs as surfactant is added at ratios of surfactant to oligomer in the range 1:2 to 1:30. As additional surfactant is added up to and beyond the critical micelle concentration the absorption and fluorescence shift back to very similar spectra such as are observed in aqueous and organic solutions. In contrast, the OPE oligomers with charged groups on the middle ring undergo a red-shift in both absorption and fluorescence and there is usually a general increase in intensity of the latter. Once again, as more surfactant is added to the solution towards and beyond the critical micelle concentration, the absorption and fluorescence spectra shift back to the original spectra.

We attribute these spectral changes to the formation of two different aggregates or dimers in the presence of small amounts of surfactant. For the end-only oligomers, all-atom molecular dynamics simulations of the interactions between the oligomers and surfactants in water suggest a face-to-face or “H” aggregate. We attribute the red-shifted spectrum for the side-armed charged OPE to the formation of a “J” aggregate where the steric effect of the side-arms prohibits an “H” aggregated configuration.

COLL 530

Precisions synthesis of nanocrystals and their use in biomedical applications

Horst Weller, *weller@chemie.uni-hamburg.de.Department of Chemistry, University of Hamburg, Hamburg, GermanyCenter for Applied Nanotechnology Hamburg (CAN), GermanyInterdisciplinary Nanoscience Center Hamburg (INCH), GermanyThe Hamburg Center for Ultrafast Imaging (CUI), Germany*

We report on the precision synthesis of CdSe/CdS/ZnS core-shell-shell nanocrystals using a preparative flow reactor. Experimental design is used to determine the crucial parameters and their influence on particle growth and size distribution.

In the second part of the talk, we will present biological applications of nanocrystals. In particular, we will present a biocompatible encapsulation technique based on amphiphilic poly(isoprene-*block*-ethylene oxide) (PI-*b*-PEO) diblock copolymers. We varied block lengths, structure and functional terminal end groups and investigated the effect on unspecific uptake. Fluorescence quenching experiments with encapsulated quantum dots show that best behavior in respect to unspecific cellular uptake is realized in those systems, in which the polymer shell yielded best protection against quenching molecules from the surrounding medium. Combination of micelle encapsulation with block copolymers and seeded emulsion polymerization finally leads to biolables for which unspecific uptake could be almost completely suppressed even under in-vivo conditions. We present various techniques for bio-conjugation with recognition molecules and show examples for specific cell and tissue targeting. In-vitro and in-vivo fluorescence and MRI data will be discussed.

COLL 531

Touch and go: Engineering surfaces for minimum bacterial contact and maximum bacterial response

Maria Santore, *santore@mail.pse.umass.edu, Bing Fang.Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003, United States*

The ongoing fight against bacterial infections in hospitals and the need for online-devices to detect bacterial threats in public places drives a need for bacterial manipulation by man-made surfaces, which in turn reveals the ignorance in the community concerning the fundamental nature of bacterial-surface contact. For instance, how much surface area is involved when a bacterium adheres to a surface? Additionally, when antimicrobial compounds attack a bacterium in solution, incorporating into the bacterial membrane on all sides, how can the same compound kill when tethered to a surface (even on long tethers)? Years of research have not enabled us to answer all these questions, however, we do know that upon initial contact, bacteria sample a relatively small surface area, often less than 100 nm in diameter. This talk addresses the use of nanoscale surface features to limit contact to small levels and then probes the effect of this small contact on bacterial adhesion and viability, compared to surfaces which offer more extensive interactions.

COLL 532

Multicompartmental carrier particles for directed cell targeting

Joerg Lahann, *lahann@umich.edu.Biointerfaces Institute, University of Michigan, Ann Arbor, MI 48109, United States*

Micro- and nanoparticles with two or more distinct compartments have high potential for drug delivery or diagnostics. A particle that is comprised of two independent compartments offers the potential for the delivery of two different drugs with fully decoupled release kinetics. In addition, the multicompartmental architecture lends itself to the design of distinct surface patches. Carrier particles with distinct surface patches, i.e., distinct regions of binding sites, can interact with biological cells in ways that are distinctly different from the isotropically modified counterparts. Specifically, the design of synthetic vectors and their interactions with biological cells will be used as an example to highlight the potential utility of multicompartmental carriers.

COLL 533

Uptake, translocation, and biological fate of engineered nanomaterials

Gabriela Romero[1], Richard Murray[1], Irina Estrela[2], Yuan Qiu[1], Edwin Donath[2], Elena Rojas[1], ***Sergio E Moya***[1]*, smoya@cicbiomagune.es.Â (1) Biointerfaces, CIC biomaGUNE, San Sebastian, Gipuzkoa 20009, SpainÂ (2) Institute of Biophysics and Medical Physics, University of Leipzig, Leipzig, Saxony, Germany*

The fate of engineered nanomaterials (ENMs) *in vivo*, is fundamental in order to assess their impact on biological functions. ENMs translocate and may finally reach the cell interior. Several issues related to the physical state of the nanomaterial, including aggregation, the interaction with biomolecules, the ENMs dynamics and intracellular dosis will determine their toxicological action.

We will focus on the use of Confocal Raman Microscopy as a label free technique for tracing ENMs intracellularly. Uptake and intracellular fate of metal oxides nanoparticles, carbon nanotubes, and poly(lactide co-glycolide) nanoparticles will be studied by

Raman Confocal Microscopy. In addition Confocal Laser Scanning Microscopy, Flow Cytometry and TEM will be applied for tracing ENMs. The intracellular dynamics of gold nanoparticles, state of aggregation and intracellular size will be studied by Fluorescence Correlation Spectroscopy. We will also present the application of Ion Beam Microscopy to quantify the intracellular dose of metal oxide nanoparticles.

COLL 534

Polyelectrolyte microcapsules for targeted magnetic delivery, cell magnetisation and retrieval of cell interior

Gleb B Sukhorukov[1], *g.sukhorukov@qmul.ac.uk, Qiangying Yi*[1]*, Samantha Gabriel*[1]*, Qingrong Wei*[1]*, Anton M Pavlov*[1]*, David J Gould*[2]*, Bruno G de Geest*[3]*.Â (1) School of Engineering and Materials Science, Queen Mary University of London, London, United KingdomÂ (2) School of Medicine and Dentistry, Queen Mary University of London, United KingdomÂ (3) University of Ghent, Belgium*

Layer-by-layer (LbL) microcapsules are designed for targeted magnetic delivery to cells. Luciferase enzyme and plasmid DNA were deliverfollowed by monitoring enzymatic activity inside cells and transfection. Magnet microcapsules were well tolerated by various cells types up to 100 times excess of capsules exposed per cells. Incorporation of magnetic capsules allows manipulation of cells via magnetic field what has been documented on immortalized neuronal and dendritic cells. Suspended cells are well affected by magnetic field whist surface adhered cells have limited effect depending on cell type.

Light addressable capsules enabling UV-induced sealing enable entrapment of cell interior and can be retrieved from cell via lysis which do not affect capsules and captured proteins from cell interior. Both magnetic and light responsive capsules demonstrate potential of the technology for cell addressing, cell therapy and visualisation as well as exploration of intracellular contents.

COLL 535

Modulation of nanoparticle activity and associated complex biological responses by the nanobiointerface

***Pablo Taboada**, pablo.taboada@usc.es.Condensed Matter Physics, Universidad de Santiago de Compostela, Santiago de Compostela, Spain*

When designing a nanoparticle (NP) system for a specific biomedical application it is necessary to bear in mind that NPs can be coated with a protein biocorona when entering a biological fluid which will determine the mutual cell− NP interactions and, subsequently, the NPs uptake and trafficking, conditioning their biodistribution and therapeutical response in vivo. Here, we will present different examples showing how the modulation of NP characteristics such as size, shape, surface roughness, or surface

functionalization, etc can drastically influence the properties of the protein biocorona, improving NP particle activity by changing the resultant main forces at the nanobiointerface and inducing, at the same time, unexpected biological responses.

COLL 536

Shape-specific stimuli-responsive hydrogel microcapsules: Effect of shape on cellular uptake

*Veronika Kozlovskaya, Jun Chen, **Eugenia Kharlampieva**, ekharlam@uab.edu.Department of Chemistry, University of Alabama at Birmingham, Birmingham, Alabama 35294, United States*

Particle shape is one of the key factors affecting particle cellular uptake and vascular dynamics. This talk will focus on synthesis and responsive properties of a novel type of shape-specific cytocompatible hydrogel microcapsules. The cubical, discoidal, and spherical capsules are obtained as hollow replicas of inorganic templates through chemical cross-linking of hydrogen-bonded layer-by-layer (LbL) films. Two related systems comprising of temperature- and pH-sensitive polymers will be presented with focus on their assembly, shape responses, and shape-controlled interactions with cells. First, we will discuss poly(methacrylic acid) (PMAA)−based hydrogel capsules of cubical geometries and demonstrate their distinctly different shape responses upon pH variations. These capsules can either turn into bulged spherical-like structures of the same size or retain their initial shape while increasing in size when transitioned from pH=3 to pH=8. These findings are quantified through comparing capsule stiffnesses. Second, we will present hydrogel capsules of poly(N-vinylcaprolactam) (PVCL) with reversible thermoresponsive behavior. We will demonstrate that the PVCL capsules retain their cubical shape when temperature was elevated from 25°C to 50°C exhibiting the size decrease. Next, the cytocompatible properties of hydrogel capsules will be demonstrated by testing viability of human cancer cells in the presence of these capsules. Finally, shape-dependent internalization efficiency will be discussed by comparinguptake by shaped andspherical capsules. Our work opens new prospects for developing biocompatible polymeric particles with predictable shape and size-changing properties for controlled drug delivery, cellular uptake, and in stimuli-regulated transport behavior in microfluidic devices.

COLL 537

Molecular dynamics study of electrophoretic alignment of carbon nanotubes and their deposition on substrates

*Mohammad Mostafa, **Soumik Banerjee**, soumik.banerjee@wsu.edu.School of Mechanical and Materials Engineering, Washington State University, Pullman, Washington 99164, United States*

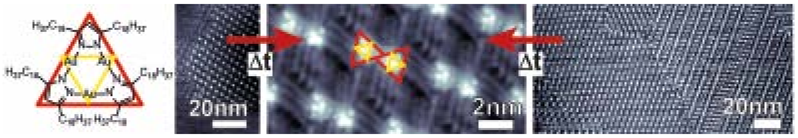
Carbon nanotubes (CNTs) have generated great interest in the scientific community due to their intrinsically high mechanical strength, chemical energy storage capacity, and thermal and electrical conductivity. These interesting properties of CNT make them usable in various applications such as high strength composite materials, transistors and super-capacitors. Since CNTs are anisotropic in nature, it is very important to leverage their orientation dependent properties such as ability to transport ions, electrons and thermal energy much quicker if aligned in a specific way. It is therefore important to identify methods for controlled deposition of aligned nanotubes on substrates for fabrication of nanocomposites. Among the different methods for controlled CNT deposition, electrophoretic deposition is promising due to cheap and simple processing, uniform deposition, and control of deposit thickness. In the present study, we have simulated various functionalized and pristine CNTs solvated in ethanol using molecular dynamics method in an effort to understand their electrophoretic alignment and deposition on substrates. We have varied intensity of the electric field and the position of the –COOH functional groups and studied the effect of these parameters on the rotational alignment dynamics and rate of deposition. We find that with the increase in the magnitude of imposed electric field, the extent of alignment and rate of CNT deposition increases. Our simulations to understand the effect of side and end –COOH functional groups in CNTs, compared to pristine CNTs, demonstrate that pristine CNTs have the fastest dynamics. Between side and end functionalized CNTs, the former show relatively faster rotational dynamics but their translation rates are similar due to similar size and mass. We also find that, in deposited films, both side and end functionalized CNTs are uniformly dispersed whereas pristine CNTs tend to form clusters.

COLL 538

Detailed studies on molecular monolayers of trinuclear metal complexes

Duncan den Boer[1,2]*, d.d.boer@tue.nl, Markrete Krikorian*[1]*, Birgit Esser*[1]*, René A. J. Janssen*[2]*, Timothy M. Swager*[1]*.Â (1) Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United StatesÂ (2) Department of Chemistry, Technical University Eindhoven, Eindhoven, The Netherlands*

Trinuclear metal complexes are very promising for the use in selective chemical sensors. For their implemention in such sensors, it is crucial to have detailed knowledge about the molecular layer. We present time-dependent Scanning Tunneling Microscopy studies on such layers at the solid/liquid interface. These detailed studies on the single-molecule level gave information on several distinct morphologies, layer evolution, cooperative dynamics, conformation of alkyl chains, chirality and subtle effects in the topographical contrasts.



COLL 539

Molecular electrostatics in the directed assembly of fullerenes

***Janice E Reutt-Robey**, rrobey@umd.edu.Department of Chemistry & Biochemistry, University of Maryland, College Park, MD 20742-2111, United States*

Since the 1985 discovery of C_{60}, fullerenes have emerged as key nanoelectronic components and promising biomedical probes. Understanding how to direct – and switch - the packing arrangements of fullerenes and their chemical derivatives at interfaces is important for advanced applications. In this talk we explore structural motifs that can be achieved in monolayer films of C_{60}, C_{70}, and their phenyl-butyric-acid methyl ester derivatives, at neat and chemically-modified Au(111) and Ag(111) substrates. On low-index metals, we observe how molecular ordering in C_{60}-PCBM and C_{70}-PCBM monolayers is frustrated by anisotropic fullerene-fullerene interactions. Transition to crystalline (hcp) fullerene arrangements is highly activated and dependent on local density. Molecular electrostatics provides a useful tool to rationalize observed packing arrangements in PCBM films and the barriers for nanocrystallization. On chemically terminated substrates, we further show how electrostatic interactions between the fullerene layer and an underlying chemical monolayer drive pattern formation. Molecular dynamics simulations reveal that interface (charge-transfer) dipoles can direct fullerene arrangements, yielding fullerene packings with reduced coordination. Finally, we describe how molecular electrostatics drive vertical phase separation in binary PCBM-ZnPc mixtures deposited from solution or vapor phase. This work was supported by the NSF-Division of Chemistry (MSN) under CHE1310380

COLL 540

Coverage-induced enhancement of the self-metalation of 2H-tetraphenylporphyrins on Cu(111)

***Hans-Peter Steinrück**, hans-peter.steinrueck@fau.de, Michael Röckert, Stefanie Ditze, Michael Stark, Jie Xiao, Hubertus Marbach, Ole Lytken.Chemistry and Pharmacy, Universitaet Erlangen-Nuernberg, Erlangen, Bavaria D-91058, Germany*

Using XPS and STM, the coverage-dependent self-metalation of 5,10,15,20-tetraphenylporphyrin (2HTPP) with Cu on Cu(111) at 400 K has been studied. At low coverages the porphyrin molecules are adsorbed as isolated molecules, and the rate of metalation is slow. As the coverage is increased beyond ~0.36 molecules/nm2 a supramolecular checkerboard structure is formed, with every second molecule slightly elevated above the surface. The appearance of this checkerboard structure coincides with a dramatic increase in the rate of metalation. This enhancement is attributed to a smaller activation barrier for the elevated molecules, which have an internal conformation similar to that of the free molecule, whereas the less reactive molecules in direct contact with the surface are strongly distorted.

COLL 541

Molecular self-assembly for single molecule devices and graphene nanoribbons

Andrew TS Wee[1]*, phyweets@nus.edu.sg, Yuli Huang*[1]*, Dacheng Wei*[1]*, Wei Chen*[2]*.Â*
(1) Department of Physics, National University of Singapore, Singapore, SingaporeÂ
(2) Department of Chemistry, National University of Singapore, Singapore, Singapore

We use the self-assembly approach to fabricate 2D molecular nanostructures on surfaces. Complementary experiments including low-temperature scanning tunneling microscopy (STM), synchrotron spectroscopy and density functional theory (DFT) calculations are used to investigate molecular-scale structures, local electronic structures, and for single molecule manipulation.

The formation of a range of tunable 2D binary molecular nanostructures on graphite using a combination of copper hexadecafluorophthalocyanine ($F_{16}CuPc$) in combination with other molecules is presented [Small2010]. Preferential adsorption on such 2D molecular templates via specific intermolecular interactions provides an efficient route to construct ordered organic nanostructures for future nanodevices. We demonstrate the preferential trapping of phthalocyanine molecules atop 2D binary supramolecular networks through intermolecular π-π interactions [JACS2011]. The formation of the second-layer supramolecular nanostructures, individual molecular dots or linear molecular chains, can be controlled by the underlying molecular networks. Reversible single-molecule manipulation is demonstrated by STM tip-induced configurational transformation of the dipole ClAlPc molecule, which makes it a promising candidate for ultrahigh density information storage [Small2012].

Graphene and novel 2D materials have recently captured the attention of researchers worldwide due to its superlative properties and potential applications. For future electronics applications of graphene, a key challenge is to make it semiconducting. One approach to opening a band gap in graphene is to reduce the dimensionality of graphene from 2D to 1D graphene nanoribbons. We present the surface-assisted bottom-up fabrication of atomically precise armchair graphene nanoribbons (AGNRs) with predefined widths, namely 7-, 14- and 21-AGNRs, on Ag(111) as well as their spatially resolved width-dependent electronic structures [SciRep2012]. The local density of states (LDOS) observed by scanning tunneling spectroscopy (STS) reveal the atomic scale electronic structure and the influence of the substrate.

COLL 542

2D molecular networks: From templating metal nanoparticle to growing organic graphenes

***Dmitrii F Perepichka**, dmitrii.perepichka@mcgill.ca.Department of Chemistry, McGill University, Montreal, Qc H3A 0B8, Canada*

Molecular self-assembly at surfaces gives a versatile framework to organize/pattern functional materials in technologically relevant environment (thin films) and with unprecedented sub-nm precision. Numerous 2D architectures with a remarkable molecular-level control have already been demonstrated. The next big step for the field will be bridging the gap between this “2D crystal engineering” and actual applications in materials science and engineering.

I will present our first humble moves in this direction in two examples. First, I will demonstrate the application of 2D molecular networks to template the epitaxial growth of metal nanoparticles at solid-liquid interface. I will show how in-registry interactions between the matching length alkyl chains can guide the growth of nanoparticle superlattices with non-centrosymmetric unit cell. Second, I will update on our continuing project in creating 2D conjugated polymers with “onmiconjugated” building blocks. I will highlight the challenges posed by the (unintuitive) chemistry of metal surfaces and discuss the electronic properties of the obtained 2D polymers.

COLL 543

Workfunction tuning of graphene with organic molecules

*Christos Christodoulou[1], **Angelos Giannakopoulos**[2], angelos@giannakopoulos.biz, Marco Vittorio Nardi[1], Giovanni Ligorio[1], Martin Oehzelt[1,3], Liping Chen[2], Georg Heimel[1], Ruslan Ovsyannikov[3], Luca Pasquali[4,7,8], Melanie Timpel[1], Oliver Monti[6], Angelo Giglia[7], Stefano Nannorone[4,7], Khaled Parvez[5], Mathieu Linares[9], Patrick Norman[9], Klaus Muellen[5], David Beljonne[2], Norbert Koch[1,3].Â (1) Department of Physics, Humboldt University of Berlin, Berlin, GermanyÂ (2) Laboratory for Chemistry of Novel Materials, University of Mons, Mons, BelgiumÂ (3) Helmholtz Zentrum Berlin fur Materialien und Energie GmbH, Berlin, GermanyÂ (4) Department of Engineering [quot]E. Ferrari[quot], University of Modena e Reggio Emilia, Modena, ItalyÂ (5) Max Planck Institute fur Polymerforschung, Mainz, GermanyÂ (6) Department of Chemistry and Biochemistry, University of Arizona, Tuscon, Arizona 85721, United StatesÂ (7) IOM-CNR, Basovizza, Trieste 34149, ItalyÂ (8) Department of Physics, University of Johannesburg, Auckland Park, South AfricaÂ (9) Department of Physics, Chemistry and Biology, University of Linkoping, Linkoping, Sweden*

Graphene has conquered the field of Cutting Edge Technology as the ultimate next generation material. However, in order to be used widely in applications, one should be able to tune its electronic properties (i.e. *work function*). This may be achieved by deposition of electron acceptor or donor molecules on the surface of Graphene. In this work, we investigate the interaction between Graphene and an organic molecule,

hexaazatriphenyl hexacarbonitrile (HATCN). HATCN is a strongly electron deficient molecule widely used in organic LEDs for hole injection [1,2]. By means of first principle computational techniques, we study the evolution in the work function of Graphene due to the adsorption of HATCN, as a function of the relative orientation and density of the doping molecules. Our modeling work points to a change from a lying-down to a standing-up configuration as the coverage increases, which is also observed in HATCN layer growth experiment over gold(111) and silver(111) surfaces [3,4]. The preferential standing-up configuration is confirmed by simulated Near Edge X-ray Absorption Fine Structure Spectra (NEXAFS) in excellent agreement with experimental data.

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COLL 544

Interfacial assembly of pristine graphene at water heptane interface

*Steven J. Woltornist[1], Andrew J. Oyer[1], Andrey V. Dobrynin[4], **Douglas H. Adamson**[1], Adamson@UConn.edu.Â (1) Department of Chemistry and Institute of Materials Science Polymer Program, University of Connecticut, Storrs, CT 06269-3136, United StatesÂ (2) Institute of Materials Science Polymer Program, University of Connecticut, Storrs, CT 06269-3136, United StatesÂ (3) Department of Physics, University of Connecticut, Storrs, CT 06269-3136, United StatesÂ (4) Department of Physics and Institute of Materials Science Polymer Programry and Institute of Materials Science Polymer Program, University of Connecticut, Storrs, CT 06269-3136, United States*

Recently we demonstrated the exfoliation and formation of transparent conductive films of pristine graphene by a solvent interface trapping technique. Placing graphite in a phase separated mixture of water and heptane results in the graphite being bound at the interface of the two solvents, despite the fact that graphite has a density roughly twice that of water. Graphite acts as a two dimensional surfactant, lowering the interfacial tension between the two solvents and effectively pinning itself at the solvent interface. Additionally, we have shown that pristine, never-been-oxidized graphene can form stable emulsions, again acting as a two dimensional surfactant.

COLL 545

Monodisperse gold nanoparticles supported by rice husk silica for heterogeneous catalysis applications

*Yan Li, Haoran Chen, Jingjing Liu, **Luyi Sun**, luyi.sun@uconn.edu.Department of Chemical & Biomolecular Engineering and Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269, United States*

Gold nanoparticles (Au NPs) based catalysts have received more and more attentions in the past two decades because of their unique catalytic properties in many important industrial processes. Both the experimental findings and theoretical predictions have demonstrated that the size of Au NPs plays a critical role in governing the catalytic activity and smaller Au NPs typically exhibit higher catalytic activity. Herein, we report a facile method to synthesize Au NPs based heterogeneous catalyst using silica from rice husks (RHs) as a support. Although silica supported Au NPs have been extensively studied, the silica supports are typically synthesized from tetraethyl orthosilicate (TEOS) via a sol-gel process. Notably, in this study, silica from RHs was first used as the catalyst support. The silica nanoparticles obtained by calcining HCl treated RHs, which possess a rough surface, was first modified by (3-aminopropyl)triethoxysilane (APTES), which was designed to play a dual role: one was to absorb Au precursor ($AuCl_4^-$) to silica surface and the other was to stabilize the resultant Au NPs obtained by reducing $AuCl_4^-$ using sodium borohydride ($NaBH_4$). Characterizations of the nanostructures revealed that the Au NPs were formed with narrow size distribution around 2-5 nm, which was very critical for essential catalytic activities. The RH silica supported Au NPs exhibited excellent catalytic activity for the reduction of 4-nitrophenol by $NaBH_4$.

COLL 546

Preparation and characterization of Ni@SiO_2 yolk-shell nanocatalyst and its catalytic performance in carbon dioxide reforming of methane to syngas

***Weiwei Yang**, hedeh@mail.tsinghua.edu.cn, Dehua He.Department of Chemistry, Tsinghua University, Haidian District, Beijing 100084, China*

Ni@SiO_2 yolk-shell nanomaterial is a kind of nanoreactor framework, and has been employed in the research on steam reforming of methane to syngas. Ni@SiO_2 yolk-shell comprises Ni cores inside hollow silica shells, which may play an important role in some reactions carried out at high temperatures. Carbon dioxide reforming of methane (CRM) to syngas is an attractive reaction for the utilization of CO_2 and CH_4, and Ni-based catalysts have been considered to be potential catalysts for the industrial utilization for CRM. However, Ni-based catalysts would deactivate rapidly due to sintering and carbon deposition. Therefore, the key issue for CRM is to develop novel Ni-based catalysts with high activity and stability. Ni@SiO_2 yolk-shell with the special structure makes it possible to have a good performance in CRM reaction. The present work aims to research on the preparation of Ni@SiO_2 yolk-shell nanocatalyst and its application in CRM reaction.

The synthesis of Ni@SiO_2 yolk-shell nanocatalyst includes three steps: Ni nanoparticles were prepared first through a polyol process, then they were coated with silica to form Ni@SiO_2 core-shell structure in the presence of porogens. Finally, the Ni cores of core-

shell structure were etched by hydrochloric acid to get Ni@SiO_2 yolk-shell structure. From the TEM images, silica hollow shell and Ni@SiO_2 yolk-shell structure could be seen.

The Ni@SiO_2 nanocatalyst was employed in CRM reaction at different conditions to evaluate the activity and stability. The results showed that the catalyst could be stable for more than 500h at 700 ^{o}C~800 ^{o}C and GHSV varied from 1.16×10^4 to 4.62×10^4 mL/g·h. The conversion of CH_4 reached 78.0%, while the conversion of CO_2 was 86.2% at 800 ^{o}C. The characterization results showed that the used catalysts still kept the structure almost the same as the catalysts before used.

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COLL 547

Uranium (VI) removal by stabilized zero-valent iron in simulated groundwater: Effects of stabilizers and water chemistry

***Xiao Zhao**, xzz0013@tigermail.auburn.edu, Wenbo Xie, Dongye Zhao.Civil Engineering, Auburn University, Auburn, AL 36849, United States*

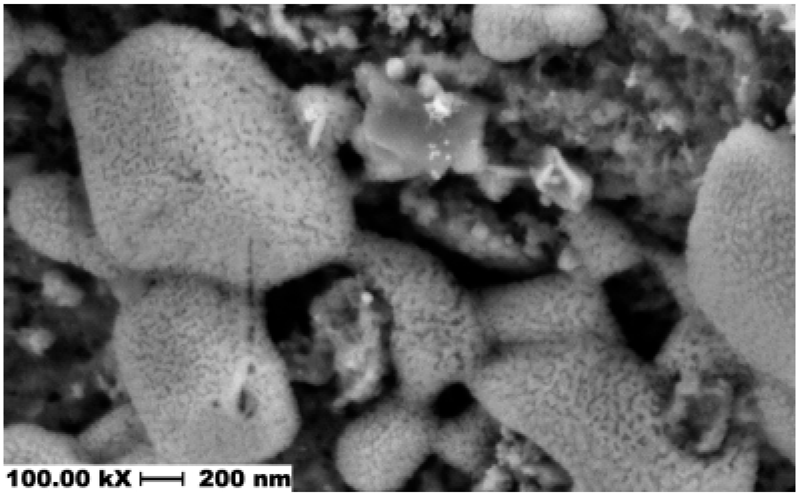
Uranium is one of the most commonly detected radionuclides in the environment. Of the two most predominant oxidation states, U(VI) is much more soluble, mobile and toxic than (IV). Consequently, converting U(VI) to its insoluble form U(IV) can facilitate removal of U from water and greatly lower its mobility and biological/human exposure. We prepared a class of highly reactive zero-valent iron (ZVI) nanoparticles using starch or carboxymethyl cellulose (CMC) as a stabilizer, and tested the effectiveness of the nanoparticles for reductive removal/immobilization of U(VI) from simulated groundwater. This work focused on effects of the stabilizers and water chemistry (pH, bicarbonate, and DOM) on the reductive removal effectiveness and possible re-oxidation of U(IV) under various conditions. At a groundwater pH of 7.0, 35 mg/L of the nanoparticles were able to precipitate 99.0% of 25 mg/L of U(VI) within 12 hours. The bicarbonate extraction tests indicated that 84% of precipitated U was in the form of U(IV) and 16% as U(VI) that was adsorbed and co-precipitated. Both starch and CMC-stabilized ZVI offered comparable removal effectiveness with that of non-stabilized ZVI particles (>96% removal in the pH range of 5.6-8.0). However, the stabilization technique facilitates soil deliverability and in situ remediation of U in soil. More effective removal was observed at lower pH. The presence of 1 and 2.5 mM of $NaHCO_3$ decreased the removal efficiency from 99% to 91% and 68% respectively. And the presence of 10 mg/L of humic acid lowered the removal from 99% to 94%. When kept under anoxic conditions, no re-dissolution of U was detected. However, when subjected to atmospheric oxidation conditions, 54% of the removed U was re-dissolved in the solution after 6 months. The results indicated that stabilized ZVI nanoparticles are highly effective for reductive immobilization of U(VI) in contaminated soil under natural groundwater conditions.

COLL 548

Arsenic (V) removal from water by iron oxide/activated carbon system manufactured by microwave heating

Alp Yurum[1], *ayurum@sabanciuniv.edu, Züleyha Özlem Kocabaş-Ataklı*[2], *Meltem Sezen*[1], *Raphael Semiat*[3], *Yuda Yurum*[2]*.Â (1) Sabancı University Nanotechnology Research and Application Center, Sabanci University, Istanbul, TurkeyÂ (2) Faculty of Engineering and Natural Sciences, Sabanci University, Istanbul, TurkeyÂ (3) Department of Chemical Engineering, Technion, Haifa, Israel*

Iron oxide nanoparticles were deposited on activated carbon (AC) with the microwave hydrothermal (MH) treatment technique. The effect of heating duration and AC's oxidation on structural properties were studied. X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), focused ion beam (FIB) microscopy, Brunauer, Emmett and Teller (BET), and porous texture analyses were utilized to characterize iron oxide/AC system. XRD characterization revealed dependence of crystal structure to heating duration. BET and porous texture analyses showed pore volume increase in iron oxide particles. With the MH technique, porous iron oxide was obtained with a high loading value of 20.27% in just 9 minutes.



Additionally, As(V) adsorption capacity of synthesized materials was studied. As(V) adsorption onto iron oxide deposited supports obeyed Langmuir and pseudo-second order models. Batch adsorption experiments revealed a high efficiency of As(V) removal with the MH synthesized materials. The maximum adsorption capacity was 27.78 mg/g, and for a loading of 0.75 g/L, 99.90% uptake was reached within just 5 minutes due to the porous nature of iron oxide. In addition, more than 99.00% of uptake was obtained within the pH range of 6-8. The results suggest that MH synthesized iron oxide particles with their porous nature and fast adsorption characteristics are promising materials for water treatment.

COLL 549

Enhanced defluoridation using hybrid polymeric cation exchangers in Al^{3+} form containing hydrated Al(III) oxide nanoparticles

Surapol Padungthon[1,2]*, surapolp@kku.ac.th, Arup SenGupta*[3]*.Â (1) Environmental Engineering, Khon Kaen University, Khon Kaen, Khon Kaen 40002, ThailandÂ (2) Center of Excellence on Hazardous Substance Management (HSM), Khon Kaen University, Khon Kaen 40003, ThailandÂ (3) Civil and Environmental Engineering, Lehigh University, Bethlehem, Pennsylvania 18015, United States*

Fluoride contamination in groundwater prevents several hundred million people worldwide from accessing clean water.Among defluoridation technologies, a fixed-bed sorption process is considered to be the most suitable method in rural and remote locations. However, the currently used fluoride selective sorbents, such as hydroxyapatite (i.e., bone char), activated alumina, and other metal oxide based-sorbents exhibit very low sorption capacity, especially at near neutral to mildly alkaline pH (6.5-8.5) of typical fluoride-contaminated groundwater. The present study provides a novel reusable hybrid nanosorbent capable of simple regeneration that can treat fluoride-contaminated groundwater across the relevant pH range. The system is essentially a packed-bed of macroporous strong acid cation exchange resin (e.g., Purolite C145) preloaded in Al^{3+} form. Once the cation exchange takes place (i.e., a hardness cation such as Ca^{2+} or Mg^{2+}, usually present in groundwater, displaces the Al^{3+} ions from the cation exchanger), the aluminium ions undergo hydrolysis reaction and form hydrated aluminium (hydr)oxide particles that precipitate onto the gel and/or within the pore phase of the macroporous cation exchanger.Fluoride is then removed from aqueous phase through Lewis acid-base interactions with freshly precipitated HAlO particles. Moreover, protons produced during the aluminium hydrolysis can promote acidic condition inside the resin phase resulting in higher sorption affinity between HAlO and fluoride ions, with effluent at pH 6. From the experimental column runs, the hybrid material can remove fluoride below WHO recommended levels (1.5 mg/L) for more than 500 bed volumes (BV) of alkaline influent (5 mg F/L, pH 8.0) and is stable for more than five exhaustion-regeneration cycles, over 12.5x greater performance than activated alumina (40 BV). The exhausted resins can be regenerated by passing nearly stoichiometric amounts of aluminium, based on the resin exchange capacity, using diluted 2% $AlCl_3$ solution.The element maps of the exhausted resin from SEM/ EDX confirm that both aluminum and fluoride were well dispersed throughout the resin.

COLL 550

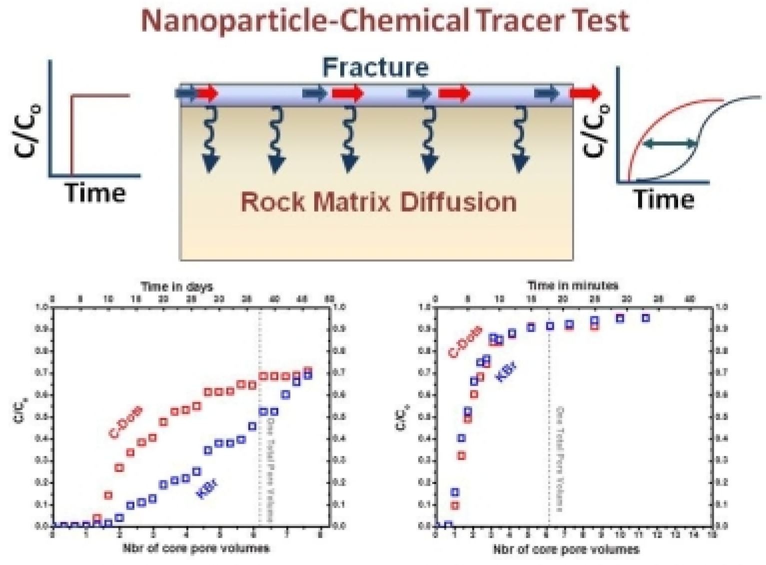
Highly mobile (non-sticky) carbon nanodots in porous media: Toward the design of smart tracer particles

Yan Vivian Li[1]*, Yan.Li@colostate.edu, Lawrence Cathles*[2]*.Â (1) Department of Design and Merchandising, Colorado State University, Fort Collins, Colorado 80523, United*

StatesÂ (2) Department of Earch and Atmospheric Science, Cornell University, Ithaca, New York 14853, United States

Nanoparticles have a diffusion constant at least an order of magnitude greater than inert chemical tracers such as KBr, and this means that they can potentially be used to measure the degree to which subsurface flow occurs through fractures. A requirement is that the particles not aggregate or stick to mineral surfaces. We inject a slug of artifical brine that contains nanoparticles into a column filled with crushed calcium carbonate, and follow this slug with particle-free brine. Eight nanoparticles are evaluated and the nanoparticles that show the least stickiness is the small 3 ± 2 nm ethanolamine carbon nanodot which has zeta potential near zero.

Figure 1a illustrates how fracture flow can be detected by passing water containing both KBr and the non-sticking carbon nanodot tracers through a portion of the subsurface. When the fluid and tracers are injected into a permeable core channel (fracture) at the rate of one core pore (fracture) volume every 5 days, the KBr tracer has time to diffuse into the surrounding halo much more than the particle tracer and arrives much sooner in the effluent (Fig 1a). When the flow is fast, neither tracer has time to diffuse into the halo and both arrive in the effluent simultaneously (Fig 1b). This success suggests that it may be possible to assess the extent of fracture-controlled flow in the subsurface by combining non-sticking nanoparticles with an inert chemical tracer.



(a) Matrix diffusion (b) Flow Channeling

COLL 551

Application of nano-colloids in fully transient electronic devices based on conjugated and organic polymers composites

*Reihaneh Jamshidi, Handan Acar, **Reza Montazami**, Reza@iastate.edu.Department of Mechanical Engineering, Iowa State University, Ames, IOWA 50010, United States*

Electronic devices are designed to last for a long period of time, under harsh chemical and physical conditions. The performance of electronic devices is to remain intact when the device is exposed to harsh environments such as high humidity and temperature. Contrary to conventional electronic devices, a new concept would be to design sophisticated electronic devices at the same performance level that are capable of undergoing rapid degradation at prescribed time and controlled rate. The sophisticated electronics used in implantable biomedical devices, military and inelegance applications can benefit from this concept. In this work, we have demonstrated a fully transient, operational electronic device that can undergo rapid full degradation in under a minute. We have designed and synthesized fully transient insulating and conductive polymers and metal dispersions that, when fabricated into an electrical circuit, exhibited reliable and repeatable electrical functionality along with rapid degradation. Synthesis of transient nano-colloid systems is a significant contribution toward realization of transient electronics. We have demonstrated that nano-colloid base electronic components can undergo full re-dispersion without mechanical mixing, and leave no traceable remains.

COLL 552

Multifunctional tungsten trioxide and zinc tungstate bilayers for methylene blue removal and electron transfer study

*Huige Wei[1], Daowei Ding[1], Henry A. Colorado[1], Haoran Chen[1], Luyi Sun[1], Lu Shao[1], **Suying Wei**[1,2], zhanhu.guo@lamar.edu, **Zhanhu Guo**[1], zhanhu.guo@lamar.edu.Â (1) Department of Chemical Engineering, Lamar University, Beaumont, TX 77710, United StatesÂ (2) Department of Chemistry and Biochemistry, Lamar University, Beaumont, TX 77710, United States*

Methylene blue (MB) removal has been studied using tungsten trioxide (WO_3) and zinc tungstate ($ZnWO_4$) bilayers with integrated functions of electrochromism and energy storage properties. The bilayers were pair-sequentially prepared onto indium tin oxide (ITO) coated glass slides by spin coating technique followed by annealing. The MB (5×10^{-6} M) was subjected to a negative potential of -0.4 and -0.8 V, in 0.5 M Na_2SO_4 aqueous solution, respectively, for 3 hrs and the removal efficiency was monitored by recording variations of the maximum absorption peak at 664 nm using a spectrophotometer. The MB removal efficiency is found to depend on both the bilayer assembly sequences and the potential applied to the solution. Furthermore, for the first time MB has been employed to serve as an indicator to study the electron transfer phenomenon across the WO_3 and $ZnWO_4$ bilayers.

COLL 553

Atomic structure and applications of supported, size-selected metal nanoclusters - and prospects for super-abundant production

***Richard E Palmer**, R.E.Palmer@bham.ac.uk.Nanoscale Physics Research Laboratory, University of Birmingham, Birmingham, United Kingdom*

Deposition of size-selected nanoclusters assembled from atoms in the gas phase is a novel route to the fabrication of <10nm surface features [1]. I will focus on the creation of monodispersed metal cluster arrays which enable new model catalysts [2,3] and protein biochips [4]. The atomic structure of the clusters – previously the province of theory - is revealed experimentally [5] by aberration-corrected scanning transmission electron microscopy (STEM) in the HAADF imaging regime; we can "count" atoms [6] and obtain 3D information not just 2D projections. Results include mass spectrometry of thiolated Au clusters [7,8], adatom dynamics on Au_{923} magic-number nanoclusters [9], first atomic imaging results for Au_{55} and Au_{20} [10,11] and a method to explore the potential energy landscape of clusters via cluster transformations [12]. A new kind of cluster beam source, to allow super-abundant generation of size-selected nanoclusters, will be proposed.

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COLL 554

Block copolymer template-directed synthesis of mono- and bimetallic nanoparticle catalysts

***David A Rider**, David.Rider@wwu.edu.Departments of Chemistry and Engineering Technology, Western Washington University, Bellingham, Washington 98225, United States*

The invention of the proton exchange membrane fuel cell (PEMFC) occurred over a half-century ago and, in spite of extensive developments of its science and its components, its widespread commercialization remains a challenge. Currently, improvements in the durability, performance and manufacturing cost of PEMFCs are required – all of which can be addressed with advances in catalyst function. Platinum (Pt) for example has long acted as the benchmark anodic and cathodic fuel cell catalyst, which makes resulting fuel cell devices less efficient due to Pt poisoning and slow kinetics for the oxygen reduction reaction (ORR). Recent work in our laboratories has shown that a *block copolymer template-directed synthesis of mono- and bimetallic nanoparticle catalysts is an attractive method for preparing high performance PEMFCs catalysts*. This presentation will describe our investigation of the underlying principles for prescribing the size, spacing and composition of nanocatalysts that can be isolated from self-assembled block copolymers loaded with metallic anions and/or cations.

The approach offers several advantageous synthetic features compared to solvothermal catalyst synthesis. The approach is highly flexible and allows for the preparation and screening of a variety of mono- and bimetallic catalysts particles. The method allows for the fine-tuning of the catalyst activity by selection of the block copolymer template precursor. The equivalent exercise of isolating and refining catalysts by solvothermal or direct metallurgy techniques often requires a vigilant redesign of the experimental conditions (ligands, solvents, temperature, pressure, new metal salt precursors, etc.) that control the growth and reduction kinetics of the reagents that create the nanocatalysts. Accordingly, the electrocatalytic activity of block copolymer template-directed Pt-based bimetallic catalysts is presented. Details for the methanol oxidation reactions and oxygen reduction reaction and tolerance to catalyst poisoning are discussed. Preliminary details on a structure–activity relationship between nanocatalysts and their self-assembled block copolymer templates is also discussed.

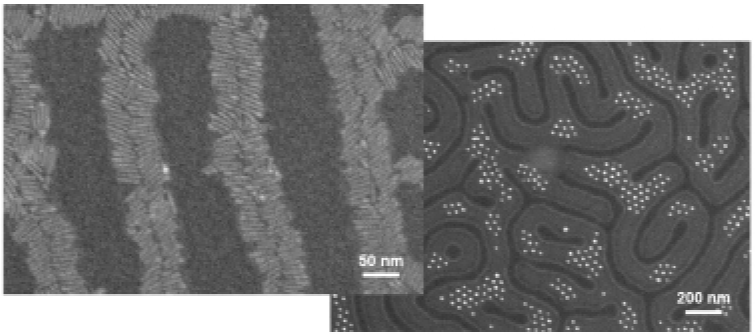
COLL 555

Controlling interparticle arrangement in nanoparticle-block copolymer composite films

***Roy Shenhar**, roys@huji.ac.il.Institute of Chemistry, Hebrew University of Jerusalem, Jerusalem, Israel*

Aggregates of metal and semiconductor nanoparticles exhibit collective properties that strongly depend on interparticle distances and the morphology of organization. Thus, the ability to assemble nanoparticles into pre-defined patterns represents an important goal since it enables controlling the ensemble properties through its morphology.

Block copolymers (polymers made of sequences of chemically distinct co-monomers) are especially suited for organizing nanoparticles, since they form periodic nanoscale structures with controlled morphologies and periodicities due to microphase separation. The presentation will discuss recent progress in our understanding of the mutual co-assembly of block copolymers and nanoparticles in thin films, and will focus on controlling the internal structure of the nanoparticles within their hosting copolymer domains.



COLL 556

Designing chemical and biochemical approaches to “staple” nanostructures onto semiconductor surfaces and to assemble magnetic materials

Andrew V. Teplyakov, *andrewt@udel.edu.Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, United States*

One of the important venues in designing novel interfaces and materials is based on the complementary functionalization of surfaces and nanostructures, so that combining them would lead to layers and materials with novel chemical and physical properties. Here we will highlight three recent research directions from our group. First, a simple application of placing a multifunctional [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) molecule on a functionalized silicon crystal will be discussed in a context of competing surface reactions, where surprisingly the most efficient pathway appears to be a direct attachment of surface aminotermination to the C-60 cage. Second, the placing of probe streptavidine-covered gold nanoparticles onto biotin-modified silicon surface will be investigated with the emphasis on passivation of the remaining surface reactive sites with alkyl thiols. Finally, the use of covalent binding to overcome the clustering of magnetic nanoparticles will take advantage of a “click” chemistry applied to iron nanoparticles to design novel materials.

COLL 557

Applications of selective derivatization of silica surfaces in catalysis and thin film deposition

Junghyun Hong, Zhihuan Weng, Lei Guo, ***Francisco Zaera****, zaera@ucr.edu.Department of Chemistry, University of California, Riverside, CA 92521, United States*

The derivatization of silica surfaces at their surface hydroxo groups can be performed by using well-established covalent chemistry. The challenge is to perform such chemistry with spatial resolution in order to achieve specific performance. In this presentation, we discuss two projects ongoing in our laboratory to prepare spatially-resolved derivatized surfaces for uses in catalysis and thin film deposition. In the first case, cinchona alkaloids, used as chiral modifiers, are being selectively tethered (using "click" chemistry with triethoxysilane-derivatized linkers) to silica sites adjacent to the Pt nanoparticles used as hydrogenation catalysts. In the latter, selective silylation of silicon oxide films is being implemented to spatially control subsequent atomic layer deposition (ALD) processes.

COLL 558

Selective deposition, reactions, and interactions of molecules and assemblies in controlled chemical environments

Paul S. Weiss*, psw@cnsi.ucla.edu.California NanoSystems Institute and Departments of Chemistry & Biochemistry and of Materials Science & Engineering, UCLA, Los Angeles, CA 90095, United States*

We control access of molecules from solution, vapor, and/or contact to substrates in order to place molecules and assemblies selectively in controlled chemical environments. Reactions of isolated molecules can proceed without disrupting surface-bound nanostructures. The reaction exothermicity of clustered molecules can disrupt the structures and can be used to enable access to the substrate and further deposition. The functionalized surfaces can be used to control chemical, biological, and physical interactions. The lability of these surfaces can be turned back off so as to preserve and to stabilize the nanostructures and chemical patterns formed.

COLL 559

Polyurethane-acrylate polymers in microcontact printing of organic molecules, thin films, and colloidal materials

Jinhai Li*, ljhhsn@gmail.com, Alexander A. Shestopalov.Department of Chemical Engineering, University of Rochester, Rochester, NY 14627, United States*

Additive contact printing in large scale has been an attractive area in last few years. The ability to structure layers of organic, inorganic and colloidal materials at micro/nano-size is essential to manufacturing of micro-electronics. In this work a serie of polyurethane-acrylate polymers is used in contact printing of various materials. It is demonstrated that surface energy of this polymer serie is controlled chemically to accommodate different printing conditions. This easy-to-tune surface property is evidenced by using polyurethane-acrylate polymers in contact printing of hydrophobic/hydrophilic self-assembled monolayers, organic thin films and self-assembled colloidal multilayers.

COLL 560

Wafer-scale sub-60 nm optical beam nanolithography with metal-coated elastomeric masks

***Jin Wu**, jwu6@e.ntu.edu.sg, Fengwei Huo.School of Materials Science and Engineering, Nanyang Technological University, Singapore, Singapore 639798, Singapore*

Developing a lithographic strategy that enables the production of high resolution features over wafer-scale areas is the central goal of lithography. Importantly, if such goal can be realized in a low-cost and high-speed manner, it can be used to fabricate various functional nanostructures for both industrial and academic applications. Herein, we developed a facile lithography tool which can be utilized to fabricate wafer-scale arbitrary patterns consisting of sub-diffraction features based on near-field photolithography with the gold-coated elastomeric pyramids or trench as the light modular. The fabricated features have the dimension as small as 50 nm and 80 nm on positive-tone and negative-tone photoresist surface respectively with controllable pitches. And the fabricated centimeter-scale nanopatterns have been successfully utilized to study cell matrix adhesion formation and migration behaviors. Unlike fabricating micrometer patterns by traditional hard photomask, the new type of elastomeric masks can be used to fabricate sub-100 nm features based on traditional photolithography maskaligner, making it as a good alternative to traditional photolithography in fabricating sub-diffraction limit patterns. This facile lithographic strategy have the advantages of low cost, high-throughput, ease of implementing compared with current nanolithographic methods that approach similar functionalities, making it as a simple and reliable method of fabricating sub-diffraction patterns.

COLL 561

Fabrication of metal nanostructures over macroscopic areas by interferometric lithography of self-assembled monolayers

*Anna Tsargorodska, Osama El Zubir, Alexander Johnson, **Graham J Leggett**, Graham.Leggett@sheffield.ac.uk.Department of Chemistry, University of Sheffield, Sheffield, S. Yorkshire S3 7HF, United Kingdom*

Interferometric lithography of self-assembled monolayers provides a fast, inexpensive, simple route to the fabrication of metal nanostructures over square cm areas. Single

exposures of self-assembled monolayers (SAMs) of alkylthiolates on gold in a Lloyd's mirror inteferometer, by irradiation at 244 nm, followed by etching in ethanolic mercaptoethylamine, yields gold wires, while double exposure yields nanostructures of varying dimensions and aspect ratios, in a variety of arrangements (square lattice, hexagonal, rows) depending on (i) the angle of rotation of the sample between exposures and (ii) the angle between the sample and the mirror in the interferometer. Structures may be fabricated with high reproducibility and structure-property relationships explored in a combinatorial fashion. For example, their optical properties depend on their dimensions (length, width, height) and packing arrangements (type of periodicity, spacing between structures). Annealing yields nanostructures with a high degree of crystallinity that exhibit strong plasmon bands. Strong coupling is observed to biomolecules, leading to highly sensitive detection, and strong enhancements are observed for Raman-active adsorbates. Exposure of SAMs of alkylphosphonates on titania cuases photocatalytic degradation, yielding nanopatterned monolayer resists that enable the fabrication of Ti nanostructures on silica with dimensions (full width at half maximum height) as small as 24 nm. These are suitable for use as re-usable for protein nanopatterning, by passivating the silica with a protein-resistant silane and by utilizing the photiocatalytic properties of the native oxide of the titania nanostructures to regenerate the surface after protein adsorption.

COLL 562

Molecular interactions between cell membranes and drug molecules as well as nanoparticles

***Zhan Chen**, zhanc@umich.edu.Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109, United States*

Molecular interactions between cell membranes and other molecules play important roles in many subjects such as drug delivery, cytotoxicity, and antimicrobial activity and selectivity. In this research, we applied sum frequency generation (SFG) vibrational spectroscopy to investigate molecular interactions between model cell membranes and a variety of different molecules and nanoparticles in situ in real time, supplemented by attenuated total reflectance (ATR) – Fourier transform infrared spectroscopy (FTIR). Our research indicates that small amphiphilic antibiotic molecules can penetrate into the cell membrane, with an orientation perpendicular to the membrane surface. The interactions between the antibiotic molecules and various cell membranes are very different, interpreting the activity and selectivity of various antibiotic molecules. Other drug molecules and molecules used for drug delivery have been studied. In addition, interactions between various nanoparticles such as Au and polymer nanoparticles and model cell membranes as well as real cells were also examined. It was found that different nanoparticles enter into cells with different pathways.

COLL 563

Phosphatidylserine compositional asymmetry in eukaryotic membranes: The role of native lipid transport and external forces in maintaining lipid distribution

*Krystal L. Brown, **John C Conboy**, conboy@chem.utah.edu.Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, United States*

The negatively charged lipid phosphatidylserine (PS) has drastic effects on cell function, ranging from blood coagulation to apoptosis. The localization of PS to one leaflet of the membrane is governed by a complex interplay between kinetic and thermodynamic factors. However, the kinetics of PS exchange has not been studied in detail. Using methods of classical surface chemistry coupled with nonlinear optical methods, we have developed a novel analytical approach, using sum-frequency vibrational spectroscopy (SFVS), to selectively probe lipid compositional asymmetry in a planar supported lipid bilayer. SFVS has been used to measure both the compositional asymmetry and kinetics of PS and phosphatidylcholine (PC) lipid flip-flop in planar supported lipid bilayers composed of 1,2-distearoyl-sn-glycero-3-phosphocholine (DSPC) and 1,2-dihexadecanoyl-sn-glycero-3-phospho-L-serine (DPPS). The transition state thermodynamics of DSPC and DPPS were measured at biologically relevant compositions ranging from 10 to 35 % DPPS. The activation thermodynamics of DSPC and DPPS and their impact on compositional asymmetry will be discussed in detail.

COLL 564

Spectroscopic study of the structure and dynamics of membrane proteins

***Feng Gai**, gai@sas.upenn.edu.Chemistry, University of Pennsylvania, Philadelphia, PA 19104, United States*

Despite being embedded in a congested milieu, membrane proteins exhibit a rich array of conformational dynamics that occur over a wide range of timescales. It is, however, difficult to probe such dynamics, especially when high temporal and spatial resolution is required. In this talk, we will show how a multifaceted approach that combines site-specific spectroscopic probes, fluorescence spectroscopy, linear and nonlinear infrared methods could be used to reveal functionally relevant structural and dynamic information about membrane proteins.

COLL 565

Measurement of nanoparticle-membrane interactions with lipid bilayer arrays

*Bin Lu, Tyler Smith, **Jacob Schmidt**, schmidt@seas.ucla.edu.Department of Bioengineering, UCLA, Los Angeles, CA 90095, United States*

Artificial lipid bilayers can serve as membrane models and mimics for ion channel studies, pore protein sensing, and permeation measurements. Our group has worked to further these applications by improving bilayer robustness, lifetime, ease of use, and

throughput. Recently we have worked with array chips which can be used to form bilayers with high yield simply following addition of solution. The repeated parallel formation and measurement of these bilayers, combined with their ease of use and the ability to control membrane and solution composition, have made this platform particularly attractive for studies of nanoparticle-membrane interactions. In particular, we have studied nanoparticle-membrane interactions as a function of ionic strength, lipid composition, membrane charge, and pH for aminated and carboxylated polystyrene nanoparticles. Electrical measurements of the bilayer arrays allowed determination of the transmembrane voltage dependence on nanoparticle-membrane interaction, estimation of the size of membrane pores formed by the nanoparticles, and measurement of membrane lifetime as a function of particle concentration. We will report on these results as well as our current work with additional conditions and particle types.

COLL 566

Structural effects on molecular transport across cell membranes studied by second-harmonic light scattering and bright-field microscopy

Hai-Lung Dai, *hldai@temple.edu.Department of Chemistry, Temple University, Philadelphia, PA 19122, United States*

Molecular transport at the membrane of living biological cells has been examined in real-time observation conditions by a combination of Bright-Field Microscopy and the surface sensitive technique Second Harmonic Light Scattering. Studies of adsorption/transport of malachite-green (MG), crystal-violet (CV), and bromocresol purple (BCP), charged or neutral hydrophobic molecules, at Gram-negative and Gram-positive bacteria, and Murine erythroleukemia (MEL) cells have revealed the effects of a) membrane surface charge, lipid bilayer packing, and protein components; and b) the charge and polarity of the molecules; on the adsorption density and molecular transport rate. The studies have also revealed new understandings of the Gram-stan mechanisms.

COLL 567

Electrostatic interactions between anionic phospholipid membranes and polycationic macromolecules: Slaved diffusion revisited

*Xiaojun Shi, **Adam W Smith**, asmith5@uakron.edu.Department of Chemistry, University of Akron, Akron, Ohio 44325, United States*

Specific binding of proteins to anionic lipids in the plasma membrane is a common motif in many cell signaling pathways. Anionic lipids can be slaved to or sequestered by adsorbing macromolecules via Columbic attraction, which leads to measurable changes in the lateral distribution and translational mobility of the lipids. Previous work suggests that the macromolecules can form nano-domains which sit on top of the membrane with

high counts of associated anionic lipids. However, the structure and dynamics of the lipid solvation around the adsorbed polymer is poorly understood. We have investigated the behavior of Alexa Fluor 568-labeled quaternized polyvinylpyridine (QPVP) on supported lipid bilayers doped with BODIPY-labeled phosphatidylserine (PS) or phosphatidylinositol phosphate (PIP) lipids using time-resolved fluorescence microscopy – including pulsed interleaved excitation fluorescence cross-correlation spectroscopy (PIE-FCCS). PIE-FCCS is a dual-color fluorescent spectroscopy that translates fluctuations in fluorescence signal into a measurement of diffusion and co-localization. In this way we measure the correlated movement of lipids and absorbed polymer and resolve the mechanism of lipid-polymer interactions. Using this approach we have systematically studied the influence of lipid charge density, solution ionic strength, and polymer chain length on the properties of the interaction between anionic lipids and polycationic polymers. PIE-FCCS was also used to investigate the behavior of dual-color labeled QPVP on unlabeled PS/PIP containing lipid bilayers. The detailed study of polymer-lipid bilayer interaction will aid our understanding of the biophysical mechanism of peptide/protein binding on the plasma membrane.

COLL 568

Lipid interaction with G protein-coupled membrane receptors studied by NMR

Olivier Soubias, Tomohiro Kimura, Walter E Teague Jr, Kirk G Hines, Alexei A Yeliseev, ***Klaus Gawrisch****, gawrisch@helix.nih.gov.Laboratory of Membrane Biochemistry and Biophysics, NIAAA, NIH, Bethesda, MD 20892,, United States*

The functional G protein-coupled membrane receptors (GPCR) bovine rhodopsin and

recombinantly expressed type II cannabinoid receptor, CB2, are reconstituted into lipid bilayers

to study the influence of membrane composition on receptor function. Lipid-GPCR interaction

is investigated directly on the lipids by a variety of solid-state NMR approaches, while receptor

function is followed by ligand binding and G protein-activation studies. Elastic deformation of

the lipid matrix from lipid-GPCR interactions is investigated by 2H-NMR on bilayers composed

of lipids with perdeuterated hydrocarbon chains. The data show that bilayers adjust elastically

to the hydrophobic length of transmembrane helices of GPCR. However, any hydrophobic

mismatch between the lipid matrix and GPCR also results in structural changes of the GPCR.

Specificity towards interaction with particular lipid species is investigated by magnetization

transfer experiments from the GPCR to lipids using 1H, 31P-, and 13C magic-angle spinning NMR

experiments. For rhodopsin, they revealed that the protein has some preference for interaction

with phosphatidylethanolamines with polyunsaturated, docosahexaenoic acid hydrocarbon

chains. Furthermore, 13C-MAS NMR relaxation studies showed that such interactions do

not result in significant immobilization of lipid molecules near the protein. Lipids in the first

layer surrounding the GPCR remain in rapid exchange with the bulk of the lipid matrix on the

timescale of microseconds. The relationship between lipid-GPCR interaction, oligomerization of

GPCR, and GPCR activation will be discussed.

COLL 569

Synthesis of Ag:SiO_2:Ag core:spacer:shell nanoparticles via the hydrogen reduction method and characterization of their optical properties

***James P Cook**, jpcook@email.wcu.edu, David D Evanoff.Department of Chemistry & Physics, Western Carolina University, Cullowhee, North Carolina 28723, United States*

Plasmonic nanostructures are of considerable interest due to their unique mechanism for light interaction and the considerable number of applications that result from, or are enhanced by, these interactions. Extensive work has been reported on the synthesis, modeling, and utilization of various morphologies of plasmonic structures. Here, the synthesis of Ag:SiO_2:Ag core:spacer:shell (CSS) particles of varying geometries is reported. CSS synthesis utilizes an adaptation of the hydrogen reduction method and results in highly crystalline particles free of surface-modifying groups. Extinction

efficiencies of the composite CSS particles as well as the effect of varying shell and spacer thicknesses on the relative ratio of the scattering and absorptive plasmon relaxation modes are reported. Likewise, the relationship between CSS particle geometry and SERS enhancement factor is explored.

COLL 570

Citrate-free synthesis of Ag nanoplates and the mechanistic study

Dong Qin, *dong.qin@mse.gatech.edu.Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States*

We report a citrate-free synthesis of Ag nanoplates with an edge length of 50 nm that involved the reduction of $AgNO_3$ by poly(vinyl pyrrolidone) (PVP) in ethanol at 80 ^oC under a solvothermal condition. Within a period of 4 hours, >99% of the initially added $AgNO_3$ could be converted into Ag nanoplates with excellent stability. To understand this remarkably simple and efficient process, we systematically investigated the roles played by various reaction parameters, which include the type of precursor, the reducing powers of PVP and ethanol, the molar ratio of PVP to $AgNO_3$, the solvent, the involvement of O_2, and the effects of pressure and temperature. Our results suggest a plausible mechanism that involves i) fast reduction of $AgNO_3$ to generate Ag multiple twinned particles (MTPs) via a thermodynamically controlled process, ii) kinetically controlled formation of plate-like seeds and their further growth into small nanoplates in the presence of Ag^+ ions at a low concentration, and iii) complete transfer of Ag atoms from the MPTs to nanoplates via O_2-mediated Ostwald ripening. We demonstrated that the molar ratio of PVP to $AgNO_3$ in ethanol plays an essential role in controlling the reduction rate for the formation of MTPs and plate-like seeds under the solvothermal condition, the transformation kinetics, and the final morphology taken by the Ag nanoplates. In particular, when the reaction temperatures were above the boiling point of ethanol, the pressure induced by a solvothermal process accelerated the oxidative etching of Ag MTPs to facilitate their complete conversion into nanoplates. The mechanistic insight could serve as a guideline to optimize the experimental parameters of a solvothermal synthesis to control the reduction kinetics and thus the formation of metallic nanocrystals with controlled shapes, and in high yields and large quantities.

COLL 571

Synthesis of iron oxide nanoparticles coated with novel surfactant bilayers and their application in stabilizing oil-in-water emulsions

Pranav S Vengsarkar, *psv0002@auburn.edu, Christopher B Roberts.Department of Chemical Engineering, Auburn University, Auburn, Alabama 36849-5127, United States*

Nanoparticles have highly tunable physicochemical properties which are extremely important in applications like catalysis, biomedicine, and environmental remediation. Unique interfacial properties resulting from the nanoparticles' small size can be used to stabilize oil-in-water emulsions, where the nanoparticles adsorb at the surface of the oil droplet in water. These emulsions are usually referred to as Pickering emulsions. Specifically, iron oxide based emulsions have been considered as alternative dispersants for oil-spill applications. The objective of this work is to investigate the effect of the primary particle characteristics and stabilizing agent chemistry on the stability of oil-in-water Pickering emulsions. Iron oxide nanoparticles were synthesized by the co-precipitation method and were then coated with layers of sodium stearoyl lactylate (SSL), an FDA approved food additive, and subsequently dispersed in aqueous and organic solvents depending upon their nature. Formation of a monolayer or a bilayer coating on the nanoparticles was also controlled through systematic changes in reagent amounts. Characterizations of these nanoparticles were performed through the use of transmission electron microscopy (TEM), dynamic light scattering (DLS) and Fourier Transform Infrared spectroscopy (FTIR) to analyze their size distribution and ligand-solvent interactions. In this study, the capacity of these bilayer coated nanoparticles to stabilize oil-in-water emulsions was systematically determined using optical microscopy and Zeta-potential analysis. These emulsion systems were also subsequently tested for their pH/salinity responsiveness to determine their applicability in oil-spill remediation applications.

COLL 572

Reactions of hydrogen and organic peroxides with titania impregnated films and coatings

Travis H. James[1]*, travis.james@okstate.edu, Cody Cannon*[1]*, Dane Scott*[2]*, Allen Apblett*[1]*, Nicholas F. Materer*[1]*.Â (1) Department of Chemistry, Oklahoma State University, Stillwater, OK 74078, United StatesÂ (2) Department of Chemistry, East Central University, Ada, OK 74820, United States*

Reactions of gaseous hydrogen peroxide with titanium isoproproxide-hydroxypropylcellulose films and coatings prepared through sol-gel formation were investigated. When exposed to peroxide vapors between 0 and 50 ppm, these films and coatings underwent a dramatic color change from clear to yellow within minutes. To determine the reaction kinetics, an experimental setup was developed to quantify the reflected light during exposure. The phenomenological reaction rate was first-order with respect to peroxide concentration and zero-order with respect to the titania loading, although lower loadings resulted in films which were not as colored and saturated faster with exposure. In addition, coatings produced on the cellulose substrate were over three times as sensitive as films produced on polycarbonate slides. Using this setup, reactions with various organic peroxides were investigated. It was determined that increasing the acidity of the films and coatings significantly increased the sensitivity.

COLL 573

Controllable synthesis and properties of rare earth nanomaterials

Chun-Hua Yan^{1,2,3}*, yan@pku.edu.cn, Ling-Dong Sun*^{1,2,3}*, Ya-Wen Zhang*^{1,2,3}*.Â (1) Beijing National Laboratory for Molecular Sciences, ChinaÂ (2) State Key Laboratory of Rare Earth Materials Chemistry and Applications, ChinaÂ (3) College of Chemistry and Molecular Engineering, Peking University, China*

In this talk, we select several representative rare earth nanomaterials to demonstrate how the basic principles in coordination chemistry could be used to direct the synthesis of rare earth nanocrystals, specifically, to control the structure, surface, particle size and morphology. Using solution-based methods such as solvothermal synthesis and thermolysis of metal complex precursors, we successfully prepared a series of novel nanostructured rare earth compounds, to name a few, ultra-small colloidal nanoceria, highly homogeneous and stable mesoporous ceria-zirconia solid solutions, and high-quality nanocrystalline rare earth oxides, fluorides, sulfides, selenides, oxyfluorides and oxysulfides. These results were obtained on the basis of elaborate control on the synthetic parameters and reaction kinetics. We also studied the assembly behaviors of these rare earth nanocrystals using methods including spin-coating, Langmuir-Blodgett technique, evaporation-induced self-assembly and liquid-liquid interface assembly. The rare earth nanocrystals display a wide range of properties in magnetic, electronics, optics and catalysis. In order to unveil the mechanisms underlying the synthesis and properties, we systematically characterized the phase, microstructure, texture and surface chemistry of the nanocrystals. We also integrated these rare earth nanocrystals with other functional units like noble metal nanoparticles and stimuli-responsive organic dyes, and fabricated a number of hybrid/composite nanomaterials. By virtue of their rich properties, the rare earth nanocrystals could find a variety of applications such as UV-absorbents, three-way catalysts, high-efficiency upconversion phosphors, high-contrast luminescent biolabels, agents for photodynamic therapy, data-recording media and environmental sensors.

COLL 574

DLVO theory and capping agents: Attaching silver nanoparticles to ceramic water filters

Anne M. Mikelonis*, amikelonis@utexas.edu, Desmond F. Lawler.Department of Civil, Architectural and Environmental Engineering, University of Texas at Austin, Austin, Texas 78712, United States*

This research explores how capping agents affect the adherence of silver nanoparticles (AgNPs) to porous ceramic water filters. AgNPs are added as an *in situ* disinfectant in ceramic pot filters used for household drinking water treatment in developing countries and could possibly be introduced into ceramic membranes in the developed world. The presentation will connect results from modeling theoretical DLVO interaction energies with experimental data collected from isotherm tests. Two types of filters were used in this work: aluminum oxide (Al_2O_3) ceramic disks (pores = 0.1 μm diameter, Whatman Anodiscs) and clay disks (pores < 20 μm diameter, produced in-house from Illite clay and sawdust). The Al_2O_3 disks are intended to represent membranes used for municipal

water treatment in developed countries, and the clay disks are intended to represent the pot filters used in developing countries. They also represent substantially different surface charges (*e.g.*, at neutral pH, Al_2O_3 filters ~ +15 mV vs clay filters ~ -40 mV). The different AgNPs studied include particles capped with: citrate, polyvinylpyrrolidone (PVP), and branched polyethylenimine (BPEI). Citrate and PVP were selected due to their differences in functional groups/stabilization and widespread use. Also, the surface charge at natural water conditions (pH 7-9) for all of these particles vary. PVP and citrate are negative (and differ in magnitude by up to 4.5 times), whereas BPEI has a positive charge. The welfare of societies depends upon safe water. A better understanding of the fundamental attachment mechanisms of differently capped AgNps represents progress towards predicting the lifespan of AgNp amendments, thus ensuring sustainability of safe water treatment processes.

COLL 575

Ligand desorption and desulfurization on silver nanoparticles using sodium borohydride in water

H.A.Ganganath S Perera, *hsp51@msstate.edu, Dongmao Zhang.Department of Chemistry, Mississippi State University, Mississippi State, Mississippi 39762, United States*

Removal of molecular adsorbates from noble metal nanoparticles (NPs) is important for NP catalytic applications and noble metal recycles and reuses. We recently reported that $NaBH_4$ can completely remove molecular adsorbates including organothiols (OTs) from gold nanoparticle (AuNP) surfaces. Presented herein is a systematic study of ligand desorption from silver nanoparticles (AgNPs) using $NaBH_4$ in water. Unlike AuNPs where the OTs can be completely desorbed or desulfurized, the OTs on AgNPs can only be partially desorbed. Complete ligand desorption from AgNPs was observed only for nonspecific ligands including organic compounds adenine and Rhodamine 6G, small anions including Cl^-, Br^- and I^-. Complete desulfurization of 2-mercaptobenzimidazole (2-MBI) and 6-thioguanine (6-TG) can be achieved with a large excess of AgNPs and $NaBH_4$. Large fraction of the desulfurized products retains on the AgNP surfaces. This is in contrast to the 2-MBI and 6-TG desulfurization on AuNPs where only the sulfide ions are adsorbed on the $NaBH_4$ treated solution.

COLL 576

Synthesis of transition metal and metal oxide nanoparticles with tunable size via use of poly(propylene imine) dendrimers

Elisabeta Mitran, *emitra1@tigers.lsu.edu, Barry Dellinger, Robin L. McCarley.Department of Chemistry, Superfund Research Program, Louisiana State University, Baton Rouge, LA 70803, United States*

The ability to control dendrimer architecture and exterior functionalities provides a powerful approach for tailoring the size and size dispersity of metal/metal oxide nanoparticles for different applications. Using a poly(propylene imine) dendrimer-based approach, we have prepared transition metal and metal oxide nanoparticles with controlled size and composition in solution and on supports. Nanoparticles of Ni(0) and Cu(0) in methanolic solution were obtained by anaerobic borohydride reduction of M(II) coordinated to the primary amines of amine-terminated poly(propylene imine) dendrimers. The metal oxide nanoparticles (NiO, CuO, Fe_2O_3) were prepared by impregnation of high-surface-area amorphous silica with metal ion-poly(propylene imine) dendrimer complexes or ferrocenoyl-modified poly(propylene imine) dendrimers, followed by thermal decomposition in air at different temperatures. High control over the diameter of the nanoparticles (2–5 nm) and size dispersity (8–21%) was possible by manipulating the dendrimer generation, metal loading, and calcination temperature.

COLL 577

Phenolic acids anchoring on magnetically responsive iron nanoparticles

Anselm I Omoike, *aomoike@uscupstate.edu, Eaves O Michael.University of South Carolina-Upstate, Spartanburg, SC 29303, United States*

Two natural phenolic compounds, ferulic acid and tannic acid, were immobilized on magnetic iron nanoparticles and the particles were characterized by attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, thermogravimetric analysis (TGA), and transmission electron microscopy (TEM). In the region 800-1,800 $cm^{-1}$where no peak was observed in the spectrum of bare magnetic iron nanoparticles (no contact with the phenolic compounds), the spectra of magnetic iron nanoparticles after exposure to ferulic acid and tannic acid showed several absorption peaks characteristic of phenolic compounds, indicating that surface immobilization had occurred. The TGA data collaborated the ATR-FTIR findings. Selective adsorption of major peanut allergens on the magnetic nanoadsorbents was evaluated and the removal capacity monitored using SDS-PAGE. Preliminary results on the potential application of the magnetic nanoparticles for the selective and efficient removal of major allergenic proteins (Ara h 1 and Ara h 2) from peanut products are presented, along with the desorption of the allergens from the particles.

COLL 578

Suppression of quenching in strongly coupled nanodimers

Kevin L Shuford, *kevin_shuford@baylor.edu.Department of Chemistry and Biochemistry, Baylor University, Waco, TX 76798-7348, United States*

This account focuses on using classical electrodynamics methods to model the optical properties of metal nanoparticles as well as the excitation dynamics of molecules interacting with them. We examine how nanoparticles couple to each other and to molecules, as well as how the nature of this coupling can affect the energy transfer process. Coupling a molecule to a nanostructure is found to drastically alter the fluorescence. Specifically, we investigate the emission characteristics of a molecule placed in the gap of a nanoparticle dimer. In contrast to the single nanosphere-molecule system, we find that the emission intensity undergoes a quenching effect only when the inter-nanoparticle gap distance of the dimer is very small, meaning that strong coupling prevails over energy engaged in the heating process unless the molecule is extremely close to the metal surface. This example highlights the importance of accurately modeling the nanoparticle and understanding the interplay between system components in plasmonic applications.

COLL 579

Alcohol oxidation electrocatalysis on CuPt core-shell nanostructures

Anne Co*, co@chemistry.ohio-state.edu, Eric Coleman, Heewon Choi.Department of Chemistry and Biochemistry, The Ohio State University, Columbus, Ohio 43210, United States*

We describe the design and synthesis of a CuPt core-shell electrocatalysts with well-defined, tunable morphology and composition. Electron microscopy and Brunauer-Emmett-Teller (BET) surface analysis indicate our catalysts have extremely high porosity, which acts to maximize mass transport, increase active surface area, and minimize the overall precious metal content. High methanol, ethanol and formic acid oxidation rates were obtained on The Cu@Pt catalysts in addition to lower carbonaceous poisoning compared to commercial Pt/C catalysts.

COLL 580

Optically modulated Ag cluster contrast agents

Robert Dickson*, dickson@chemistry.gatech.edu.School of Chemistry & Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332-0400, United States*

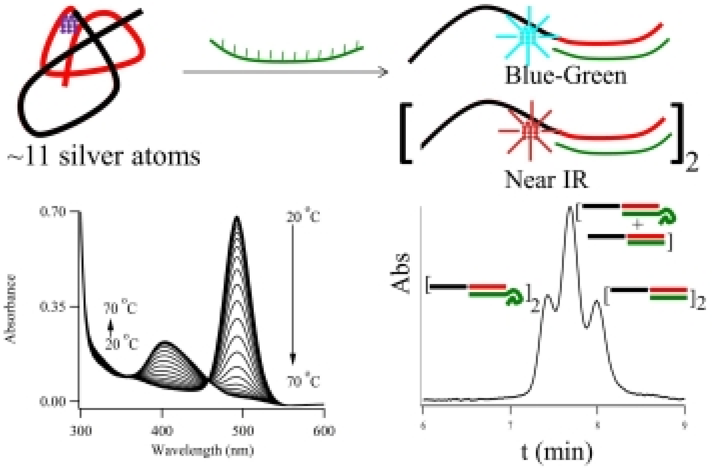
A multitude of imaging modalities and contrast agents have been devised to improve detection, dynamics, and resolution. Whether imaging low copy number proteins in cells or detecting small pathologies in vivo, materials and detection schemes must be specifically tailored to visualize weak signals buried within high backgrounds. Working toward real-world applications, we have tailored bright Ag cluster chromophores and ultrasensitive optical spectroscopies for their selective visualization, even when buried deep within highly absorptive/emissive and highly scattering tissue. Our few-atom Ag nanocluster fluorophores exhibit extremely bright and stable fluorescence, but it is their very long-wavelength absorbing *dark* states that enable ground state populations to be optically modulated. By optically shifting steady-state population between dark and bright state manifolds, we marry molecular modulation schemes characteristic of absorption spectroscopy with both multi-label fluorescence imaging and photoacoustic detection, to recover only Ag cluster signals without interfering background. Such modulated optical contrast has enabled signal recovery from metal clusters buried multiple cm within tissue-mimicking phantoms. Finite element computational models nicely match experimental results giving predictive insight for future studies and for potential medical applications.

COLL 581

DNA-templated silver clusters

Jeffrey T Petty[1]*, jeff.petty@furman.edu, Orlin O Sergev*[1]*, David A Nicholson*[1]*, Ian C Miller*[1]*, D Ryan McMullan*[1]*, Stuart K Graham*[1]*, Banabihari Giri*[1]*, Peter M. Goodwin*[2]*.Â (1) Chemistry, Furman University, Greenville, SC 29613, United StatesÂ (2) Los Alamos National Laboratory, Los Alamos, NM 87545, United States*

Single-stranded DNA encapsulates silver clusters, and we consider blue-green and near-infrared chromophores whose spectra are directed by DNA structural changes. We show how these changes are used to detect oligonucleotides. A common type of DNA template has two components: the 3' sequence hybridizes with target oligonucleotides and the 5' sequence forms specific silver clusters. These composite strands exclusively harbor an ~11 silver atom cluster that absorbs at 400 nm with limited emission. When a target hybridizes with these single-stranded conjugates, cluster absorption shifts and strong emission develops. Fluorescence anisotropy, fluorescence correlation spectroscopy, size exclusion chromatography, elemental analysis, and temperature-dependent spectral measurements identify two structural and thermodynamic changes accompanying hybridization. First, the violet cluster folds its single-stranded host and inhibits DNA hybridization. Second, the violet cluster dimerizes its DNA host and forms a near-infrared cluster. Our key conclusion is that silver clusters are both chromophoric reporters and ligands that modulate analyte-sensor interactions.



COLL 582

Fluorescent molecular-like metal nanoclusters

Jennifer S Martinez[1]*, jenm@lanl.gov, James H. Werner*[1]*, Hsin-Chih Yeh*[2]*, Jaswinder Sharma*[3]*, Andrew P. Shreve*[4]*.Â (1) Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, NM 87545, United StatesÂ (2) Biomedical Engineering, University of Texas Austin, Austin, TX 78712, United StatesÂ (3) Oak Ridge National Laboratory, Oak Ridge, TN 37831, United StatesÂ (4) Center for Biomedical Engineering, University of New Mexico, Albuquerque, NM 87131, United States*

Fluorescent metal nanoclusters are gaining much interest because of their desirable photophysical properties, smaller size than quantum dots, and biocompatibility. As a compliment to quantum dots and molecular fluorophores, fluorescent metal nanoclusters have been produced using templates of dendrimers and polymers, small

molecular ligands, or within biological materials of interest, such as DNA. The specificity of complementary base pairing has made DNA an attractive template for the synthesis of two- and three-dimensional nanostructures and also for templating and organizing inorganic nanoparticles. We exploit the chemical and structural specificity of DNA to not only template fluorescent nanoclusters, but to also enable their use in medical diagnostics and in the bottom-up assembly of heterostructures.

COLL 583

Biological applications of gold nanomolecules

***Christopher J Jeffries**, ackerson@colostate.edu.Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-1872, United States*

Thiolate Monolayer Protected Gold Clusters (MPCs) are applied in biological contexts as contrast markers and less frequently as radiofrequency hyperthermia agents. Their use as contrast markers is well established in biological electron cryomicroscopy, and emergent for whole organism x-ray contrast and optical contrast. Fundamental properties of MPCs may enable additional contrast modes. Our work on the biological applications of MPCs including molecular, whole cell and whole animal contrast, as well as radiofrequency hyperthermal manipulations of biological molecules is presented.

COLL 584

Ultrasmall photoluminescent metal nanoclusters at the nano-bio interface

*Li Shang, **G. Ulrich Nienhaus**, uli@uiuc.edu.Institute of Applied Physics, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany*

Metallic nanoclusters (such as Au and Ag NCs) composed of only a few atoms possess strong, robust, size-dependent photoluminescence, making them attractive as markers for many applications [1]. Interesting biological and biomedical applications of these NCs have been reported, including in vitro and in vivo imaging, ultra-sensitive bioassays and therapy. Despite intense research on in recent years, knowledge about their behavior in the biological environment is still fairly limited [2]. We have investigated the interaction of photoluminescent Au and Ag NCs with proteins and live cells [3]. Interactions with proteins may alter the photophysical properties of metal NCs and the subsequent biological effects on cells and organisms. Recently, we have systematically engineered the surface charge of a model protein, human serum albumin (HSA), to explore the role of Coulomb forces in the interactions of AuNCs with proteins and the ensuing effects on cellular uptake. By using confocal microscopy with quantitative image analysis, we have investigated cellular uptake in detail. Ultrasmall AuNCs are internalized by HeLa cells via multiple active mechanisms; clathrin-mediated endocytosis and macropinocytosis play a predominant role.

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COLL 585

Bioimaging applications of luminescent gold nanoparticles

***Jie Zheng**, jiezheng@utdallas.edu.Chemistry, The University of Texas at Dallas, Richardson, TX 75080, United States*

Inorganic nanoparticles (**NPs**) with large surface areas, tunable material properties and strong signal output potentially serve as a new generation of contrast agents for advancing our fundamental understanding of cell biology and also catalyzing the shift of our current medical paradigm to “earlier detection and prevention”. After decades' efforts, luminescent gold NPs that can give intrinsic emission without conjugation of any fluorophores start emerging a class of fluorescent probes for biomedical imaging. In this talk, we will summarize the synthetic strategies for creating different sized luminescent gold nanoparticles, their unique photophysical properties and their bioimaging applications at both in vitro and in vivo level.

COLL 586

PEGylation and zwitterionization: Pros and cons in the renal clearance and tumor targeting of near-IR-emitting gold nanoparticles

***Jinbin Liu**, jxl101000@utdallas.edu, Mengxiao Yu, Xuhui Ning, Chen Zhou, Shengyang Yang, Jie Zheng.Department of Chemistry, The University of Texas at Dallas, Richardson, Texas 75080, United States*

PEGylation and zwitterionization, which are used in minimizing serum protein adsorption and nonspecific reticuloendothelial system (RES) uptake of nanoparticles (NPs), have a distinct impact on tumor targeting of luminescent gold nanoparticles (AuNPs), although both strategies provide AuNPs with effective renal clearance. The renal-clearable NIR-emitting PEGylated AuNPs was synthesized through a facile one-step method, and these NPs exhibit photophysical properties and core size almost identical to the zwitterionic glutathione coated AuNPs (GS-AuNPs). Systematic studies of the renal clearance, pharmacokinetics, and passive tumor targeting of PEG-AuNPs and GS-AuNPs in mice bearing MCF-7 tumors showed that the PEG-AuNPs can effectively target tumors with an efficiency three times higher than that of the GS-AuNPs, although the two of them exhibited comparable low RES uptake. The high tumor-targeting efficiency of the PEG-AuNPs is fundamentally a result of the fact that

PEGylation can enhance the enhanced permeability and retention (EPR) effect of renal-clearable luminescent AuNPs relative to zwitterionization by increasing their retention time and concentration in the blood. However, the limitation of PEGylation in tumor imaging is that it took much longer for the PEG-AuNPs to reach the desired contrast index threshold than it took the zwitterionic GS-AuNPs because of the slow tumor accumulation and normal-tissue clearance of the PEG-AuNPs. These differences suggest that appropriate surface chemistries for NPs should be rationally selected upon their exact applications in cancer diagnosis and therapy.

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COLL 587

Heterogeneous distribution and cell internalization dynamics of Au nanoclusters with enhanced near IR luminescence

Cecil V Conroy[1], *cconroy4@student.gsu.edu, Jie Jiang*[1]*, Chen Zhang*[1]*, Tarushee Ahuja*[1]*, Zhenghua Tang*[2]*, Jonathan W Padelford*[1]*, Gangli Wang*[1]*.Â (1) Department of Chemistry, Georgia State University, Atlanta, Georgia 303032, United StatesÂ (2) Department of Chemistry, University of Miami, Coral Gables, Florida 33146-0431, United States*

The defined chemical compositions and atomic structures make the molecular-like gold nanoclusters fundamentally interesting because structure-function correlations could be established. This category of nanomaterials also received much attention due to their exciting physicochemical properties, chemical stability and flexibility for further functionalizations. Our group has been working on the control of core-ligand interfacial bonding via a multi-dentate approach, with a focus on the corresponding impacts on the electrochemical activity and near IR luminescence. In this report, we describe the quantum efficiency enhancement of the near IR emission from prototype thiolate stabilized Au nanoclusters via a combined thermo and thiol-etching treatment. Up to ten fold enhancement has been achieved with the emission max beyond 700 nm, a preferred spectrum window with less autofluorescence and other cellular interference. The as-synthesized, thermo-optimized, and PEGlated Au nanoclusters chemical and luminescence properties are evaluated in a wide pH range, and in a range of common buffers and cell media. Cell internalization of Au nanocluster at different dosage and incubation duration are studied with confocal microscopy. Quantification/ analysis reveal heterogeneous distribution in different subcellular organelles. The pathway is proposed based on further analysis of internalization kinetics. Nucleus entry is attributed to

passive diffusion and validated by co-localization of nucleus stain/dye and z-stack analysis.

COLL 588

Heterogeneous catalysis probed by sum frequency generation

Gabor Somorjai, *somorjai@berkeley.edu.Chemistry, UC Berkeley, Berkeley, CA 11111, United States*

Recent developments in the application of vibrational SFG to heterogeneous catalysis will be discussed.

COLL 589

Aqueous interfaces: Localized and collective vibrations probed with nonlinear spectroscopy

Mary Jane Shultz[1], *Mary.Shultz@Tufts.edu, Patrick Bisson*[2], *Tuan Vu*[3], *Jing Wang*[1]*.Â (1) Chemistry, Tufts University, Medford, Massachusetts 02155, United StatesÂ (2) Thayer School of Engineering at Dartmouth, Darmouth College, Hanover, NH 03755, United StatesÂ (3) Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, United States*

Despite the fundamental role that aqueous interfaces play in shaping the world and the numerous efforts to generate a molecular-level model of these interfaces, the picture is not yet sharply in focus. The challenge lies in the nature of hydrogen-bond interactions: experimentally sharp molecular vibrations spread over hundreds of wavenumbers producing broad, overlapping resonances. Spectral breadth challenges molecular-level interpretation of spectral changes. This contribution will discuss recent success in identifying resonances in the hydrogen-bonded interface using single-crystal ice and the nonlinear spectroscopy, sum frequency generation (SFG). This work combines the anisotropy of ice and the polarization interference of SFG to identify localized and long-range vibrational modes. Localized modes are used to quantify *intra*molecular coupling.

COLL 590

Time-resolved SFG measurements of molecules under extreme conditions

Christopher M. Berg, Yuxiao Sun, ***Dana D Dlott****, dlott@illinois.edu.School of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

Ultrafast vibrational sum-frequency generation spectroscopy is used to study the dynamics of molecules adsorbed on metal surfaces and their responses to ultrafast temperature jump and ultrafast shock compression.

COLL 591

Linear and nonlinear optical studies of structure, organization, and reactivity across solid/liquid interfaces

***Rob A. Walker**, rawalker@chemistry.montana.edu, Brittany L. Woods, Eric A. Gobrogge.Chemistry and Biochemistry, Montana State University, Bozeman, MT 59717, United States*

Surfaces change the properties of solvents from bulk solution limits, often in ways that are difficult to predict. This talk will explore how surface induced anisotropy creates markedly different solvating properties with two polar solvents, acetonitrile and methanol. Specifically, resonance enhanced second harmonic generation (SHG) is used to measure the surface activity and electronic structure of two adsorbed 7-amino-coumarin solutes, Coumarin 151 (C151) and Coumarin 152 (C152) at silica/liquid interfaces, and time resolved fluorescence measurements performed in a total internal reflection geometry (TR-TIRF) measure the emission lifetimes of these two solutes in the near-surface region. Across the silica/liquid interface, acetonitrile forms a local solvation environment that is more polar than bulk solution, whereas the silica/methanol interface is significantly less polar than bulk solution. These differences are assigned to differences in solvent structure imposed on the interfacial region by the substrate. TR-TIRF data from C151 and C152 adsorbed to silica/methanol interfaces support the SHG measurements, but similar experiments performedTR-TIRF data from silica/acetonitrile interfaces appear to contradict SHG results with the fluorescence lifetime showing little evidence of the polar solvation implied by the excitation wavelengths. This discrepancy may reflect differences in the properties measured by the two types of experiments: SHG samples adiabatic excitation energies and is sensitive to the solvent organization around solutes in their ground excited states, whereas TR-TIRF measures the response of excited state solvent molecules with solvation structure equilibrated to the solute's excited state.

COLL 592

Structure and activity of chemically immobilized peptides and proteins on surfaces

***Zhan Chen**, zhanc@umich.edu.Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109, United States*

Molecular structures of peptides and proteins chemically immobilized on SAM and polymer surfaces were deduced using sum frequency generation (SFG) vibrational spectroscopy and attenuated total reflectance (ATR) – FTIR. A variety of peptides including cecropin P1, MSI-78, tachyplesin I, and FSD-1 were investigated. It was found that both the peptide surface immobilization site and the surface coverage affect the conformation and orientation of surface immobilized peptides. The different orientation and conformation also led to different activities. Two enzyme molecules, 6-phospho-β-

galactosidase (β-Gal) and nitroreductase (NsfB) were examined using SFG and ATR-FTIR. The enzymes were immobilized onto the surface via specific cysteine sites and the orientations were detected using SFG and ATR-FTIR. This research demonstrated the feasibility to control the surface immobilized enzyme orientation, and showed that enzymes with the optimized orientation enhance the activity.

COLL 593

Award Address (ACS Award in Colloid and Surface Chemistry sponsored by the ACS Division of Colloid and Surface Chemistry). Studies of biomolecular interactions at interfaces by nonlinear spectroscopy

***Kenneth Eisenthal**, kbe1@columbia.edu.Chem, Columbia, New York, NY 10000, United States*

The applications of nonlinear spectroscopy at surfaces including those of colloidal systems will be discussed in the context of biomolecuiar interactions.

COLL 594

Award Address (Arthur W. Adamson Award for Distinguished Service in the Advancement of Surface Chemistry sponsored by the ACS Division of Colloid and Surface Chemistry and the ACS Publications Journal Langmuir). In search of perfection: The quest for atomically flat silicon and the mechanism of silicon oxidation

***Melissa A. Hines**, Melissa.Hines@cornell.edu.Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853, United States*

Driven by the demands of technology, silicon surface chemists seek the creation of truly perfect surfaces — surfaces that are atomically flat, free of contaminants, and perfectly terminated with precisely defined monolayers. To meet this goal, most have sought to understand silicon reactivity in terms of the majority species — the ideal terrace sites on an atomically flat surface. Here, I will show that the chemistry of perfection actually lies in the defects.

Because of its importance to the microelectronics industry, silicon oxidation has been studied intensely for decades; however, the disordered nature of the oxide makes this reaction notoriously difficult to understand. In this work, the oxidation reaction is coupled with a subsequent etching reaction, allowing oxidation to literally write an atomic-scale record of its reactivity into the etched surface — a record that can be read with a scanning tunneling microscope (STM) and decoded into site-specific reaction rates, and thus chemical understanding, with the aid of simulations and spectroscopy. This record overturns the long-standing and much-applied mechanism for the aqueous oxidation of the technologically important face of silicon, Si(100), and shows that the unusually high reactivity of a previously unrecognized surface species leads to a self-propagating etching reaction that produces near-atomically flat Si(100) in a beaker at room-temperature — a long-standing technological goal. These findings show that, contrary to expectation, the low-temperature oxidation of Si(100) is a highly site-specific reaction and suggests strategies for functionalization by low-temperature, solution-based reactions.

COLL 595

Award Address (ACS Award in the Chemistry of Materials sponsored by E. I. du Pont de Nemours and Co.). Emerging science of nanocrystals

A. Paul Alivisatos*, paul.alivisatos@gmail.com.Department of Chemistry, University of California, Berkeley, CA 94720, United States*

This talk will chart the development of a fundamental building block of nanoscience—colloidal inorganic nanocrystals. We will examine fundamental scaling laws for size and shape-dependent properties; the ability to synthesize nanocrystals with controlled composition, topology, and connectivity; the deep applications of artificial nanostructures in biology; the study of nanocrystals at the single particle level; the emergence of collective behavior when nanocrystals are coupled together; and the prospects for nanocrystals to play an important role in energy science and technologies.

COLL 596

Structural design and synthetic chemistry of integrated nanocatalysts

Hua Chun Zeng*, chezhc@nus.edu.sg.Chemical and Biomolecular Engineering, National University of Singapore, Singapore, Singapore*

Despite decades of research, the prevailing catalyst technology for heterogeneous catalysis remains largely as an art than as a science. Rapid development of nanotechnology and materials chemistry in recent decades however provides us new capacity to reexamine the existing catalyst design and processing methods. An important advancement from the above research is that the catalytic materials can now be prepared in a greater precision. With newly gained controllability over particle composition, structure, shape and dimension, researchers in this field will be able to enter next phase of catalyst development for general heterogeneous catalysis if they find new bridging ways between the old and new technologies. One possible way seems to be integrating active nanostructured catalysts onto design-built catalyst supports which are “not-so-nano” in dimension but with accessible hierarchical pore and cavity spaces. Note that such catalyst devices still remain the essence of traditional catalysts (i.e., “catalyst-plus-support”), but they involve different design and integration processes in construction and they show good advantages in performing catalysis.

In this presentation, we will report some of our recent progress in this technologically important area – development of state-of-the-art catalytic nanomaterials.[1-6] In particular we will first address the current issues of nanocatalysts research, and then introduce various possible forms of design and types of integration for catalyst fabrication with increasing compositional and structural complexity, including tunable smart features and functionalities. It is further proposed to anchor sub-nanometer metal-clusters, organometallic complexes, organocatalysts and enzymes onto surfaces of device-walls and shell-pores of this type of catalysts. At the same time, we will also address the important roles of surface analytical techniques in the development of these new-generation heterogeneous catalysts.

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COLL 597

Vinyl acetate formation pathways and selectivity on model metal and alloy catalyst surfaces

***Wilfred T Tysoe**, wtt@uwm.edu.Chemistry and Biochemistry, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53211, United States*

Surface reaction pathways are explored on model single crystal catalyst surfaces using a combination of surface science experiments in ultrahigh vacuum, in-situ monitoring of the surface intermediates during reaction, and by using density functional theory (DFT) calculations. This approach enables detailed reaction pathways to be obtained and is illustrated using palladium- and palladium-gold alloy catalyzed synthesis of vinyl acetate monomer (VAM). It is shown that vinyl acetate is formed on a Pd(111) model catalyst

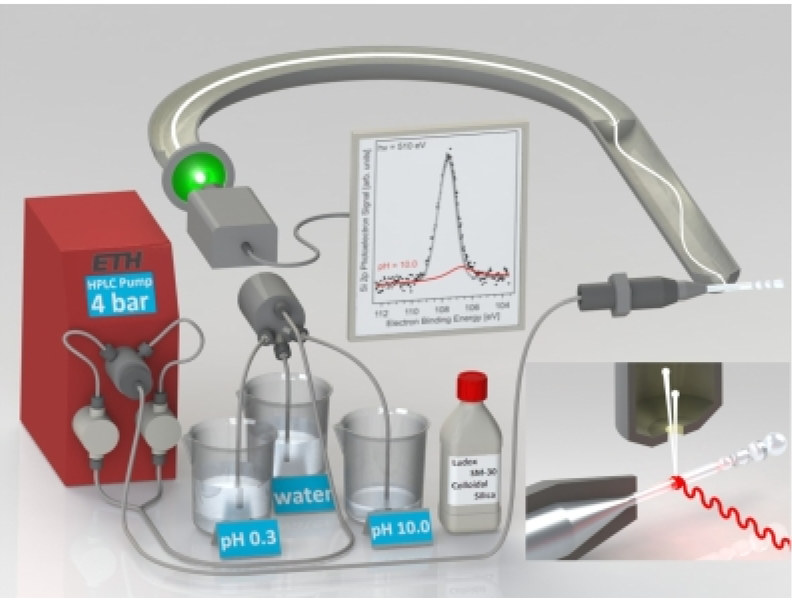
via the so-called Samanos pathway, where reaction is initiated by coupling between ethylene and surface acetate species to form an acetoxyethyl intermediate that decomposes by β-hydride elimination to form VAM. The way in which adsorbate coverage affects both reactivity and selectivity is discussed. Gold-palladium alloys are found to improve the selectivity of the commercial catalyst. The origins of the catalytic selectivity and activity of the alloys are also investigated by exploring reactions on well-characterized Au/Pd(111) and Au/Pd(100) model alloys.

COLL 598

In situ XPS and XAS at the liquid-nanoparticle interface

Matthew A. Brown[1], *matthew.brown@chem.ethz.ch, Jeroen A. van Bokhoven*[1,2]*.Â (1) Institute for Chemical and Bioengineering, ETH Zurich, Zurich, SwitzerlandÂ (2) Swiss Light Source, Paul Scherrer Institute, Villigen PSI, Switzerland*

In situ electron spectroscopy is a fast emerging field that provides unique opportunities across several disciplines. Here we describe our recent extension of in situ XPS and XAS for applications at the solution-oxide nanoparticle interface using a liquid microjet. In situ electron spectroscopy at the liquid-oxide NP interface provides a means to investigate the local interface structure with unprecedented detail. We give some examples from our current area of interest, the water-silica nanoparticle interface, which have identified a size-dependent surface charge density, the role of surface charge density in the affinity of the particles' for the vapor-liquid interface, the true surface potential at the interface, and the response to specific ions (Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ba^{2+}, and Al^{3+}) in basic solutions. We conclude by giving a general outlook of the method with potential applications for catalysis, soft-matter, and ultra fast time dependent processes.



COLL 599

In situ surface-enhanced Raman spectroscopic studies of formic acid electrooxidation on Pd and Pd/Pt thin films deposited on silica core-gold shell (SiO_2@Au) nanoparticle arrays

***Charles K Dotse**, dotseck@miamioh.edu, Shouzhong Zou.Chemistry & Biochemistry Department, Miami University, Oxford, Ohio 45056, United States*

Direct formic acid fuel cells (DFAFCs) have attracted much attention recently due to several advantages of using formic acid as the fuel over hydrogen or methanol. DFAFCs are less sensitive to fuel 'crossover', have fast oxidation kinetics, and have a much higher theoretical cell voltage than hydrogen fuel cell or direct methanol fuel cells (DMFCs). Even though DFAFCs have lower volumetric energy density (2104 WhL^{-1}) than neat DMFCs, this is compensated for by the use of high concentration of formic acid. Pt- and Pd-based catalysts are commonly used in DFAFCs. However, problems of low catalytic activity and/or instability of Pt- and Pd-based catalysts are issues of great concern, and formic acid oxidation mechanism is under active debate. A number of spectroscopic techniques such as infrared reflection absorption spectroscopy (IRAS), sum frequency generation (SFG), electron energy loss spectroscopy (EELS), surface-enhanced infrared absorption spectroscopy (SEIRAS) with attenuated-total reflection (ATR) etc. have been used in previous studies to elucidate molecular speciation, bonding and reactivity of adsorbates on metal surfaces. These methods have provided valuable information on understanding the formic acid oxidation mechanism. In this study, we will use surface-enhanced Raman spectroscopy to study formic acid oxidation on Pd and Pd/Pt thin films. The SERS will be supported on uniform arrays of SiO_2@Au core- shell nanoparticle arrays. The Pd and Pd/Pt thin films are deposited by a redox

replacement method. With the advantage of high surface sensitivity provided by the core-shell nanoparticles and the ability of SERS to probe low frequency vibration modes, we expect the study will provide new insights into formic acid oxidation on Pd and Pd/Pt surfaces. Results from SERS studies will be discussed and compared with previous vibrational spectroscopic studies.

COLL 600

In-operando characterization of the structural dynamics of nanoscale catalytic materials

***Ralph Nuzzo**, r-nuzzo@illinois.edu.Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana-Champaign, Illinois 61801, United States*

The electronic and atomic structural properties of nanoscale metal catalysts exhibit complex structural/dynamical influences with origins related to impacts due to particle size, metal-support interactions, and specific—and strongly condition-dependent—features of metal-adsorbate bonding. The experimental investigation of these factors, as well as the elucidation of the impacts they have on mechanisms in catalysis, are hindered by their interdependency in working catalysts. In this talk I will discuss methods suitable for characterizing such features using combined high spatial/energy resolution methods of electron microscopy and x-ray absorption spectroscopy methods—illustrating their application to both model systems and functional catalysts. I will explore the emerging understandings coming from recent collaborative studies that examine dynamical features that underpin both condition responsive bond-strains and perturbations of electronic structure in supported heterogeneous catalysts, and the complexities that arise due to the interplay of metal-support and metal-adsorbate bonding effects. The work extends insights into the fluxional structural dynamics that are manifested in these systems, a feature harboring significant consequences for understandings of both their properties and mechanisms of action.

COLL 601

Design and synthesis of advanced metal catalysts with atomic layer deposition

***Junling Lu**[1], junling@ustc.edu.cn, Jeffrey W. Elam[2], Peter C. Stair[3,4].Â (1) Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230026, ChinaÂ (2) Energy Systems Division, Argonne National Laboratory, Argonne, IL 60439, United StatesÂ (3) Chemical Sciences & Engineering Division, Argonne National Laboratory, Argonne, IL 60439, United StatesÂ (4) Department of Chemistry, Northwestern University, Evanston, IL 60208, United States*

Supported metal nanoparticles are among the most important catalysts for many practical reactions. The catalytic performance strongly depends on the size, composition, and structure of the metal nanoparticles as well as the underlying support. Conventional synthesis methods including impregnation, ion exchange, and deposition-

precipitation have been used to control and tune these factors, to establish structure-performance relationships, and to develop better catalysts. Meanwhile, the stability of metal nanoparticles against sintering has been improved by the application of protective layers, such as polymers and oxides that encapsulate the metal particle. This often leads to decreased catalytic activity due to a lack of precise control over the thickness of the protective layer.

A promising new method of catalyst synthesis is atomic layer deposition (ALD). ALD is a variation on chemical vapor deposition wherein metals, oxides, and other materials are deposited on surfaces via a sequence (usually binary) of self-limiting reactions. The self-limiting character of the reactions makes it possible to achieve uniform deposits on high-surface-area porous solids. Hence, design and synthesis of advanced catalysts at the nanoscale becomes possible through precise control over the structure and composition of the underlying support, the catalytic active sites, and the protective layer. In this presentation, I will describe the application of ALD to synthesize highly uniform supported metal catalysts and to apply oxide overcoats with atomically-precise thickness control for stabilization of metal nanoparticles while preserving their catalytic function. [1-4]

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COLL 602

Coverage-mediated reaction mechanisms at ordered metal surfaces

***Kai Wu**, kaiwu@pku.edu.cn.College of Chemistry, Peking University, China*

Coverage effect on surface reaction mechanism has been noticed. Previously, people recognize that surface coverage affects the reaction mechanism by tuning the adsorption and activation sites of molecules at surfaces. This is a static picture. However, as surface may possess mobile adatoms, molecules may change their binding modes with these adatoms or substrate atoms to form different reaction intermediates, and hence mediate the reaction mechanisms at surface upon coverage change. We here present several case studies showing this coverage mediation effect. The prototype reactions employed are the Ullmann coupling reactions of 4-bromophenyl and its derivatives on ordered noble metal surfaces by using scanning tunneling microscopy, x-ray photoemission spectroscopy and density functional theory calculations. The Ullmann coupling reaction was first reported by Ullmann and Bielecki

in 1901 on the homocoupling of aromatic halides on Cu-catalyst at elevated temperatures, leading to various coupling products carrying different functional groups via the dehalogenation and novel C-C bond formation between the aromatics carrying the halogen atoms. Afterwards, other metal-containing catalysts such as Pd- and Ni-catalysts were utilized to catalyze the coupling reactions, aiming at lowering the reaction energy barrier and achieving higher yields. In our study, we obtained direct experimental evidence showing that at full coverage, the catalytic cycle of the 4-bromophenyl molecule on silver involves the detachment of the bromine atom from the initial reactant to form an organometallic intermediate containing one silver adatom connected by biphenyls. The silver atom in the intermediate may reside either on two-fold bridge or three-fold hollow sites. The hollow site turns out to be catalytically more active than the bridge one, allowing the achievement of site-mediated reaction from the intermediate to the final coupling product, p-quaterphenyl, at different temperatures. However, at submonolayer coverage, the above-described organometallic intermediates turn into clover intermediates pinned down to the substrate metal atoms, in which the orientations of the biphenyl groups are dictated by the underlying lattice structures at higher temperatures, enabling us to tune the reaction pathways. More reaction examples will be also presented to form a general picture for the Ullmann coupling reactions at noble metal single crystal surfaces.

COLL 603

Operando characterization of supported Pd nanoparticles during CO oxidation

Susannah L Scott[1,2]*, sscott@engineering.ucsb.edu, Ryan C Davis*[1]*, Zachary Jones*[1]*.Â (1) Department of Chemistry & Biochemistry, University of California, Santa Barbara, Santa Barbara, California 93106, United StatesÂ (2) Department of Chemical Engineering, University of California, Santa Barbara, Santa Barbara, California 93106, United States*

The highly dispersed metal nanoparticle catalysts Pd/Al_2O_3 and Pd/CeO_2/Al_2O_3 respond dynamically to changes in the reactive atmosphere during CO oxidation in a packed-bed reactor. A combination of IR spectroscopy of adsorbed CO and X-ray absorption spectroscopy at the Pd K-edge reveal that surface and sub-surface Pd atoms undergo non-simultaneous redox changes as the temperature increases. The temperatures required to trigger these changes depend on the inlet P(CO)/P(O_2) ratio, as well as the presence of absence of CeO_2. Under lean conditions (P(O_2) >> P(CO)), a dramatic and abrupt enhancement in reactivity occurs simultaneous with formation of a surface oxide as the temperature of Pd/Al_2O_3 increases. In the absence of ceria, the surface oxide is barely observable under near-stoichiometric conditions (P(O_2) ~ P(CO)), and the catalyst is less active over the entire temperature range, while the ceria-promoted catalyst is readily oxidized even at low temperature and is more active.

COLL 604

Ultrasound imaging, gamma scintigraphy and HIFU therapy with perfluorocarbon loaded iron-silica nanoshells

Alexander Liberman[1], *aliberma@ucsd.edu, Zhe Wu*[2]*, Christopher Barback*[2]*, Robert Viveros*[4]*, Sarah L. Blair*[5]*, David Vera*[2]*, Lesley G. Ellies*[6]*, Robert F. Mattrey*[2]*, William C. Trogler*[3]*, Andrew C. Kummel*[3]*.Â (1) Material Science and Engineering Program, University of California, San Diego, La Jolla, California 92093, United StatesÂ (2) Department of Radiology, University of California, San Diego, San Diego, California 92093, United StatesÂ (3) Department of Chemistry and Biochemistry, University of California, San Diego, San Diego, California 92093, United StatesÂ (4) Department of Nanoengineering, University of California, San Diego, San Diego, California 92093, United StatesÂ (5) Moores Cancer Center, University of California, San Diego, San Diego, California 92093, United StatesÂ (6) Department of Pathology, University of California, San Diego, San Diego, California 92093, United States*

The reported positive margin rate from wire localized excisions of breast cancers is approximately 20-50%; however, by preoperatively injecting a radioactive seed into the tumor under CT guidance, the excision rate is halved because the surgeon can constantly reorient the dissection to place the seed in the center of the specimen. Unfortunately, radioactive seed localization has several safety challenges, only single focus can be localized, and incisions are required to implant the seeds, so it is rarely employed. As a safe alternative, perfluoropentane-filled Fe-SiO_2 particles have been developed, which can be used for ultrasound-guided surgery even for multiple foci. The particles are synthesized through a sol-gel method with tetratmeyl orthosilicate and iron ethoxide on a polystyrene template, and calcined to create hollow, rigid nanoshells. *In vitro* studies have shown that continuous particle imaging time is up to approximately 45 minutes. *In vivo* particle injection longevity studies have been performed in tumor bearing mouse models show signal presence up to ten days post injection. To study biodistribution, nanoshells were functionalized with DTPA and radiolabeled with Indium-111 and then imaged by gamma scintigraphy over 72 hours. Scintigraphic imaging and gamma counting confirm that particles undergoing IV delivery to tumor bearing mice will passively accumulate in the tumors.

Perfluorocarbon filled silica shells break under acoustic excitation to increase acoustic energy absorption and reduce acoustic cavitation threshold. Therefore they may also be employed as a sensitizing agent in high intensity focused ultrasound (HIFU) therapy. It was found that nanoshells systemically adminstered to breast tumor bearing mice could be cavitated by HIFU 24 hours after administration. This mechanical cavitation caused liquification within the focal volume of the HIFU which contained the nanoshells within seconds of the HIFU application. This may potentially allow for a larger area to be ablated in less time with less power.

COLL 605

Oh so sweet! Carbon nanoparticles from natural sweeteners for cancer theranostics

***Shaneen F Braswell**, braswel2@illinois.edu, Sumin Kim, Dipanjan Pan.Department of Bioengineering and Beckman Institute of Advanced Science and Technology and Carle Foundation Hospital, University of Illinois at Urbana Champaign, Urbana, Illinois 61801, United States*

There has been a surge of interest in utilizing carbon nanoparticles as optical imaging agents driven in large part by their inherent chemical inertness, strong luminescence properties and biocompatibility. However, current carbon nanoparticles are cumbersome in preparations that rely on conventional methods, albeit reliable, but cannot scale to large quantities for clinical use. Here, we have designed and synthesized for the first time, luminescent carbon nanoparticles from commercial food grade, agave nectar and molasses. A simple and inexpensive single-pot green chemistry approach has been developed, which entails surface passivation of these naked carbon nanoparticles with a dendritic or hyperbranched organic macromolecule. Interestingly, the surface passivation with hyperbranched polymers (generation 2-4) facilitated the absorption of the particles in the near infrared region. The as-synthesized carbon nanoparticles (8-25nm) were prepared using a domestic microwave. The particles had a tunable fluorescence properties within 650-800nm, which is ideal for in vivo imaging. The syntheses also involved the use of clinically adopted anticancer agents (e.g. doxorubicin, paclitaxel) to generate nanoparticles with 'theranostic' properties. Dissolution studies indicated an ~90% encapsulation efficiency for the drug moelcules. We will discuss characterization of these particles using dynamic light scattering, Fourier Transform Infrared spectroscopy, Atomic Force microscopy, Transmission Electron microscopy, Scanning Electron microscopy, Raman spectroscopy, electrophoretic potential, and cytotoxicity analysis for evaluation of their chemical structure, morphology and biocompatibility. This approach holds immense promise towards clinical scalability, reduced procedural expense and improved patient outcomes. We envision that these colloidal nanoscale theranostic agents will provide invaluable information on the progression of cancer as well as enable enhanced therapy and diagnosis.

COLL 606

Enhancing targeted tumor treatment by near IR light-activatable photodynamic-photothermal synergistic therapy using theranostic nanoplatform

***Paresh Ray**, paresh.c.ray@jsums.edu.Chemistry & Biochemistry, Jackson State University, Jackson, MS 39232, United States*

Recent advances with our better understanding of the molecular underpinnings of cancer & cell signaling pathways, it has become apparent that a single therapeutic agent show limited efficiencies, poor tolerability, and resistance profiles. Here we will discuss our recent reports on the development of methylene blue (MB) bound nanoplatform, which is capable of delivering targeted diagnostic and combined synergistic photothermal & photodynamic treatment of cancer. We show <tt></tt> that, once nanoparticle binds with the target cell surface, it can detect LNCaP human

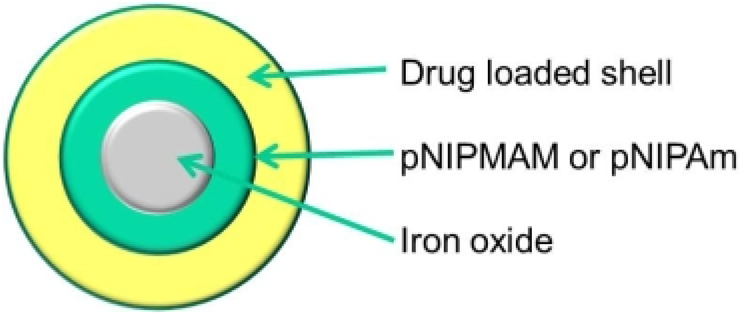
prostate cancer cell selectively using fluorescence imaging. Our result shows that the therapeutic actions can be controlled with external NIR light. Our data for targeted photodynamic & photothermal treatment using NIR light, show that the multimodal treatment regime can dramatically enhance the possibility of destroying cancer cells in vitro.

COLL 607

Investigation of core-shell N-alkyl substituted acrylamides for theranostic delivery of chemotherapeutics

Jonathan T Peters[1]*, jonathan.peters@utexas.edu, Isha Verma*[2]*, Nisha Lizana*[2]*, Nicholas A Peppas*[1,2,3]*.Â (1) Department of Chemical Engineering, The University of Austin at Texas, Austin, Texas 78712, United StatesÂ (2) Department of Biomedical Engineering, The University of Austin at Texas, Austin, Texas 78712, United StatesÂ (3) College of Pharmacy, The University of Austin at Texas, Austin, Texas 78712, United States*

N-Alkyl acrylamide polymers, such as poly(N-Isopropylacrylamide) (pNIPAm) have been extensively investigated due to their lower critical solution temperature (LCST) near physiological temperature. Issues are encountered when these systems are used to deliver small molecule drugs, such as model chemotherapeutics like doxorubicin and 5-fluorouracil, as the concentration gradient between the polymeric drug and blood steam leads to mild release of the toxic drugs [1]. In order to counteract this phenomenon, a new polymeric system should be devised in order to limit the premature release of the devastating payload. N-alkyl substituted acrylamides demonstrate a useful burst-like release when intensely heated by internal magnetic nanoparticles. This release can be used to force out drugs loaded into a shell of a non-responsive hydrogel system designed to interact with the predominately hydrophobic chemotherapeutics. In order to develop this system a number of hydrogel systems are analyzed for hydrophobicity and chemotherapeutic interaction. The hydrogel systems are comprised of Tert-butylmethacrylate (TBMA), N-vinylpyrrolidone (NVP) , and methyl methacrylate(MMA) were compared to pNIPAM and p(N-isopropylmethacrylamide) (pNIPMAM) and copolymers comprised of the various monomers. These systems are then combined into core shell systems [Figure 1] and tested for magnetically triggered release to determine the effect of the shell on the externally triggered release.



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COLL 608

Novel targeted theranostic tools for cancer applications

***Jianghong Rao**, jrao@stanford.edu.Department of Radiology, Stanford University, Stanford, CA 650-736-8563, United States*

Our main research focus is to design, synthesize and evaluate novel molecular probes for imaging or manipulating targeted biomolecules in normal and diseased states. New projects often begin by identifying an important molecular target and then designing specific probes for that target. Next we evaluate new probes by performing cellular and *in vivo* imaging experiments. We also develop novel biosensors, new strategies for early biomarker detection in biological samples, and improved methods of high throughput drug screening, and drug delivery. Our favorite targets are often enzymes that catalyze specific biochemical transformations, such as proteases, beta-lactamases, ribozymes, and kinases.

COLL 609

“Nano-flares” for the analysis of circulating cancer cells

***Chad A. Mirkin**[1], chadnano@northwestern.edu, C. Shad Thaxton[2], Tiffany L Halo[1], William E. Briley[1], Nicholas L. Angeloni[2], Kaylin M. McMahon[2].Â (1) Department of Chemistry and International Institute for Nanotechnology, Northwestern University, Evanston, IL 60208, United StatesÂ (2) Department of Urology, Northwestern University, Chicago,, IL 60611, United States*

Cancer metastasis is the leading cause of mortality among cancer patients. Indeed, most traditional methods for diagnosing it rely on analysis of secondary tumor sites after metastasis has already occurred. Therefore, the ability to detect metastatic cancer cells from patient blood samples, before the development of secondary tumors, would represent a revolutionary advance in cancer diagnostics. We have designed and synthesized a nanoparticle-based system, which moves toward accomplishing this goal. Nano-flares are spherical nucleic acid (SNA)-gold nanoparticle constructs, which are bound to displaceable fluorescent reporter strands. These structures have the ability to efficiently enter cells without the use of transfection agents and provide an intracellular fluorescence signal correlated with the concentration of a target molecule. Therefore, they can be used to translate traditional extracellular diagnostic approaches to an intracellular environment. Advantageously, this nanoconjugate system exhibits all of the novel cooperative properties of SNA-gold nanoparticle conjugates, including enhanced target hybridization, resistance to enzymatic breakdown and low immune response and can be easily combined with gene regulation technologies. Specifically, we have developed a functional assay for detecting multiple putative metastatic markers (such as Twist, vimentin and fibronectin) in circulating breast cancer cell populations. Furthermore, we have coupled nano-flare technology with flow cytometry to isolate these small breast cancer cell populations in cell culture and from whole blood samples for individual analysis. We are currently working to validate this novel nano-flare-based approach against traditionally-used assays, as well as to improve the sensitivity and specificity of nano-flares. We are also extending the capability of the system to address the need for multiplexed approaches, which allow for semi-quantitative detection of multiple mRNA targets simultaneously.

COLL 610

Nanotheranostics for passive and active drug targeting to tumors

Twan Lammers, *tlammers@ukaachen.de.Experimental Molecular Imaging, RWTH Aachen University, Aachen, NRW 52074, Germany*

Many different drug delivery systems and drug targeting strategies have been designed and evaluated over the years, especially for the treatment of cancer. Examples of routinely used drug delivery systems are liposomes, polymers, proteins and micelles, and examples of commonly employed drug targeting strategies are passive targeting, active targeting to cancer cells, active targeting to endothelial cells and triggered drug release. In the present lecture, I will address the principles, progress and pitfalls of passive and active drug targeting. In particular, the high variability observed in EPR-mediated passive drug targeting, the often over-interpreted potential of active drug targeting, and the relatively disappointing clinical performance of tumor-targeted nanomedicines will be addressed. Strategies to overcome these shortcomings, based on the use of nanotheranostics and non-invasive imaging techniques, as well as on nanomedicine-based combination therapies, will also be discussed.

COLL 611

Pd-catalyzed C-C coupling of aryl bromide on a Au(111) surface: Activation energy determination and mechanistic investigations

Jinne Adisoejoso[1,2]*, Jinne.adisoejoso@chem.kuleuven.be, Tao Lin*[2]*, Xue Song Shang*[3]*, Ke Ji Shi*[3]*, Aditi Gupta*[2]*, Pei Nian Liu*[3]*, Nian Lin*[2]*.Â (1) Department of Chemistry, Katholieke Universiteit Leuven, Heverlee, BelgiumÂ (2) Department of Physics, The Hong Kong University of Science and Technology, Kowloon, Hong Kong Special Administrative Region of ChinaÂ (3) Shanghai Key Laboratory of Functional Materials Chemistry and Institute of Fine Chemicals, East China University of Science and Technology, Shanghai, China*

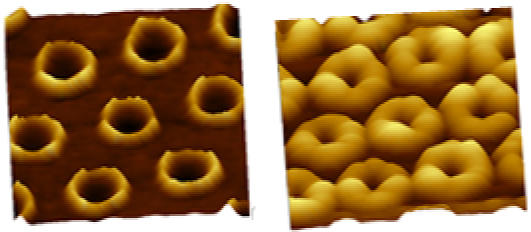
Palladium is one of the most versatile catalysts of C-C bond formation in solution; it is widely used in homo-coupling and cross-coupling reactions. Although great success has been achieved for the Pd catalysis in solution, to the best of our knowledge, the surface confined covalent C-C formation catalyzed by Pd has never been reported. Here we describe Pd-catalyzed covalent C-C bond formation between molecules of 5,15-bis-(4-bromo-phenyl)-10,20-diphenyl porphyrin. We also aimed to determine reaction rate constants and activation energy in order to gain detailed mechanistic insights. This remains a challenge for on-surface reactions because the myriad techniques developed for reactions in solution do not apply, necessitating single-molecule techniques.Therefore we analyzed reaction products in situ using scanning tunneling microscopy (STM) at single-molecule resolution under isothermal conditions. We also compared our kinetic and thermodynamic findings for the Pd-catalyzed reaction with those for the corresponding Cu-catalyzed reaction. This qualitative comparison, together with Monte Carlo simulations, suggests that Pd and Cu catalyze the coupling reaction differently.

COLL 612

Spatially-confined chemical reactions: Application of particle lithography for studies of surface self-assembly

***Jayne C Garno**, jgarno@lsu.edu.Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, United States*

Particle lithography offers a versatile approach to generate well-defined surface platforms of organosilanes, organothiols, nanoparticles or proteins. With particle lithography, billions of nanostructured test elements can be prepared with high throughput, with relatively few defects. Procedures for particle lithography are based on the natural and spontaneous processes of self-assembly to define the arrangement of latex or silica mesospheres to produce a surface mask. When the mesosphere masks are removed by a rinsing step, the area of contact between the spheres and the surface defines discrete locations for further reactions. Exposed sites of the substrate provide nanoscale containers for confining surface reactions to defined areas to construct supramolecular assemblies. For nanopatterns of self-assembled monolayers, the interfacial endgroups can be designed to spatially define the surface selectivity for adsorption of proteins, nanoparticles or electrolessly deposited metals. An emerging challenge is to investigate physical changes for surfaces or materials in response to environmental parameters at the nanoscale. Multilayer nanostructures of octadecyltrichlorosiloxane provided a test platform for scanning probe studies of solvent-responsive properties where the sides of designed ring structures expose a 3D interface for studying the interaction of solvents with molecular side-groups. Nanostructures change significantly in size and shape when imaged in certain liquid media or with heated conditions. Approaches for nanoscale lithography will be described for preparing molecular test platforms suitable for scanning probe studies of surface reactions.



AIR ETHANOL

COLL 613

On-surface synthesis of gold-organic polymers

Haiming Zhang[1], ***Lifeng Chi***[1,2], *chi@uni-muenster.de.Â (1) Physikalisches Institut, Universitaet Muenster, Muenster, NRW 48161, GermanyÂ (2) Institute of Functional Soft- and Nanomaterials, Soochow University, Suzhou, Jiangsu, China*

Covalently-connected metal-organic polymers have been predicted as an intermediate state by theoretical simulations both on Cu and Ag and verified experimentally in recent STM studies. However, less addressed is the existing of stable gold-organic hybrid intermediates in aryl-aryl coupling reactions on gold surface, which is of particular interest as its local electronic structures studied by scanning tunnelling spectroscopy (STS) may allow a basic understanding of the electron transport through covalent Au-C bonds.

In this talk, we will present the recent studies concerning on-surface synthesis of gold-organic hybrids under UHV-conditions via surface assisted coupling reactions by using several precursor molecules containing halogen-substitutions. Some precursors lead to stable gold-organic polymers, while others serve as the intermediate state and lead to the formation of graphene nanoribbens during the further annealing process. Surface temperature related reaction pathways and species is proposed based on experimental data and supported by the DFT calculations.

COLL 614

Controlling chemical processes at the level of single molecules

Leonhard Grill, *leonhard.grill@uni-graz.at.Department of Physical Chemistry, University of Graz, Graz, Austria*

The use of functional molecules and their assembly into pre-defined architectures are key challenges in nanotechnology and of interest in various fields from molecular electronics over novel materials to molecular machines. We study chemical processes of single functional molecules on surfaces by scanning tunneling microscopy under ultrahigh vacuum conditions and at low temperatures, thus allowing submolecular resolution analysis. The central objectives are (i) to control and understand these functions at the single-molecule level, (ii) the controlled molecular assembly in two dimensions, and (iii) to investigate the influence of the atomic-scale environment, i.e. interactions of the molecules with other adsorbates and the surface.

Various examples of how to control chemical processes will be discussed, ranging from covalent molecular linking to intramolecular reactions. The first is realized by on-surface polymerization [1] where specifically designed molecular building blocks are connected to two-dimensional networks or one-dimensional chains, which can act as molecular wires [2,3]. The polymerization process can be catalytically controlled via the surface material and precise structure [4]. Furthermore, a hierarchical growth mode could be achieved by the sequential creation of reactive sites within the molecules on demand [5]. On the other hand, chemical processes within individual molecular can be controlled via their environment. This was observed for molecular switches, where the atomic-scale surroundings cause drastic changes in their switching probability and lead to a spatially periodic switching pattern [6]. Recently, we could show that the rate of an intramolecular hydrogen transfer reaction can be tuned up and down by single atoms in the vicinity of the molecule [7].

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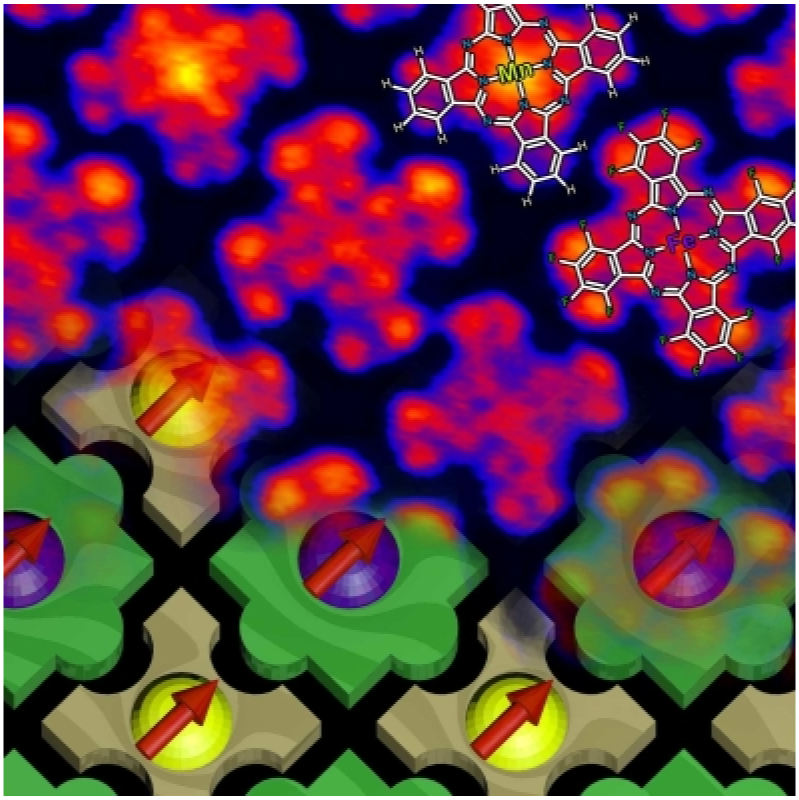
COLL 615

On-surface chemistry and supramolecular chemistry: Engineering with molecules at interfaces

***Thomas A. Jung**, thomas.jung@psi.ch.Molecular Nanoscience, Paul Scherrer Institute, Villigen PSI, Switzerland*

By combination of supramolecular-, coordination- and magneto-chemistry we create self-assembled on-surface architectures also consisting of spin-bearing complexes. We discuss the interplay of electronic[1] and spin states[2] at specifically designed interfaces. Reversible control of the spin-state, as well as variation of the sign and strength of the exchange coupling with the magnetic substrate is demonstrated. The physics and chemistry of these unique functional systems provides insight into novel materials and their electronic and spintronic properties which emerge from the interaction of their components on many scales, down to single atoms and molecules.[3]



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COLL 616

On-surface click chemistry, a novel metal coordination network and conformational dynamics in molecular self-assembly

Trolle Linderoth*, trolle@inano.au.dk.Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Aarhus, Denmark*

I will describe recent results concerning molecular reaction and organization on surfaces as studied by STM and XPS in collaboration with chemical synthesis and DFT modeling. Within the field on on-surface synthesis, we have explored the prototypical ”click”-reaction of azide-alkyne cycloaddition for reactants adsorbed on a Cu(111) surface under UHV conditions [1]. The reaction is shown to proceed and azide decomposition is identified as the factor limiting the yield. Secondly, we have identified a novel metal coordination network formed through dehydrogenation of tetrahydroxybenzene [2]. Finally, we have investigated a model system of binary conformational switches based on a series of Oligo-Naphthalene Ethynylenes [3]. Using time-resolved STM we have visualized the dynamics of conformational switching and quantified the selection of conformational states in self-assembled structures.

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COLL 617

From (supra)molecular assemblies to covalently coupled nanostructures on surfaces: Insight from scanning tunneling microscopy and photoemission experiments

***Meike Stöhr**, m.a.stohr@rug.nl.Zernike Institute for Advanced Materials, University of Groningen, Groningen, The Netherlands*

Supramolecular recognition is a useful tool to realize highly organized and periodic structures at the nanometer scale. The understanding of the interplay of the underlying intermolecular and molecule substrate interactions is highly important since the resulting molecular structures are determined by them. Since supramolecular recognition is based on non-covalent interactions the stability of the resulting structures is quite often weak. Thus, for the formation of molecular structures with improved stability and conductivity, the concept of on-surface polymerization [1] has been introduced recently.

In my presentation, I will discuss different examples for the formation of supramolecular as well as polymeric structures on surfaces from specially designed molecular building blocks. For the supramolecular structures the self-assembly of an achiral triphenylamine derivative featuring cyano functionalities [2] as well as a binary H-bonded system will be discussed. For the two systems, the substrate influence both on the development of the intended intermolecular interactions and on the formation of periodic structures was studied. To obtain polymeric structures on surfaces, a biphenyl derivative featuring protecting groups was employed [3]. Control over the reactivity and the size of the polymeric structures was in the focus of these investigations.

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COLL 618

Role of the byproducts in on-surface polymerization

Josh Lipton-Duffin[1]*, duffin@emt.inrs.ca, Marco Di Giovannantonio*[2]*, Gianluca Galeotti*[1]*, Stefano Tebi*[2]*, Giorgio Contini*[2]*, Dmitrii Perepichka*[3]*, Federico Rosei*[1]*.Â (1) Centre Ã‰nergie, MatÃ©riaux et TÃ©lÃ©communications, Institut National de la Recherche Scientifique, Varennes, QC J3X 1S2, CanadaÂ (2) Istituto di Struttura della Materia, Consiglio Nazionale della Ricerca, Rome, RM 00133, ItalyÂ (3) Department of Chemistry, McGill University, Montreal, QC H3A 2K6, Canada*

Recent interest in two-dimensional materials has inspired numerous efforts toward the synthesis of polymeric materials on surfaces. With the substrate's ability to template growth in two dimensions, we may thereby create analogues of graphene with tailored chemical functionalities. While a handful of researchers have demonstrated the ability to grow well-ordered 2D structures, achieving long-range order in 2D polymers is challenging, and our understanding of the factors driving the growth is incomplete. In this talk I will describe the of our group's effort into the synthesis of these novel materials, and our characterizations using traditional methods of surface science. By simplifying the experiment to single-dimensional polymers, we have determined that the reaction intermediates play a significant role in the growth, and may have important consequences for producing ordered structures in 2D.

COLL 619

Environment-friendly epoxy magnetic nanocomposite with reduced flammability

Xi Zhang[1]*,* ***Suying Wei***[2]*, suying.wei@lamar.edu,* ***Zhanhu Guo***[1]*, zhanhu.guo@lamar.edu.Â (1) Department of Chemical Engineering, Lamar University, Beaumont, TX 77710, United StatesÂ (2) Department of Chemistry and Biochemistry, Lamar University, Beaumont, TX 77710, United States*

Due to the outstanding physical properties, epoxy resin attracts more attention as one of the most important engineered polymers, and it shows wide applications in industry field, including structural material, surface coatings and adhesive. However, the utilization of epoxy is limited by its flammability, and the widely used flame retardant for epoxy resin would generate toxic and corrosive fumes during combustion.[1] Thus, environmental concerns and legislation demands for new flame retardant agents for epoxy resin.[2]

In this project Fe@C, Gr and Gr/Fe@Fe_2O_3 nanoparticles have successfully serve as nanofiller for obtaining magnetic epoxy resin nanocomposite (PNCs) with reduced flammability. The effects of nanofiller loading levels on the thermal stability, flammability, mechanical and magnetic properties were systematically studied. In the TGA test, although the introduction of all three nanofillers caused lower onset decomposition temperature of the PNCs, the Fe@C and Gr/Fe@Fe_2O_3 were found to favor the char

formation from the epoxy resin. The enhanced char residue was also observed during the flammability tests. The flammability performance was evaluated by microscale combustion calorimetry considering the heat release capacity (HR capacity), peak heat release rate (pHRR), total heat release (total HR), and the char residue. And all three kinds of nanocomposite show reduced pHRR and total HR. In addition, foam char layer can be clearly observed in the PNCs with Gr/Fe@Fe_2O_3. The tensile strength observed in the PNCs with 1.0 wt% Gr/Fe@Fe_2O_3 and 5.0 wt% Fe@C nanoparticles is 58% and 60% higher than that of the pure epoxy, respectively. Finally, the magnetic properties of the PNCs with Fe@C and Gr/Fe@Fe_2O_3 are studied and the value of coercivity (*H*c) is observed depends on the loading of the nanofiller.

COLL 620

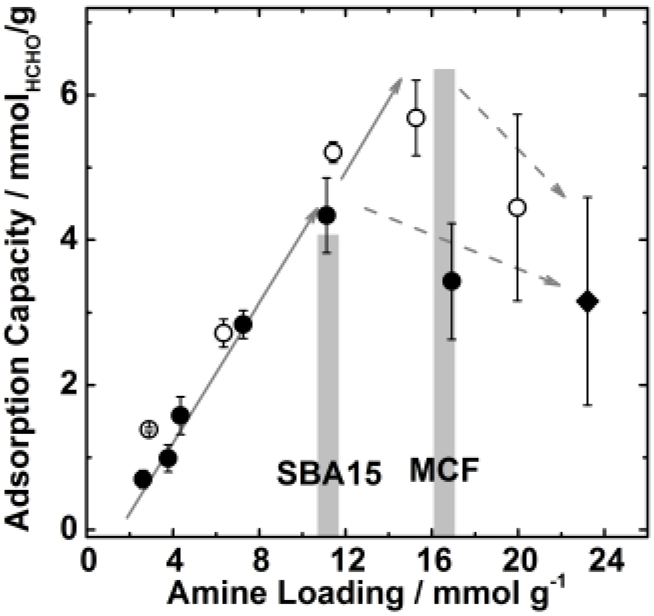
Polymeric amine incorporated porous silicas as adsorbents for trapping of formaldehyde indoor air pollutants

***Akihiro Nomura**, akihiro.nomura@chbe.gatech.edu, Christopher W Jones.Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States*

Indoor air quality is an area of emerging importance for human health and well-being. Here we report that polymeric amine incorporated porous silicas (aminosilicas) have excellent adsorption properties for airborne formaldehyde, which is among the main irritant indoor air pollutants. Branched poly(ethyleneimine) (PEIBr) was incorporated into the ordered mesoporous silica SBA-15 and mesocellular foam silica (MCF).

Â	Â Surface area S_{BET} / m^2 g^{-1}	Pore volume V_p / cm^3 g^{-1}	Pore diameter D_p / nm
Â SBA-15	Â 891	Â 0.90	Â 6.9
Â MCF	740	2.4	26

Figure 1 shows the adsorption capacity of the aminosilicas by SBA15 (●) and MCF (○) under a 100-200 ppm contamination level of airborne formaldehyde. An adsorption capacity of PEIBr bulk polymer (♦) was also plotted. The gray bars in Figure 1 show the maximum amine loadings at which PEIBr could be stored inside of the silica pores of each silica support.



The adsorption capacity increased along with amine loading before reaching the maximum amine loading, showing the highest amine capacity of 4.3 mmol$_{HCHO}$/g for SBA-15 and 5.7 mmol$_{HCHO}$/g for MCF aminosilicas. Once PEIBr was over incorporated, the adsorption performance decreased, with the extra aminopolymer behaving as a bulk polymer, rather than an accessible dispersed phase. These results indicate that the nanostructures of the support play a crucial role in effectively dispersing the aminopolymer and in adsorbing formaldehyde vapor. Because the adsorbed formaldehyde was chemically attached to aminosilica surface by covalent bonds, as verified by ^{13}C solid state NMR analysis, it did not desorb from the aminosilicas under 130 ºC. These adsorption characteristics suggest that aminosilicas can act as effective indoor air purifying materials. The adsorption mechanism will also be discussed.

COLL 621

Reactivity of chromium anchored Al-MCM-41 nanomaterial: An FT-IR study of detoxification of organic compounds

***Dilip K Paul**, dpaul@pittstate.edu.Chemistry, Pittsburg State University, Pittsburg, KS 66762, United States*

The acidity of Cr-incorporated Al-MCM-41 nanomaterials was investigated by adsorbing pyridine using transmission infrared spectroscopy. Both Lewis and Bronsted acid sites were found to be present as determined by corresponding IR modes on surfaces. Adsorption of acetaldehyde was used a model compound to understand the reactivity of the nanoparticles towards catalytic degradation. During adsorption at low temperature, the acetaldehyde molecule binds through H-bonding with surface –OH groups. In addition, a fraction of acetaldehyde adsorbed through Lewis acid sites- Cr (IV) and Al (III). The combination of both H-bonded and Lewis acid sites bound acetaldehyde underwent condensation reaction forming aldol which then dehydrated at elevated temperature forming 2-butenal. Acetaldehyde underwent photodecomposition to CO_2 during photooxidation at 273 K and 173 K This oxidation involves photoactive acetyl radical and Cr ion. A variety of condensation products also identified using TPD during photochemical reaction.

COLL 622

Adsorption of heavy metals on functionalized magnetic mesoporous silica nanoparticles

***Sarah C Larsen**, sarah-larsen@uiowa.edu, Shani Egodawatte.Chemistry, University of Iowa, Iowa City, IA 52242, United States*

Heavy metals, such as Cr, As and Hg, can lead to groundwater pollution and undesirable human health effects. Mesoporous silica has a very high surface areas and a readily modifiable surface. Covalant modification of mesoporous silica is routinely used to optimize the adsorption of heavy metal contaminants through enhanced binding and/or favorable electrostatic interactions. In this study, the adsorptive properties of mesoporous silica and the magnetic properties of iron oxide were combined to prepare a high surface area composite nanomaterial that can adsorb heavy metals and can be recovered using magnetic separation. Magnetic iron oxide nanoparticles were coated with mesoporous silica (MCM-41) to prepare magnetic mesoporous silica (m-MCM-41) with an overall diameter of approximately 100 nm. The resulting materials were functionalized with organosilanes containing amine and thiol functionalities. The magnetic MCM-41 nanoparticles exhibited the highest adsorption capacity for Cr(III) at pH=5.4 relative to the parent, nonmagnetic MCM-41. The Cr(III) adsorption capacity was attributed to a synergistic effect between the iron oxide cores and the MCM-41. Spectroscopic studies are in progress to better understand the molecular details of the adsorption of heavy metals. The magnetic MCM-41 samples showed relatively low arsenic adsorption capacities.

COLL 623

Efficient cesium recovery from fluid flows using a silica-alumina microhoneycomb including Prussian Blue analog nanoparticles

***Shin Mukai**, smukai@eng.hokudai.ac.jp, Yoshinao Kimura, Seiichiro Yoshida, Isao Ogino.Division of Chemical Process Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan*

A serious amount of radioactive Cesium has been widely dispersed around the Fukushima Daiichi nuclear power plant, due to the accident caused by the earthquake which hit the east coast of Japan on March 11, 2011. The development of methods to efficiently recover and safely store such radionuclides is now an urgent issue.

Various materials are known to have the ability to efficiently recover Cesium. Among them Prussian Blue Analogues (PBAs), ferrocyanide insolubilized using bivalent metal cations, is a promising candidate, as it selectively recovers cesium even though it is extremely inexpensive. However, as it is usually obtained in the form of nanoparticles, it is difficult to use them in large-scale processes, especially when they are to be used for high throughput processing.

In this presentation, we attempted to obtain a Cesium adsorbent which can be used for high throughput processing by immobilizing PBA nanoparticles in a silica-alumina microhoneycomb. First, a silica-alumina sol including ferrocyanide was prepared, and after the solution became viscous, bivalent cations that can insolubilize the dispersed ferrocyanide were added. The sol was aged, and then the resulting hydrogel was froze unidirectionally. Ice crystals which appeared within the hydrogel, and elongated in the freezing direction acted as templates, and the hydrogel was molded into a microhoneycomb

Due to the unique structure of microhoneycombs, monoliths having straight and aligned micrometer-sized channels which are formed by walls with a thickness also in the micrometer range, efficient recovery of Cesium from fluid flows without causing a severe hydraulic resistance was found to be achievable. It was confirmed that the microhoneycombs can adsorb Cesium at amounts at least 3 wt% of their total weight (including the weight of the silica-alumina substrate), even at equilibrium concentrations at about 10 ppm.

COLL 624

Ag nanoprism synthesis using cellulose nanofibrils for surface enhanced Raman spectroscopy

***Feng Jiang**, fjiang@ucdavis.edu, You-Lo Hsieh.Fiber and Polymer Science, University of California Davis, Davis, CA 95616, United States*

Silver (Ag) nanospheres and nanoprisms were robustly synthesized using TEMPO oxidized cellulose nanofibrils (CNF) to cap as well as to regulate the shape of Ag nanoparticles. Ag nanospheres were synthesized by reducing $AgNO_3$ by $NaBH_4$ in CNF suspensions and their sizes reduced and size uniformity increased with increasing Ag^+:CNF ratios. The as synthesized Ag nanospheres could be transformed to nanoprisms, showing a sharp peak at 340 nm due to the out-of-plane quadruple resonance and shifting the in-plane dipole resonance from 760-870 nm. Further tuning Ag^+**:** CNF ratio as well as the H_2O_2 etching agent quantity, a wide spectrum of color ranging from red, purple, blue, and turquoise could be obtained, showing widely spanned in-plane dipole resonance peaks from 420 nm to 900 nm. TEM images confirmed the formation of Ag nanoprisms with size ranging from 80-200 nm. Free standing films of CNF/Ag nanoprisms were fabricated and characterized for light transmittance (UV-Vis spectroscopy), elemental compositions (Energy-dispersion X-ray spectroscopy), and crystalline structure (X-ray diffractions). The CNF/Ag nanoprims composites films showed strong surface enhanced raman spectroscopy of Rhodamine 6G with analytical enhancement factor of 3.5x10^3.

COLL 625

Application of porous silicon particulates for lithium ion batteries

Sibani Lisa Biswal, *biswal@rice.edu.Rice University, United States*

There is great interest in developing rechargeable lithium batteries with higher energy capacities and a longer cycle lifetimes. Silicon has very high lithium ion capacity of 4200 mAh/g, and has been suggested as a potential high capacity lithium battery anode material. However, it has been encumbered with serious expansion/ contraction during cycling, increasing internal resistance and resulting in cell failure. Severe silicon pulverization can be triggered by a large volume change (>300%) during lithium alloying (to form LixSi) and de-alloying (to reform Si), which results in electrically disconnected smaller particles. These disconnected particles cause a rapid decrease in cycling stability. Porous silicon structures have been suggested as a potential means to accommodate silicon expansion/contraction while maintaining continuity. We will report on our fabrication of a nanoporous silicon structure by electrochemical etching process. We find that the specific capacity of the battery cell after 1000 cycles with a capacity of 1000 mAh/g.

COLL 626

Synthesis and applications of gold nanoprisms

Beatriz Pelaz[1], *beatriz.pelazgarcia@physik.uni-marburg.de, Pablo del Pino*[3], *Jesús M. de la Fuente*[2]*.Â (1) Physik Department, Philipps UniversitÃ¤t-Marburg, Marburg, GermanyÂ (2) Instituto de Nanociencia de AragÃ³n, Universidad de Zaragoza, Zaragoza, SpainÂ (3) CIC biomaGUNE, San SebastiÃ¡n, Spain*

The optical properties of metallic nanoparticles (NPs) come mainly dictated by their plasmon band. The plasmon band of anisotropic gold nanoparticles can be set in the NIR range by tailoring the anisotropy of the NPs. Most of the methods to produce NIR absorbing gold nanoparticles rely on challenging synthesis with several steps and/or seed-mediated approaches with cetyltrimethylammonium bromide (CTAB) as a surfactant. CTAB is the most widely used and convenient surfactant to synthesize Au nanorods and nanoprisms although it is a well-known toxic cationic surfactant.

Herein, we present a straightforward one-pot synthetic method produce single-crystalline flat-thin triangular gold nanoprisms using “green” reagents. The edge length can be tuned by adjusting the final concentration/molar ratio of gold salt and reducing agent (sodium thiosulfate). This allows tuning the surface plasmon band of nanoprisms along the NIR range.

The biocompatibility and suitability of functional nanoprisms as photothermal agents were studied in cell cultures. Due to their biocompatibility, ease of production, ease of functionalization and remarkable heating features, the nanoprisms discussed herein represent a significant advance in the biocompatibility of nanoparticles and serve as an attractive alternative to those currently in use as plasmonic photothermal agents. Importantly, gold nanoprism are also capable of high resolution visualization of probes under photoacoustic imaging and these can therefore simultaneously deliver anatomical, functional and molecular information with both high resolution and penetration capabilities.

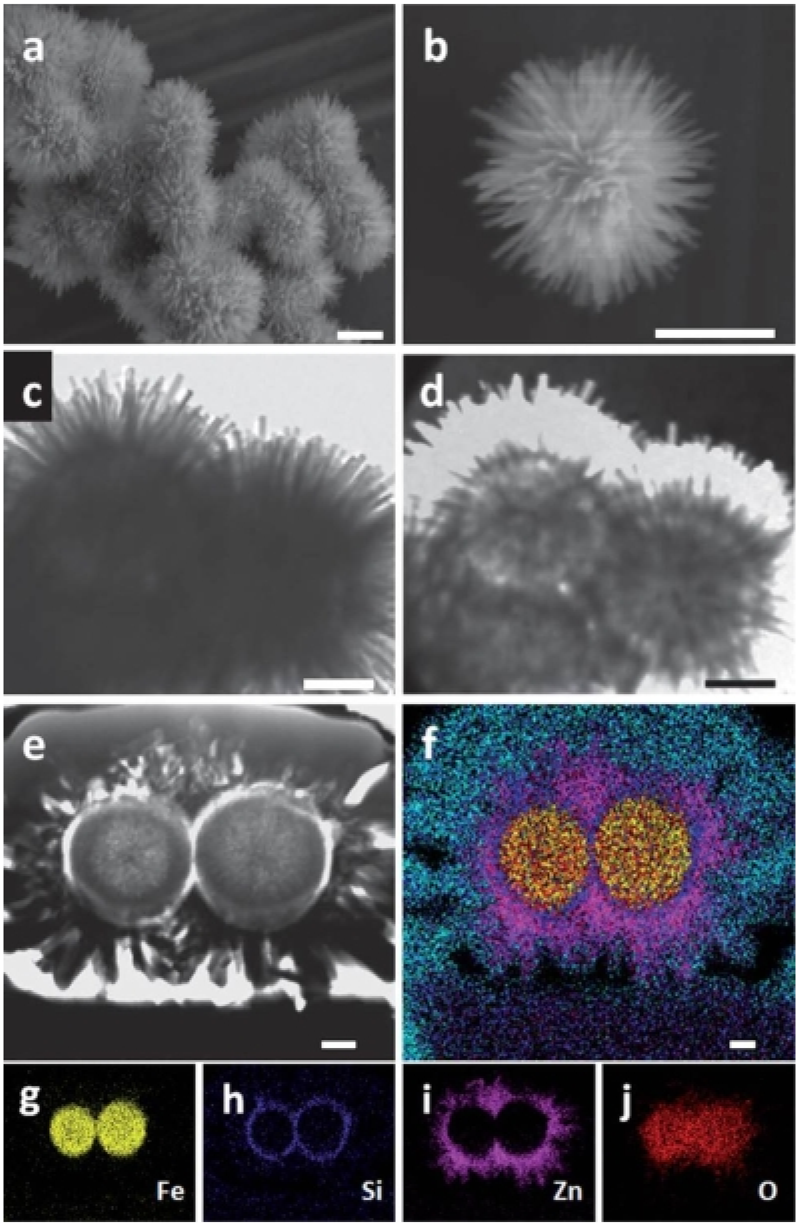
Finally, as a proof of concept, these nanoprisms have been applied in the design of a new ultrafast high-sensitivity plasmonic-driven thermal biosensor. This sensor is able to detect cancer markers up to the attomolar range in real patiente samples.

COLL 627

Urchin-like hierarchical Fe_xO_y@SiO_2-ZnO koosh ball architecture with tunable magnetic core, fluorescent nanowire shell and enhanced photocatalytic property

***Zheng Ren**[1,2], zheng.ren@uconn.edu, Yanbing Guo[1,2], Pu-Xian Gao[1,2].Â (1) Department of Materials Science and Engineering, University of Connecticut, Storrs, Connecticut 06269, United StatesÂ (2) Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269, United States*

A facile wet chemical method has been developed to synthesize three-dimensional (3D) urchin-like koosh ball nanostructure comprised of a tunable magnetic iron oxide core (Fe_xO_y) and a 3D fluorescent ZnO nanowire shell.(Figure1) This multicomponent architecture demonstrates enhanced photocatalytic activity towards dye degradation under UV irradiation. As shown in Figure 2, the phase transition of the magnetic iron oxide core and the native defects induced fluorescence of the nanowire shell can be simultaneously manipulated by post hydrogen annealing to produce urchin-like koosh balls with retained morphology but different magnetic and photocatalytic properties. This unique architecture initiates the three-dimensional nanowire growth on the micro-scale spherical substrate and enables the rational combination of multiple desired functionalities originating from dissimilar constituents.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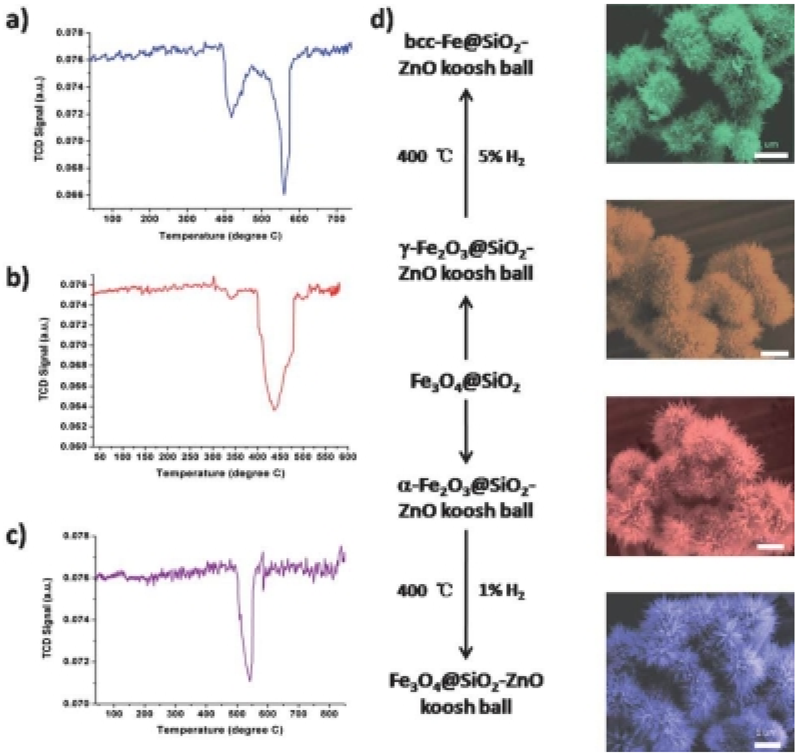


COLL 628

Controllable sonochemical synthesis of $Cu_2O/Cu_2(OH)_3NO_3$ composites toward synergy of adsorption and photocatalysis

Songbo Wang, *wangsongbo@tju.edu.cn,* ***Ji-Jun Zou***, *jj_zou@tju.edu.cn, Lun Pan, Zhen-Feng Huang, Feng-Min Zhao, Li Wang, Xiangwen Zhang, Xu Jia.School of Chemical Engineering and Technology, Tianjin University, Tianjin, Tianjin 300072, China*

Herein we report a facile sonochemical synthesis of Cu_2O(nanoparticles)/$Cu_2(OH)_3NO_3$(sheet) composites with tunable composition using only copper powders and $Cu(NO_3)_2$ as precursors. The composites can be controlled from almost pure Cu_2O (98.1%) to pure $Cu_2(OH)_3NO_3$ (95.9%) through adjusting the initial ratio of Cu^{2+}:Cu or sonication time. Controlled experiments show that Cu_2O nanoparticles are formed first via the redox reaction between Cu^{2+} and Cu, after that $Cu_2(OH)_3NO_3$ are produced from the reaction between Cu_2O, NO_3^- and OH· radicals generated from sonolysis of water. $Cu_2(OH)_3NO_3$ synthesized using the present method exhibits outstanding adsorption capability toward organic dyes (MO), whereas Cu_2O can degrade MO quickly, so $Cu_2O/Cu_2(OH)_3NO_3$ composites are very efficient to remove MO due to the synergetic effect of adsorption and photocatalysis. In particular, composites with 30.6% of $Cu_2(OH)_3NO_3$ and 69.4% of Cu_2O shows the highest removal capability and good stability. Therefore, composite materials having maximized adsorption and rapid photocatalysis may be an attractive alternative for pollutant removal.

COLL 629

Galvanic-assiated co-reduction route to the formation of Ag-Au hollow nanostructures with enhanced SERS and chemical stability

***Dong Qin**, dong.qin@mse.gatech.edu, Yin Yang.Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States*

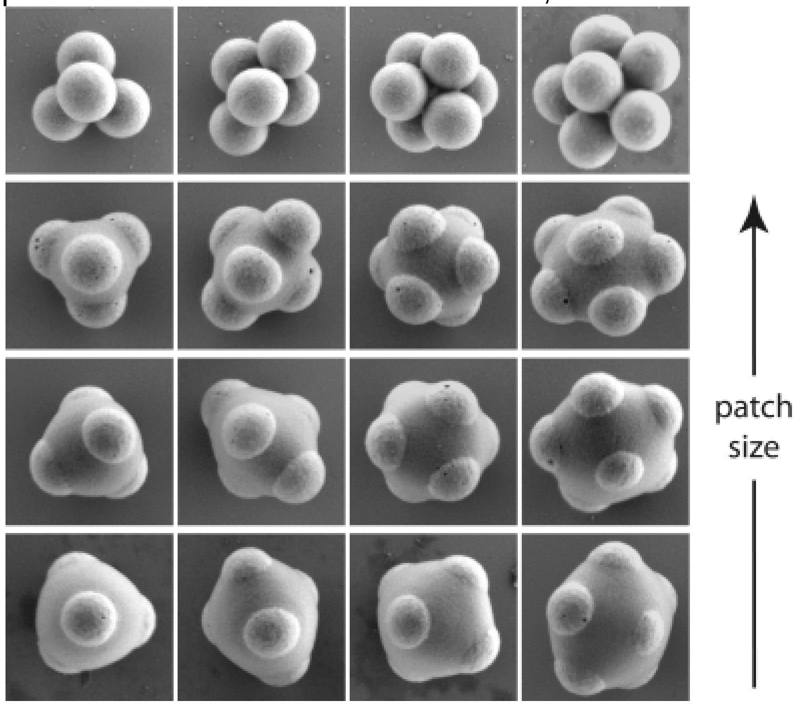
In this talk, we report a facile route to the formation of Ag-Au hollow structures with morphologies, compositions, and optical properties different from those previously reported for Ag-Au nanoboxes and nanocages. Specifically, with the involvement of a strong reducing agent such as ascorbic acid, we demonstrate that co-reduction could complement galvanic replacement to retard the loss of Ag component to form hollow nanostructures with enriched elemental Ag. We found that most (>80%) of the Ag^+ ions released from the galvanic replacement could be effectively reduced into Ag atoms by AA, and ultimately re-deposited back onto the Ag templates. Additionally, co-reduction could also significantly inhibit the dealloying process associated with the galvanic replacement, leading to the formation of hollow nanostructures with a continuous layer of Ag-Au alloy on the surface. For the first time, we observed distinctive SERS properties for the Ag-Au hollow nanostructures at visible and near-infrared excitation wavelengths. For example, the SERS properties with 532 nm excitation were extremely weak, which indicates the presence of plasmon dephasing at interband transition of Au at 2.5 eV (~500 nm). However, by changing the excitation wavelength to 785 nm, we demonstrated the ability to optimize the SERS properties by tailoring morphology and composition of Ag-Au nanostructures. More significantly, we revealed that the SERS of Ag-Au hollow nanostructures with enriched Ag elements was 15 times stronger than those of Ag nanocubes with near-infrared excitation wavelength. Remarkably, these nanostructures with exceptional SERS activity also embraced significantly improved stability in an oxidizing environment. We believe that this new class of nanomaterials is an excellent candidate to develop potential SERS detection for biomedical applications.

COLL 630

Kinetically-controlled inorganic patchy particle fabrication

***Yu Wang**[1], yw534@nyu.edu, Yufeng Wang[1], Xiaolong Zheng[1], Gi-Ra Yi[2], Stefano Sacanna[1], David Pine[3], Marcus Weck[1].Â (1) Molecular Design Institute and Department of chemistry, New York University, New York City, New York 10003, United StatesÂ (2) Department of Polymer Science and Engineering, Sungkyunkwan University, Suwon, Republic of KoreaÂ (3) Center for Soft Matter Research and Department of Physics, New York University, New York City, New York 10003, United States*

Imparting inorganic compositions into patchy particles will allow functional materials to be coupled in complex architectures that have potentially new emergent properties. Here we demonstrate a kinetically-controlled approach which can encapsulate inorganic clusters into patchy particles. This method avoids the swelling process and is only relevant to the cluster's surface property. Silicon dioxide and titanium dioxide patchy particles are obtained with various numbers of patches that adopt highly symmetrical geometries . The patchy size can be varied systematically via the modification of three parameters: amount of matrix material, surfactant concentration and reaction time.



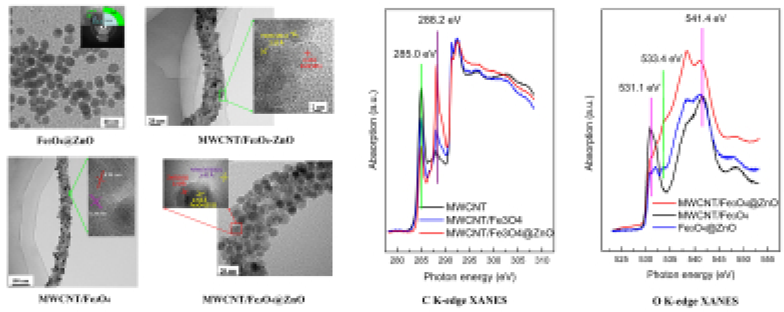
COLL 631

Dielectric-magnetic hybrids: Interface engineering, electronic structure and absorption on electromagnetic waves

Zhijiang Wang[1]*, wangzhijiang@hit.edu.cn, Jigang Zhou*[2]*, Zhaohua Jiang*[1]*.Â (1) School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin, ChinaÂ (2) Canadian Light Source Inc., Saskatoon, Saskatchewan S7N 0X4, Canada*

Extraordinary electron systems may be generated at well-designed interfaces of hybrids where the novel charge layers are induced and the carrier density are varied. The derived synergistic properties can endow the hybrids with enhanced properties and novel functions not available in the single-phase nanostructures. By controlling the nuclei site-selective anchoring location and subsequente growth behavior of nanoparticles, we have synthesized dielectric-magnetic hybrids of MWCNT/Fe_3O_4, Fe_3O_4@ZnO, MWCNT/Fe_3O_4-ZnO, and MWCNT/Fe_3O_4@ZnO. Their electronic structures were studied by analyzing their C K-edge, O K-edge, Fe L-edge and Zn L-edge X-ray absorption near-edge structures. It is found that charges are redistributed in

the hybrids through C-O-Zn, C-O-Fe and Fe-O-Zn bondings. Multiple electronic phases at the interfaces are generated. These redistributions result in the complementarity between the dielectric loss and magnetic loss. Under an altering electromagnetic field, the spawned interfacial polarization and synergetic interaction between magnetic and dielectric components extensively attenuate microwaves, protecting biological systems from the destroying of electromagnetic waves on the immune system and DNA strands. The excellent microwave absorption ability of the prepared hybrids makes them attractive candidate as materials for microwave absorption applications. The continued development of other high-performance microwave absorbers could be further expanded based on current report.



COLL 632

Organic solution synthesis of 2D transition metal chalcogenides

Zhen Liu, David Raciti, ***Chao Wang****, chaowang@jhu.edu.Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, Maryland 21218, United States*

The past decade has witnessed a remarkable growth of research interests in two-dimensional (2D) layered nanomaterials. Composed of layered MX_2 (M is a transition metal of groups 4–10 and X is a chalcogen) crystals, 2D transition metal chalcogenides (TMCs) offer versatile and appealing chemical properties that are promising for a variety of applications including electronics, sensing, energy storage and catalysis. Synthesis of 2D TMCs, however, has largely been limited to physical/chemical exfoliation of bulk crystals (top–down) and chemical vapor deposition (CVD) on appropriate substrates. Despite the progress that has been made, reliable production of 2D TMCs with control over the size, layer thickness, composition and structure has been challenging with existing methods. Moreover, feasible methods for manipulation of these 2D nanomaterials for functional applications are yet to be developed. These problems have become the main obstacles for practical implementation of the 2D nanomaterials in large scale.

Our group has been dedicated to the development of organic solution synthesis of 2D nanomaterials. Previously this method has been demonstrated to robust for the preparation of monodisperse and uniform colloidal nanocrystals, including zero-dimensional (0D) nanoparticles and one-dimensional (1D) nanorods and nanowires. Recently we have developed a two-step method for the synthesis of 2D TMCs in organic solutions. Transition metal or transition metal oxide nanoparticles were first synthesized, and then applied as seeds for chalcogenation to form TMC nanoparticles. 2D TMCs were produced either by *in situ* solvothermal exfoliation, or by post-synthesis liquid exfoliation. Control over the size, shape and stacking degree of produced nanosheets was achieved by tuning the morphology of the seeding nanoparticle and reaction conditions (e.g., temperature, stabilizing ligands) for chalcogenation/exfoliation. In addition, starting with composite metal or metal oxide nanostructures (e.g., alloy and core/shell nanoparticles), bimetallic 2D TMCs were obtained with control over composition. The obtained 2D TMCs were further demonstrated to be efficient electrocatalysts for the hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR).

COLL 633

Magneto-fluorescent core-shell supernanoparticles

***Ou Chen**, chenou@mit.edu, Moungi Bawendi.Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

The design and fabrication of materials that simultaneously contain more than one type of functional components, so-called multifunctional materials, is an active research area with the potential to impact a wide range of technological applications. In particular, co-assembling two types of nanocrystals with distinct properties into larger colloidal particles, especially at the mesoscopic scale, offers the possibility of producing new classes of nanoparticles (i.e., supernanoparticles, SPs) with a set of combined properties, all the while maintaining the colloidal nature of their building blocks. Here, we report a simple and effective method for assembling CdSe-CdS QDs with Fe_3O_4 MNPs into colloidal SPs with a “core-shell” (CS) superstructure. Additional thermal annealing drives the crystallization of the “core” MNPs into a highly ordered supercrystal with an ideal fcc superlattice. The CS-SPs can be easily coated with a thin silica layer, providing surface functionality and colloidal stability as well as biocompatibility. Importantly, these silica-coated CS-SPs for the first time simultaneously satisfy all the design criteria needed for various applications: uniform and tunable sizes, high magnetic content loading, maximized fluorophore loading on the surface, substantial colloidal stability, and versatile surface functionality. These features allow the utilization of these magneto-fluorescent SPs for *in vitro* intracellular manipulation and *in vivo* MR/MP dual-modal imaging.

COLL 634

Plasmon and exciton interaction in metal nanoparticles and quantum dots complexes

***Jing Zhao**, jing.zhao@uconn.edu, Xiangdong Tian.Chemistry, University of Connecticut, Storrs, CT 06269, United States*

The localized surface plasmon resonance (LSPR) of metal nanoparticles is sensitive to molecules/nanoparticles in the proximity. In Ag nanosphere dimers and trimers, the LSPR spectra significantly differ from that of the single Ag nanospheres by correlated structural and optical studies. The additional peaks in the LSPR spectra of Ag nanosphere dimers and trimers are attributed to the coupling between the nanoparticles and they depend on the polarization of the incident light. In the case when colloidal quantum dots adsorb onto single metal nanoparticles, the LSPR spectra of the nanocomplexes shifts in wavelength and changes in the lineshape compared to single metal nanoparticles. The strong exciton-plasmon interaction results in dips in the LSPR lineshape of nanocomplexes.

COLL 635

Applying molecular veneers on MoS_2 sheets

***Stanley S. Chou**[1,2], schou@sandia.gov, C. Jeffrey Brinker[1,2].Â (1) Sandia National Laboratory, Albuquerque, New Mexico 87106, United StatesÂ (2) Department of Chemical and Nuclear Engineering, University of New Mexico, Albuquerque, New Mexico 87106, United States*

In carpentry, veneering refers to the application of a thin strip of material to facade a piece of wood, thus giving it new function and appearance. Similarly, protective finishes can be applied to improve the durability of a core structure. Using this analogy, we explore methods than enable us to apply molecular veneer and finishes on two-dimensional colloids, such as MoS_2 sheets, for the purpose of modifying self-assembly behavior. Firstly, we will discuss assembly of proteins on MoS_2 surfaces using native electrostatic interactions, measurement of assembly dynamics through activity and spectroscopic assays and effects of near-infrared irradiation on protein structure and activity. Secondly, we will discuss ligand attachments that can alter biomolecular interactions *in vitro* and *in vivo*, and in particular, ways to modulate hemolytic activity. Lastly, we will discuss tuning the optical and catalytic properties of MoS_2 sheets by molecular deposition, thus altering the way in which it interacts with its environment. In the end, our goal is to design molecular strategies to dictate the way two-dimensional colloids, such as MoS_2 sheets, behave in different chemical environments, and to use it to shape self-assemblies for applications ranging from drug delivery to catalysis.

COLL 636

Spectroscopic characterization of P3HT/SWNT composites synthesized using *in situ* GRIM methods: Improved polymer ordering *via* nanoscaffolding

***David S Boucher**[1], boucherds@cofc.edu, Hayden P Barrett[1], William J Kennedy[2].Â (1) Department of Chemistry and Biochemistry, College of Charleston, Charleston, SC*

29424, United StatesÂ (2) Structural Engineering Division, NASA Johnson Space Center, Houston, TX 77058, United States

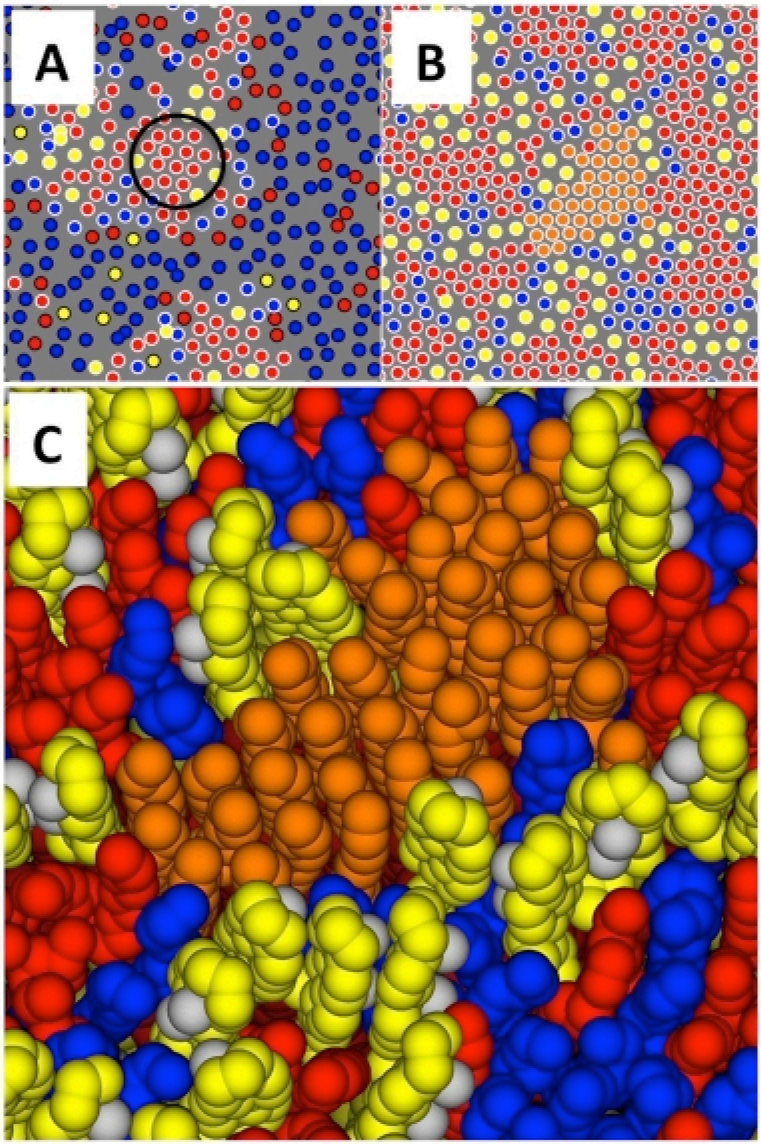
We have synthesized poly(3-hexylthiophene)/single-walled carbon nanotube (P3HT/SWNT) composites using an in-situ Grignard metathesis approach at low (0-1%) weight fractions of SWNT. We studied the structural properties and photophysics of the materials using a multitude of techniques, including ^{1}H NMR, FTIR, UV–vis absorption, Raman, photoluminescence (PL), and transient absorption spectroscopies. The composites have a high degree of P3HT regioregularity (rr > 96%). However, Raman spectroscopy reveals an increase in the dispersion rate parameter with increasing SWNT concentration, indicating close overlap and strong interactions between P3HT and the carbon nanotubes. Changes in the solution-phase PL quantum yields and excited state lifetimes relative to pure P3HT support these conclusions, and indicate that strong interactions persist even after the composites are dispersed in organic solvents. The high regioregularity and enhanced polymer-nanotube interactions are promising attributes for improving the morphology and efficiency of functional P3HT/SWNT materials.

COLL 637

Molecular structure of the liquid ordered phase

***Edward Lyman**, elyman@udel.edu.Physics and Astrophysics; Chemistry and Biochemistry, University of Delaware, United States*

Molecular dynamics simulations reveal substructures within the liquid-ordered phase of lipid bilayers. These substructures



, identified in a 10 μsec all-atom trajectory of liquid-ordered/liquid-disordered coexistence (L_o/L_d), are composed of saturated hydrocarbon chains packed with local hexagonal order, and separated by interstitial regions enriched in cholesterol and unsaturated chains. Lipid hydrocarbon chain order parameters calculated from the L_o phase are in excellent agreement with ^{2}H NMR measurements; the local hexagonal packing is also consistent with ^{1}H-MAS NMR spectra of the L_o phase, NMR diffusion experiments, and small angle X-ray- and neutron scattering. The balance of cholesterol-rich to local hexagonal order is proposed to control the partitioning of membrane components into the L_o regions. The latter have been frequently associated with formation of so-called rafts, platforms in the plasma membranes of cells that facilitate interaction between components of signaling pathways.

COLL 638

Simple models for biomembranes

***Frank L. H. Brown**, flbrown@chem.ucsb.edu.Department of Chemistry and Biochemistry, University of California, Santa Barbara, Santa Barbara, CA 93106, United States*

Simulation of biomembranes over length and time scales relevant to cellular biology is not currently feasible with Molecular Dynamics including full atomic detail. Barring an unforeseen revolution in the computer industry, this situation will not change for many years. We will present aggressively coarse-grained membrane models, which enable practical calculation of various biophysical phenomena at minimal computational expense. Applications will be discussed.

COLL 639

Coupled phase transitions in lipid bilayer membrane systems

***Mikko P Haataja**, mhaataja@princeton.edu.Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544, United States*

The leaflets comprising a lipid bilayer membrane are strongly coupled to their environments and susceptible to thermo-mechanical perturbations. This coupling results in several related intriguing phenomena, such as registration of compositional lipid domains across the two bilayer leaflets in supported membranes or vesicles and spatial correlation of compositional lipid membrane domains with co-existing bulk phases in giant vesicles.

In this talk, I will provide an overview of our on-going studies of coupled phase transition phenomena in lipid membrane systems. In particular, I will focus on the development of a physically-based, coarse-grained continuum simulation framework to investigate such phenomena.

COLL 640

Membrane interaction mechanisms and curvature sorting of BAR domain proteins

***Tobias Baumgart**, baumgart@sas.upenn.edu.Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States*

Membrane curvature has developed into a forefront of membrane biophysics. Numerous proteins involved in membrane curvature sensing and membrane curvature generation have recently been discovered, including proteins containing the crescent-shaped BAR domain as membrane binding and shaping module. Accordingly, the

structure determination of these proteins and their multimeric complexes is increasingly well-understood. Substantially less understood, however, are thermodynamic and kinetic aspects and the detailed mechanisms of how these proteins interact with membranes in a curvature-dependent manner. New experimental approaches need to be combined with established techniques to be able to fill in these missing details. Here we use model membrane systems in combination with a variety of biophysical techniques to characterize mechanistic aspects of BAR domain protein function. This includes a characterization of membrane curvature sensing and membrane generation. We also establish kinetic and thermodynamic aspects of BAR protein dimerization in solution, and investigate kinetic aspects of membrane binding. We present two new approaches to investigate membrane shape instabilities and demonstrate that membrane shape instabilities can be controlled by protein binding and lateral membrane tension.

COLL 641

Photooxidation-induced morphological deformation of lipid bilayers: Kinetics of surface area changes

***Noah Malmstadt**, malmstad@usc.edu, Shalene Sankhagowit.Department of Chemical Engineering and Materials Science, University of Southern California, Los Angeles, California 90089, United States*

Lipid oxidation has been implicated as a potential molecular mechanism of oxidative damage in a variety of disease states, including atherosclerosis, neurodegenerative diseases, and hyperbaric oxygen toxicity. We have studied the kinetics of photo-induced phospholipid bilayer oxidation using giant unilamellar vesicles (GUVs) as model membranes. Incorporating rhodamine-labeled 1,2-dipalmitoyl-sn-glycero-3-phosphoethanoamine (Rh-DPPE) as photosensitizer to generate highly reactive singlet oxygen at the surface of 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) GUVs, we observed a two-phase morphological transformation. Within minutes of irradiation, the membrane area increased, resulting in vesicle flattening and high-amplitude membrane fluctuations. After reaching a maximum area, the membrane began contracting, causing the GUVs to became tumid with a surface tension sufficient to exceed the critical limit for pore formation. The periodic micron-scale opening of pores was observed as step-decreases in vesicle size below pre-oxidation dimensions. The growth and shrinkage behaviors were analyzed as consecutive rate-limiting reaction steps, allowing estimates of molecular size changes and the rate constants of the underlying chemical events. Dependence of these kintetics on irradiation intensity and on concentrations of Rh-DPPE and DOPC were considered. Furthermore, experiments varying membrane DOPC content were repeated at ten-fold increased aqueous viscosity to slow down fluid leakage and allow for more accurate measurement of pore closure rates. The calculated decreased line tension with higher DOPC concentration suggests that oxidation products stabilize pores and compromize membrane barrier properties.

COLL 642

Bottom-up approach to curvature directed patterning of lipids, functional groups, and proteins

***Marjorie L Longo**, mllongo@ucdavis.edu.Chemical Engineering and Materials Science, University of California, Davis, Davis, California 95616, United States*

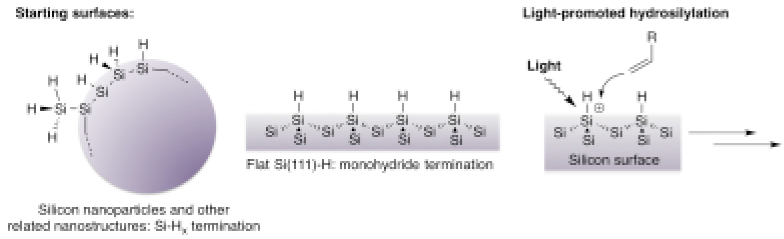
We have shown that coexisting lipid bilayer phases, varying in composition, form a pixilated pattern in response to the curvature pattern of an underlying substrate formed by electron beam lithography. These results are strongly indicative that the transfer of a nanoscale curvature pattern to a compositional lipid pattern may be a viable way of positioning functional groups. In collaboration with Darryl Sasaki at Sandia National Labs, we have moved this bottom-up approach toward application by using curvature to compositionally pattern phase-specific lipids functionalized with a metal chelating iminodiacetic acid (IDA) headgroup. The IDA headgroup coordinates to divalent transition-metal ions and sequesters proteins rich with histidine (His) moieties. Therefore, we characterize the spatial patterning of His-tagged green fluorescent protein (GFP) targeted to phase specific IDA-lipids (such as DSIDA or DOIDA) that are spatially patterned by a nanoscale curvature pattern. We show that this method can be used to form defect-free arrays of His-GFP, in small areas, suggesting the possibility of using this approach for the localization of protein, DNA, or optically active molecules. Defects in the His-GFP pattern were also interesting and may be of future use. We also briefly discuss metastablity, dynamics, and the potential to pattern other functionalities.

COLL 643

Illuminating the surface chemistry of silicon

***Jillian M. Buriak**, jburiak@ualberta.ca.Department of Chemistry, University of Alberta, Edmonton, AB T6H 3T5, CanadaNational Institute for Nanotechnology, Edmonton, AB T6G 2M9, Canada*

Light-driven reactions on silicon to form silicon-carbon bonds are a fascinating approach to functionalizing the surface of this important material because they require few reagents, and are very intriguing from a mechanistic perspective. Shining light on a hydrogen-terminated silicon surface in the presence of an alkyne or alkene was, at least initially, expected to proceed via a radical mechanism, in much the same manner as silicon-based molecules (silanes, R_3Si-H for instance). Research over the past decade has shown that the mechanisms that may be in operation are far richer and more diverse than ever thought. The underlying electronics of the silicon play an important role in enabling the chemistry of the surface, and under many circumstances, can dominate. In this talk, we will discuss how the environment and reaction conditions can favor one reaction mechanism over another, and how to distinguish between them.



COLL 644

Relay reaction mechanisms in semiconductor surface chemistry

Mathew D Halls[1]*, mat.halls@schrodinger.com, Alain Estève*[2]*, Yves J Chabal*[3]*.Â (1) SchrÃ¶dinger Inc., San Diego, United StatesÂ (2) LAAS-CNRS, Toulouse, FranceÂ (3) Department of Materials Science & Engineering, University of Texas at Dallas, Dallas, United States*

First-principles simulation has been shown to be an invaluable tool for gaining insight into the atomistic details, reaction energetics and reaction mechanisms for the chemical reactions involved in thin-film deposition and processing on semiconductor surfaces. For simplicity, the vast majority of this work has studied the interaction between the surface reaction site and a single co-reactant species; neglecting cooperative effects and the possibility of more complex reaction mechanisms. In this presentation, we will summarize our work suggesting that reaction pathways involving multiple co-reactant species give significantly more favorable reaction energetics than was previously estimated. This is illustrated by an in-depth look at surface reactions involving hydrogen transfer, where a Grotthuss-type relay mechanism leads to lowered kinetic barriers. Relay reaction mechanisms may therefore have general applicability, as illustrated by surface and co-reactant examples involving heavy-atom transfer.

COLL 645

Building atom-scale circuitry

Robert Wolkow*, rwolkow@ualberta.ca.Physics, University of Alberta, Edmonton, Alberta T6G2B5, Canada*

Quantum dots are small entities, typically consisting of just a few thousands atoms, that in some ways act like a single atom. The constituent atoms in a dot coalesce their electronic properties to exhibit fairly simple and potentially very useful properties. It turns out that collectives of dots exhibit joint electronic properties of yet more interest. Unfortunately, though extremely small, the still considerable size of typical quantum dots puts a limit on how close multiple dots can be placed, and that in turn limits how strong the coupling between dots can be. Because inter-dot coupling is weak, properties of interest are only manifest at very low temperatures (milliKelvin). In this work the ultimate small quantum dot is described – we replace an “artificial atom” with a true atom - with great benefit.

It is demonstrated that the zero-dimensional character of the silicon atom dangling bond (DB) state allows controlled formation and occupation of a new form of quantum dot assemblies - at room temperature. Coulomb repulsion causes DBs separated by less than ~2 nm to experience reduced localized charge. The unoccupied states so created allow a previously unobserved electron tunnel-coupling of DBs, evidenced by a pronounced change in the time-averaged view recorded by scanning tunneling microscopy. It is shown that fabrication geometry determines net electron occupation and tunnel-coupling strength within multi-DB ensembles and moreover that electrostatic separation of degenerate states allows controlled electron occupation within an ensemble.

It appears a new “atomic electronics” based upon these results can be fabricated. Recents steps toward that end will be described.

COLL 646

Molecular modulation of conductivity on chemically modified silicon-on-insulator substrates

Gregory Lopinski, *gregory.lopinski@nrc-cnrc.gc.ca.Measurement Science and Standards, National Research Council Canada, Ottawa, ON K1A 0R6, Canada*

Electrical transport of semiconductor surfaces and nanostructures are strongly influenced by interfacial processes. Adsorption and reaction events which result in charge re-distribution can modulate near surface conductivity through long-range electric field effects. These effects are being exploited to tailor the electronic properties of nanomaterials and devices as well as in the development of electrically-based chemical and biological sensors. Silicon-on-insulator (SOI) substrates are particularly well-suited for investigating the effects of surface processes on electrical transport. SOI substrates also facilitate formation of point contact pseudo-MOSFETs, allowing transistor characteristics to be obtained without the need for device fabrication. This method is demonstrated to be a simple and straightforward way to monitor the effect of adsorption and reaction events on the electronic properties of the silicon substrate. Adsorption of certain polar molecules (water, pyridine and ammonia) on hydrogen terminated H-SOI substrates (with both (100) and (111) orientations), results in large reversible increases in conductivity. These conductivity changes are attributed to charge transfer effects that induce accumulation of majority carriers on n-type and formation of minority carrier channels (inversion) on p-type substrates. Adsorption of the prototypical electron acceptor tetracyanoethylene (TCNE) results in a strong decrease in conductivity on n-type substrates due to depletion of carriers. This effect is not fully reversible due to reactions of TCNE with the H-terminated surface. Gas phase photochemical reaction of alkenes has been used to chemically passivate these surfaces while maintaining a low density of electrically active defects ($<1x10^{11}$ cm^{-2}).

Alkyl monolayer passivated SOI surfaces show a large reversible response to TCNE, suggesting that these monolayers function as good ultrathin gate dielectrics for the fabrication of molecular sensors. Application of chemically modified SOI to the electrical detection of other high electron affinity compounds will also be shown.

COLL 647

Composite models for investigating structures and chemical reactions of adsorbates on semiconductor surfaces

Krishnan Raghavachari*, kraghava@indiana.edu, Benjamin C Gamoke.Department of Chemistry, Indiana University, Bloomington, IN 47405, United States*

The accurate modeling of adsorbates and chemical reactions on periodic surfaces at low or intermediate coverage is computationally inefficient with most current methods, typically requiring large unit cells to minimize unphysical intercell interactions. We propose novel composite methods that effectively cancel any unphysical adsorbate-adsorbate interactions that may otherwise be present in such slab calculations. Our composite approach provides a good description of the entire potential energy surface, and yields geometrical relaxations at low, intermediate and high coverages of adsorbates on small, computationally efficient unit cells. The foundations of the method along with a range of chemical reactions on silicon surfaces will be discussed.

COLL 648

Surface chemistry of diamond films and nanoparticles: Applications in catalysis and environmental science

Robert J Hamers*, rjhamers@wisc.edu.Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706, United States*

While diamond has many unique properties, its extraordinary chemical and electrochemical stability makes in an idea material to use in emerging areas such as catalysis and environmental science. Recently we have been developing new approaches to using diamond as a catalytic material using the direct emission of solvated electrons from hydrogen-terminated diamond as a way to initiate novel reduction reactions such as the reduction of N_2 to NH_3 and CO_2 to CO. The surface chemistry of diamond plays a key role in its ability to emit electrons. Functionalized diamond nanoparticles are also playing a role in environmental science as chemically inert tracers for studying the interaction of nanoparticles with biological systems.

COLL 649

GaSb (001): New adventures in III-V surface chemistry

***Victor M. Bermudez**, victor.bermudez@nrl.navy.mil.Electronics Science and Technology Division, Naval Research Laboratory, Washington, DC 20375, United States*

GaSb is probably the least-studied of all III-V semiconductors from the perspective of fundamental surface science. However, new areas of application have led to increased interest in this material. A critical issue is the production of high-quality gate oxides with a low defect
density on either side of the oxide/substrate interface, the most viable approach to which involves atomic layer deposition (ALD). This talk will describe recent and on-going experimental and computational work at NRL that is aimed at understanding and optimizing oxide ALD on the GaSb (001) surface. The most stable reconstruction, the so-called α-(4x3), consists of 4 Ga-Sb adatom dimers per unit cell on the Sb termination layer, which also comprises 1 Sb-Sb dimer. This surface is non-metallic with no surface states in the band gap. Molecular adsorption of H_2O *via* a Ga---OH_2 dative bond is exothermic, but dissociation is highly unfavorable. Hence the formation, *via* direct dissociation of H_2O, of the OH-terminated surface necessary for the initiation of ALD is problematic. An alternative is to produce (somehow) a high-quality native oxide, which will presumably form OH sites when exposed to H_2O. The key issue is how to accomplish this while avoiding the well-documented problem of defective III-V/oxide interfaces.
Careful measurement of the Fermi-level pinning position vs. O_2 exposure shows that O_2 can passivate defects as well as cause them, which is supported by recent electrical measurements performed at NRL. This in turn has led to efforts to understand the mechanism whereby O_2
exposure generates GaSb surface defects. Preliminary results have revealed a process, which is apparently unique to GaSb (001), in which O_2 dissociates with little or no barrier and forms sub-surface defects. A practical outcome of this work is a set of tentative suggestions for how best to form a GaSb native oxide.

COLL 650

Ligand-protected superatoms and superatomic molecules: Synthesis and characterization

***Tatsuya Tsukuda**, tsukuda@chem.s.u-tokyo.ac.jp.Department of Chemistry, The University of Tokyo, Japan*

It is known that an icosahedral gold cluster Au_{13}^{5+} with a closed electronic structure (8 valence electrons) constitutes a superatomic core in ligand-protected Au clusters. Recent X-ray crystallographic studies demonstrated a formation of a variety of dimeric structures of Au_{13}^{5+} via different bonding modes: a vertex-sharing Au_{25}^{9+} (16 e), face-sharing Au_{23}^{9+} (14 e) and non-sharing Au_{26}^{10+} (16 e). These examples suggest that we can artificially create a new world of quasi-molecules made of superatoms (superatomic molecules), which is in parallel with the familiar world of molecules made of atoms. We launched a project for chemical synthesis of the superatoms and superatomic molecules. The first strategy is to synthesize superatoms or superatmic molecules by enclosing by bulky arenethiols, such 2,6-diphenylbenzenethiol (DppSH). We expect that the obtuse angle between the two substituent Ar groups will regulate the size and structure of the Au core. The second strategy is to fuse phosphine-protected superatoms during the ligand exchange, as we demonstrated in the synthesis of a vertex-sharing bi-icosahedral Au_{25}^{9+}. This paper focuses on our recent results toward this goal. The first topic concerns the selective synthesis of $Au_{25}(SDpp)_{11}$. We proposed the formation of a new type of bi-icosahedral Au_{25}^{11+} (14 e) core based on high-energy X-ray diffraction data. The second topic is the production of bi-icosahedral $PdAu_{24}^{8+}$ (16 e) alloys by the aggregation of superatomic alloys.

COLL 651

Gold thiolate molecules: Nanoparticles of molecular definition

***Amala Dass**, amal@olemiss.edu.Department of Chemistry & Biochemistry, University of Mississippi, University, Mississippi 38677, United States*

Correlating nanoparticle structure (atomic arrangement) to function, properties and reactivity can facilitate the optimization of its use in catalysts and solar cells. To make this possible, it is important to obtain nanoparticles of precise composition and structure. This talk will present my research group's efforts towards the synthesis of gold thiolate (Au-SR) molecules. Typical examples include $Au_{25}(SR)_{18}$, $Au_{36}(SPh)_{24}$, $Au_{38}(SR)_{24}$, $Au_{102}(SPhCOOH)_{44}$, $Au_{144}(SR)_{60}$. Using a combination of high resolution experimental techniques (mass spectrometry, HR-TEM, synchrotron based x-ray methods, electrochemistry, and spectroscopy) and theoretical simulations, we study the composition, crystal structure, electronic structure and redox behavior of Au-SR molecules.

COLL 652

Toward the creation of functionalized metal nanoclusters and highly active photocatalytic materials by the use of thiolate-protected magic gold clusters

***Yuichi Negishi**, negishi@rs.kagu.tus.ac.jp.Department of Applied Chemistry, Tokyo University of Science, Shinjuku-ku, Tokyo 162-8601, Japan*

Advances in the development of nanotechnology have encouraged the creation of highly functionalized nanomaterials. Thiolate-protected gold clusters ($Au_n(SR)_m$), in addition to their nanoscale size (<2 nm), exhibit size-specific physical and chemical properties that are not observed in bulk metals; thus, they have been attracting significant attention as functional units or building block in nanotechnology. Among these, the highly stable, magic $Au_n(SR)_m$ clusters have especially great potential as new nanomaterials. We are engaged in the following subjects for magic $Au_n(SR)_m$ clusters: (1) establishing methods to enhance their functionality, (2) developing high-resolution separation methods, and (3) utilizing them as active sites in photocatalytic materials. Through these studies, we aim at the creation of highly functionalized metal clusters, and through their application, the creation of highly active photocatalysts. The results of our efforts to date are reported in this presentation.

COLL 653

Molecular silver nanoparticles

Terry P. Bigioni*, Terry.Bigioni@utoledo.edu.Department of Chemistry, University of Toledo, Toledo, OH 43606, United StatesSchool of Solar and Advanced Renewable Energy, University of Toledo, Toledo, OH 43606, United States*

Magic-number theories have been used to explain the anomalous stability of small Au nanoparticles, but generalization of these theories requires their application to other materials systems. To this end, we have found that small Ag nanoparticles can also be synthesized as a family of discrete sizes and structures. Gel electrophoresis and mass spectrometry results show the discrete nature of the different nanoparticle sizes. The smallest Ag and Au nanoparticles cover a comparable size range, although the Ag nanoparticle size range extends to much larger sizes. I will discuss the optical properties of these materials as a function of size and contrast them with those of gold. The stability of the Ag nanoparticles has been a major obstacle so I will present the results of studies on their decomposition mechanism, which enables the prevention or acceleration of nanoparticle decay. I will also present very recent work on a 44-atom Ag nanoparticle that is extremely stable, in stark contrast to other Ag nanoparticles. The unprecedented stability of this nanoparticle resulted in (i) a truly single-sized molecular product, (ii) ~140 g of pure product from a single batch, and (iii) an opportunity to crystallize the nanoparticle and understand its protective ligand shell, atomic and electronic structure, and thereby its stability.

COLL 654

Enhanced optical properties in gold and silver metal clusters

Theodore Goodson*, tgoodson@umich.edu.Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109, United States*

Metal nanoparticles under 2 nm are considered nanoclusters. Nanosystems at this scale have many fascinating optical properties directly related to their size and topology. Nanoclusters of gold have been studied extensively and many promising applications in the fields of imaging and optical limiting are presently being investigated. Our results with these gold clusters will be presented. Silver nanocluster of similar topology to the well known gold nanoclusters were also studied, in particular silver nanocluster with a 32 metal core and 19 thiolate ligand shell. $Ag_{32}(SG)_{19}$ has been synthesized. Enhanced emission has been observed for the $Ag_{32}(SG)_{19}$ cluster. Using time-resolved fluorescence measurements, the kinetics of the emission were investigated. The quantum efficiency for the emission is found to be approximately two orders of

magnitude higher than the gold (25) system. The emission can also be excited by a two-photon process and a cross-section of ~1000 GM was obtained. The absorption dynamics of the silver cluster system will also be discussed

COLL 655

Interfacial engineering and functionalization of nanoparticle materials

Shaowei Chen, *shaowei@ucsc.edu.Department of Chemistry and Biochemistry, University of California Santa Cruz, Santa Cruz, CA 95064, United States*

Organically capped metal nanoparticles represent a unique class of functional nanomaterials. Traditionally the material properties can be manipulated by the chemical nature of the organic ligands as well as the metal cores. Recently we found that the metal-ligand interfacial bonding interactions may also play a significant role in controlling the nanoparticle optical and electronic properties. In this presentation we will discuss several examples of transition-metal nanoparticles functionalized by various metal-ligand covalent bonds including metal-carbon and –nitrene pi bonds where extensive intraparticle charge delocalization occurs, and highlight the impacts of such unique interfacial interactions on the nanoparticle electrochemical and photoluminescence properties, and in particular, on nanoparticle catalysis for fuel cell electrochemistry.

COLL 656

Exploring chalcogen interfacial chemistry for charge transfer in monolayer-protected metal nanoparticles

Yuan Gao, Yangwei Liu, ***YuYe J. Tong****, yyt@georgetown.edu.Department of Chemistry, Georgetown University, Washington, DC 20057, United States*

Monolayer-protected metal nanoparticles (MPNs) are the fundamental functioning units/building blocks for many promising applications in the emerging fields of nano-electronics, nano-optics, nano-sensing, and nano-medicine. The chemistry of metal core–protecting monolayer interface, which consists of bonds between the anchoring element from the protecting monolayer and the underlying metal surface atoms, largely governs, among others, the metal NP stabilization, electrical conductance through metal–molecular wire junctions, and chemical reactions taking place at the interface. This chemistry is also fundamentally relevant to the field of molecular electronics. While S has been and still is the prevailingly used anchoring element in MPNs, increasing evidence has shown that the most studied Au–S bond may not be the optimal one according to Pearson's hard and soft acids and bases (HSAB) principle. As such, research on alternative anchoring elements or groups that would offer better enabling capability has been gaining increasing tractions recently. In this presentation, we will discuss results from our recent research on exploring chalcogen, particularly heavier

chalcogen (Se and Te), interfacial chemistry and its effect on charge transfer in MPNs and their assemblies.

COLL 657

New method for controlling hydrogen spillover, reaction, and storage: The molecular cork effect

***Charles Sykes**, charles.sykes@tufts.edu.Department of Chemistry, Tufts University, Medford, MA 02155, United States*

Hydrogen activation, uptake and reaction are important phenomena in heterogeneous catalysis, fuel cells, hydrogen storage devices, materials processing, and sensing. Much attention has been devoted to materials that exhibit facile activation and weak binding of hydrogen, as these properties lead to the best energy landscape for storage or chemical reactivity. Spillover is a common method by which a reagent can be activated at one location and then reacted at another, and it is commonly invoked to explain the synergistic relationship between metals in an alloy or metal/metal oxide mixtures. The traditional view of these processes involves molecules adsorbing somewhat uniformly over a surface, migrating to preferred/active sites, followed by reaction or desorption. For example, in heterogeneous catalysis hydrogen spillover from metal particles to reducible oxide supports is implicated as an important step in a variety of reactions including hydrogenations, hydroisomerizations, and methanol synthesis. Hydrogen spillover has also been shown to significantly enhance the performance of hydrogen storage materials such as metal organic frameworks, zeolites and many carbon-based nanostructures. Despite these advances, the mechanism of spillover in most systems remains poorly understood, and with the exception of hydrogen bridges in storage systems, methods for mediating the spillover pathway do not exist.We discovered a system in which the uptake and release of hydrogen from a copper surface occurs solely through 1% of the surface sites which are individual, isolated, catalytically active palladium atoms. The surface can either be kept free of hydrogen by pre-adsorption of carbon monoxide or that hydrogen can be trapped on the surface by post-adsorption. In this way the coverage of the surface as a whole can be controlled by the addition of a single molecule to a minority atomic-scale site which we term a *molecular cork* effect. This non-equilibrium effect can be used to produce superheated hydrogen atoms, a more reactive form than regular surface bound hydrogen. We also demonstrate in a model system that the molecular cork effect could offer a new method for mediating the kinetics of hydrogen uptake and release from storage materials that rely on spillover from small metal particles.

COLL 658

MP-SPR: New optical characterization method for molecular interactions and ultrathin films

Niko Granqvist^{1,2}*, niko.granqvist@bionavis.com, Annika Jokinen*^{1}*, Janusz Sadowski*^{1}*.Â (1) BioNavis Ltd, Ylojarvi, FinlandÂ (2) Department of Biopharmaceutics and Pharmacokinetics, University of Helsinki, Helsinki, ETELA-SUOMEN LAANI 00710, Finland*

Surface Plasmon Resonance (SPR) has been used few decades for label-free detection and characterization of biochemical kinetics and affinities for many different types of analysts. The physical phenomena is not limited to biochemistry, but is applicable to many other nanoscale characterization.[1]

Aside of the traditional interactions, Multiparametric Surface Plasmon Resonance (MP-SPR) can be utilized to determine unique refractive index (*RI*) and thickness (*d*) of ultrathin films (d 0.5-100 nm) without knowledge of the RI of the material. These are important properties for many thin film coating industries and applications, and important knowledge in biomaterials also. The new method allows measurement of these properties for both dielectric layers, but also for metals and metal-like coatings that are difficult to measure with other optical methods.

Two new methods utilizing MP-SPR have recently been introduced, either measuring in two different media (2M) with high *RI* difference, such as air and water [1-3], or at two or more different wavelengths (2W) of light [2,3] in order to characterize properties of ultrathin films.

Strongly light absorbing materials, such as metals and semiconductors, have been difficult to measure with traditional thin film measuring optical methods, such as ellipsometry because they are mostly non-transparent materials [4]. For plasmon generation needed for MP-SPR this is not as crucial issue and even multilayered nanolaminates can be characterized.

With the ability to characterize both kinetics and nanoscale layer properties, MP-SPR is an effective tool for nanomaterial, biomaterial and biochemical interactions research. This makes the MP-SPR a powerful tool for multidisciplinary research, where both material physical- and interaction properties are characterized.

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[3] Granqvist et al. Langmuir **29** (27), 2013, 8561-8571

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[5] Sadowski et al. Opt.Eng., **34** (9), 1995, 2581-2586

COLL 659

Characterization of fly ashes from incinerators in China

Elisabeth Feld*, efeld1@tigers.lsu.edu, Slawomir Lomnicki, Barry Dellinger.Chemistry, Louisiana State University, Baton Rouge, LA 70803, United States*

Fly Ash samples collected from multiple waste incinerators in cities throughout China were studied to characterize their propensity to form Environmentally Persistent Free Radicals (EPFRs). The elemental composition of the samples was analyzed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Surface composition of the samples and oxidation state of the metals were analyzed using X-ray Photoelectron Spectroscopy (XPS). The combustible fraction of the fly ashes was evaluated by thermal treatment of the samples at 500 C and 800 C. Electron Paramagnetic Resonance (EPR) studies were used to analyze the behavior of paramagnetic metal ions (iron, in particular) upon thermal treatment. Differently treated fly ash samples will be further exposed to the EPFR precursors to analyze their capability to form EPFRs at different stages of the incinerator. Exhaust treated samples are compared to “as is” fly ash samples in respect of their EPFR quality and quantity.

COLL 660

Alloy catalysis across alloy composition space: $Au_xCu_yPd_{1-x-y}$

Andrew J Gellman*, gellman@andrew.cmu.edu, James B Miller, Gamze Gumuslu.Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States*

High throughput methods have been developed for study of the properties of Cu_xPd_{1-x} and $Cu_xAu_yPd_{1-x-y}$ alloys used in hydrogen purification membranes and as hydrogenation catalysts. These alloys have been deposited on Mo substrates as Composition Spread Alloy Films to form high throughput libraries that span all of composition space, $x = 0 \rightarrow 1$ and $y = 0 \rightarrow 1-x$. Using a high throughput microreactor we have measured the kinetics of catalytic H_2 dissociation via H_2-D_2 exchange and the kinetics for ethylene hydrogenation across all of binary and ternary alloy space. Analysis of the Cu_xPd_{1-x} alloys using UPS has allowed measurement of the position of the *d*-band center at all compositions and correlation of the barriers to hydrogen adsorption and desorption with the position of the *d*-band. XPS has been used to map out the regions of the composition space over which the alloy exists in fcc versus bcc structures.

COLL 661

Molecular perspective on water structure and motion at the surface of climate-active ice nucleating proteins

Ravindra Pandey[1], *pandey@mpip-mainz.mpg.de, Janine Fröhlich*[2], *Ruth Livingston*[1], *Ulrich Pöschl*[2], *Mischa Bonn*[1], *Tobias Weidner*[1]*.Â (1) Max Planck Institute for Polymer Research, Mainz, GermanyÂ (2) Max Planck Institute for Chemistry, Mainz, Germany*

Specific bacteria, such as Pseudomonas syringae, attack plants by using ice-nucleating proteins anchored to their outer cell surfaces. Ice nucleating proteins promote the massive crystallization of ice at temperatures that would otherwise not allow ice formation. The frost damage caused by ice crystals then facilitates bacterial invasion of the affected plants. Ice nucleating proteins not only play an important role for agriculture, but are also very important for atmospheric processes: airborne ice-nucleating proteins have been shown to be among the most effective promoters of ice particle formation in the atmosphere. A recent NASA survey of bacteria in the troposphere has discovered large emissions of biogenic ice nucleators from large forest areas like the amazon, which likely change precipitation patterns and may affect the global climate. To understand biogenic ice formation, a detailed molecular level picture of the mechanism by which ice-nucleating proteins interact with water molecules is important. Sum frequency generation (SFG) spectroscopy – owing to its inherent interface sensitivity – is ideally suited to determine the structure and dynamics of water molecules at interfaces. Here, we report on the interaction a layer of the ice-nucleating protein inaZ with water using static and time-resolved SFG spectroscopy. When cooling the sample from room temperature to near-freezing temperatures (~5°C for D2O), inaZ significantly increases the structural order of water molecules in contact with inaZ proteins. This effect was not observed for liquid water surfaces without the protein or for protein monolayers which are not ice nucleators. The data indicates the activation of a specific binding mechanism at lower temperatures. Femtosecond, time- resolved 2-dimensional SFG spectroscopy was used to quantify the energy transfer from intrfacial water towards the protein contacts.

COLL 662

Photochemistry of methanol at 3D networked aerogels of TiO_2 and Au/TiO_2

John R. Morris[1], *jrmorris@vt.edu, Paul A. DeSario*[2], *Jeremy J Pietron*[2], *Dimitar A Panayotov*[1], *Debra R Rolison*[2]*.Â (1) Department of Chemistry, Virginia Tech, Blacksburg, VA 24061, United StatesÂ (2) Surface Chemistry Branch, U.S. Naval Research Laboratory, Washington, District of Columbia 2375, United States*

Photocatalytic production of hydrogen from methanol offers tremendous promise for the generation of clean fuel for use in combustion and fuel cells. With the objective of gaining a more complete understanding of the mechanism and kinetics of methanol photocatalytic oxidation, we employ high-vacuum surface-sensitive infrared spectroscopy as a probe of molecular and electronic changes to the system during catalysis *(J. Phys. Chem. C* 2012, *116*, 6623). The catalysts we have studied are a unique class of ultraporous TiO_2 and TiO_2-supported Au aerogels that feature a nanoscale solid network interpenetrated in three dimensions (3D) by mesopores and small macropores. The 3D networks significantly stabilize metallic Au particles against

thermal migration, provide open pathways for mass transport to and from the active centers, and significantly increase the number of metal–semiconductor junctions where charge transport and surface chemistry may occur. The utility of IR spectroscopy in semiconductor photochemistry stems from its ability to simultaneously probe both the discrete vibrational transitions of surface adsorbates and the electronic population within or close to the continuum of the semiconductor conduction band *(J .Phys. Chem. C* 2012, *116*, 4535). Our experiments show that the initial uptake of methanol at 3D TiO_2 and Au–TiO_2 aerogels is governed by dissociation to methoxy adsorbates within both systems and that UV irradiation of the porous solids efficiently oxidizes methoxy species to surface-bound formates. Further, we find that networked-entrained Au particles sensitize the oxide nanoarchitecture and activate it toward photochemistry that extends well into the visible range with photooxidation rates at 550-nm that nearly match those at the UV-irradiated TiO_2 aerogel *(J. Phys. Chem. C* 2013, *117*, 15035).

COLL 663

In-operando scanning tunneling microscopy study of Cu-Pd surface alloys

***Niv Levy**, nlevy@bnl.gov, Gayani Perera.Center for Functional Nanomaterials, Brookhaven National Lab, Upton, NY 11973, United States*

Bimetallic surface alloys have been shown to enhance catalytic activity, selectivity and prevent catalyst deactivation in several reactions. However, atomic scale imaging of surface alloys *in-operando* remains relatively unexplored. Recent studies[1] have shown improved selectivity for partial Acetylene hydrogenation using an ultra dilute Cu-Pd surface alloy. The imaging studies reported by Kyriakou *et al.* were conducted in a cryogenic ultra high vacuum environment, leaving open the question as to the evolution of the structure and the active sites under typical reaction conditions. We will present scanning tunneling microscopy images of a range of Cu-Pd surface alloys under realistic reaction conditions, highlighting the changes due to increased pressures and temperatures.

1. Kyriakou, G. *et al.* Isolated Metal Atom Geometries as a Strategy for Selective Heterogeneous Hydrogenations. *Science* **335,** 1209–1212 (2012).

COLL 664

Surface modification strategies for GaP(111)A and GaP(111)B surfaces by X-ray photoelectron and infrared spectroscopy and spectral response

***Elizabeth S Brown**, esbrow@umich.edu, Sabrina L Peczonczyk, Stephen Maldonado.Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, United States*

The development of chemical strategies for surface modification of gallium phosphide (GaP) is vital for the implementation of GaP as a photoelectrode in solar energy

systems. GaP(111)A (Ga-rich) and GaP(111)B (P-rich) surfaces have been modified using either a chlorination/Grignard reaction sequence or a Williamson ether-type synthesis, respectively. The native oxide creates surface states that serve as trap sites which facilitate charge recombination. Previous surface modifications in the literature based upon thiol chemistry are not sufficiently durable for extended photoelectrochemical applications. However, utilizing an alternate modification of covalent Ga-C or P-O-C bonds could impart stability while reducing deleterious surface states. Methods of attachment of organic groups (straight-chain alkyls of varying lengths, benzyl groups, or terminal olefins) to either Ga atop atoms or P atop atoms on controlled single-crystalline surfaces are compared using X-ray photoelectron spectroscopy and grazing-angle attenuated total reflectance infrared spectra. The quantum yield from photoresponse measurements in the visible spectrum exhibits a decrease in surface states after surface modification. These versatile reaction strategies exhibit controlled variations in the electrochemical behavior of GaP electrodes.

COLL 665

Reactivity and structural dynamics of supported metal nanoclusters using electron microscopy, *in situ* X-ray spectroscopy, and electronic-structure theory and simulations

***Judith Yang**, judyyang@pitt.edu.Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA 15203, United States*

Heterogeneous catalysis, which impacts the worldwide economy and sustainability due to its ubiquitous role in energy production, depends sensitively on the nano-sized 3-dimensional structural habits of nanoparticles (NPs) and their physicochemical structural sensitivity to the environment. Very small metal clusters can exhibit patterns of reactivity and catalytic activity that are dramatically distinct, and sometimes completely opposite, than behaviors seen with larger clusters. It therefore remains a significant need in research to fundamentally understand and predict the local structure and stability of catalytic materials that can be specifically tailored by design and optimized for an application in technology. Our focus is on the development of integrated characterization and modeling tools and their applications appropriate for carrying out detailed studies on metallic nanoscale clusters comprised of a few to as many as 100 metal atoms. Two state of the art methodologies, synchrotron X-ray absorption fine-structure (XAFS) and quantitative scanning transmission electron microscopy (STEM) methodologies are used and specially designed for determining the 3D structure and structural habits, both individually and as an ensemble, critical for understanding metallic nanoclusters. The experimental work is integrated with theoretical calculations. It is now clear that the structural dynamics of small metallic clusters is actually quite complex. For example, we have shown that the structures of Pt NPs may be both ordered and disordered, depending on its size, support and adsorbates. While bulk amorphous Pt is unstable, its existence in NPs is a manifestation of their mesoscopic nature. Furthermore, theoretical simulations show that the Pt NPs are not static, but show highly fluxional dynamics. To bridge the theory-

experiment gap, we are producing model Pt/g-Al_2O_3 systems using oxidation of NiAl(110) to form a thin film of single crystal g-Al_2O_3 . To bridge the complexity gap, we are developing an universal environmental cell that is compatible currently with synchrotron XAFS and environmental TEM.

COLL 666

IR investigations of CO oxidation on well-defined Pd oxide surfaces

Feng Zhang[1], *zhangfeng@ufl.edu, Tao Li*[1], *John T Diulus*[1], *Li Pan*[2], *Aravind Asthagiri*[2], *Jason F Weaver*[1]*.Â (1) Chemical Engineering, University of Florida, Gainesville, Florida 32611, United StatesÂ (2) William G. Lowrie Department of Chemical & Biomolecular Engineering, The Ohio State University, Columbus, Ohio 43210, United States*

Interest in the surface chemistry of late transition-metal oxides has been stimulated by observations that the formation of metal oxide layers tends to dramatically alter the catalytic performance of transition metals in applications of oxidation catalysis. For example, *in situ* investigations of CO oxidation over single crystal surfaces of the Pt-group metals have revealed significant changes in surface reactivity as a function of the oxidizing conditions, with these changes attributed to the formation of distinct types of metal oxide layers or surface oxygen phases. In this talk, I will discuss results of recent experiments in which we used reflection absorption infrared spectroscopy (RAIRS) and mass spectrometry to investigate the oxidation of CO on well-defined “surface” and “bulk” Pd oxide surfaces that were grown on Pd(111) in ultrahigh vacuum using oxygen atom beams. We find that both the Pd_5O_4 surface oxide and a multilayer PdO(101) film are reactive toward CO, but the PdO(101) surface is significantly more reactive than the surface oxide.

We investigated the evolution of CO binding states on Pd oxide surfaces during both temperature programmed reaction (TPR) and isothermal reaction experiments. We find that RAIRS can distinguish CO bound on distinct types of surface sites that develop as the Pd oxide surfaces undergo reduction during reaction with CO, including oxygen vacancies and sites associated with metallic domains as well as the surface vs. bulk oxides. During TPR experiments, reaction of a single monolayer of CO on PdO(101) initially produces oxygen vacancies which agglomerate to form metallic domains over a narrow temperature range near 400 K. Further heating above about 450 K causes the metallic domains to be oxidized by oxygen from the subsurface, thereby regenerating PdO(101) surface sites before CO reaction or desorption is complete. We observe a different evolution of surface sites and phases when Pd oxide surfaces react isothermally in a constant CO background. At 400 K, CO oxidation on the PdO(101) film initially produces surface oxygen vacancies and the CO_2 production rate increases toward a maximum. After the rate maximum, RAIRS reveals the loss of PdO(101) domains and the formation of coexisting metallic and Pd_5O_4-like domains. The Pd_5O_4 structure remains on the surface once the CO oxidation rate drops to zero, thus demonstrating that the surface oxide is less reactive toward CO than PdO(101) for the conditions studied. Lastly, I will also discuss results of DFT calculations that have

identified many of the IR features for CO bound on specific sites of the Pd_5O_4 and PdO(101) surfaces. Overall, our results demonstrate the dynamic nature of Pd oxide surfaces during reaction with CO, and provide new information for understanding elementary processes which occur during CO oxidation on these surfaces, including IR signatures for CO bound on specific Pd oxide structures.

COLL 667

Enhanced CO oxidation rates at the interface of mesoporous oxides and Pt nanoparticles and their in situ characterizations

Kwangjin An[1,2]*, akj007@berkeley.edu, Selim Alayoglu*[1,2]*, Nathan Musselwhite*[1,2]*, Gabor A. Somorjai*[1,2]*.Â (1) Department of Chemistry, UC Berkeley, Berkeley, California 94720, United StatesÂ (2) Chemical Sciences Division and Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States*

The interaction of metal and support in oxide supported transition metal catalysts has been proven to have extremely favorable effects on catalytic performance. Despite large amounts of research on oxide-metal interfaces, the mechanism which causes the enhanced catalytic properties is not fully understood. This is due mainly to a limitation of insight to the catalytic workings of the interfaces under reaction conditions.

Herein, mesoporous oxides (Co_3O_4, NiO, MnO_2, Fe_2O_3, and CeO_2)were synthesized and loaded with size controlled Pt nanoparticles to investigate the oxide-metal interface effects on catalytic CO oxidation reactions in both excess O_2 and excess CO. *Insitu* studies show that the redox behavior of the oxides provides the charge that changes the mechanism of CO oxidation from covalent bond chemistry to so-called acid-base, or charge transfer chemistry. This change of mechanism was found to be a general phenomenon for all the oxide-metal interfaces studied. Through the utilization of Near Edge X-ray Absorption Fine Structure (NEXAFS) and Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) under catalytically relevant reaction conditions, we were able to demonstrate a strong correlation between the oxidation state of the oxide support and the catalytic activity at the oxide-metal interface.

COLL 668

On the structures and adsorption properties of the model ZrO_2- and CeO_2-supported metal catalysts

*Yong Han, Shanwei Hu, Dandan Kong, **Junfa Zhu**, jfzhu@ustc.edu.cn.National Synchrotron Radiation Laboratory, University of science and Technology of China, Hefei, Anhui 230029, China*

ZrO_2 and CeO_2 are the two very important oxides which have been widely used in many technical applications such as gas sensors, protective coatings and heterogeneous catalysis. In particular, in heterogeneous catalysis, these two oxides

have been used in many catalytic reactions not only as the metal catalysts' supports but also sometimes as the pure catalysts. Especially, as supports for metal catalysts, despite their vast industrial applications, however, there are still many fundamental uncertainties regarding to the interaction between metal catalysts and these two oxides, the electronic properties of metals, and the morphological evolution of the catalysts before and after the catalytic reactions. To address these uncertainties, we have recently in-situ studied several metal/ ZrO_2 and metal/CeO_2 model catalysts by using a variety of surface science techniques including synchrotron radiation, ultraviolet and X-ray based photoelectron spectroscopies (SRPES, UPS and XPS), scanning tunneling microcopy (STM), low energy electron diffraction (LEED) and temperature programmed desorption (TPD). In this presentation, we will show our recent results on the electronic structures, growth modes, sintering behaviors, and adsorption properties of Ag and Ni on CeO_2(111), and Au, Ag and Cu on ZrO_2(111). The interaction of these metals with the oxide supports as well as its influences on the surface chemistry of these metal/oxide catalytic systems will be discussed.

COLL 669

Solid-state HRMAS NMR as a powerful method for investigating linkers and catalysts immobilized on oxide supports

***Janet Bluemel**, bluemel@tamu.edu, Jacqueline Pope, Johannes Guenther.Department of Chemistry, Texas A&M University, College Station, TX 77843, United States*

Immobilized catalysts ideally combine the recyclability of heterogeneous catalysts with the activity and selectivity of homogeneous systems. Molecular catalysts can be immobilized by tethering them to solid supports with bifunctional linkers. Typical linkers are mono-, bi-, or tridentate phosphines that coordinate the metal complex and they incorporate an ethoxysilane group which binds the linker to the oxide support covalently. Silica and alumina are favorable supports due to their mechanical stabilities, high specific surface areas and availability with different pore sizes. The most powerful method for characterizing immobilized linkers and catalysts is solid-state NMR spectroscopy. Measuring the spectra with classical CP/MAS (cross polarization and magic angle spinning) NMR provides information about the dry materials. However, reactions employing immobilized catalysts are run in solvents. HRMAS (high-resolution MAS) methods allow measurements in the presence of solvents and therefore provide information about *in situ* processes. Linkers and immobilized catalysts are mobilized to some degree by the solvents and therefore anisotropic interactions are reduced. Very narrow lines result and this dramatically improved spectral resolution allows unprecedented insights. For example, side-products of reactions are easily identified, and leaching of trace amounts of linkers or catalysts can be detected. Furthermore, HRMAS allows to quantify the mobilities of linkers with different alkyl chain lengths bound to the support in various ways. With *in situ* HRMAS measurements the migration of a metal fragment from linker to linker on the surface can be observed and the timeline for this process is easily established. The fundamental insights gained by HRMAS in combination with CP/MAS allow us to generate immobilized catalysts with

unprecedented lifetimes and recyclabilities. As examples, Rh catalysts tethered to silica (*Adv*. *Synth*. *Catal*. **2011** , *353*, 443-460) and the immobilized Sonogashira catalyst system (*Chem*. *Commun*. **2011** , *47*, 2059-2061) will be presented.

COLL 670

Impact of metal-support interaction of Pt/Ce-Al_2O_3 catalysts for hydrogen production probed by *in situ* techniques

*Debora M. Meira[1], Renata U. Ribeiro[1], Jose Maria C, Bueno[1], **Daniela Zanchet**[2], daniela@iqm.unicamp.br.Â (1) Department of Chemical Engineering, SÃ£o Carlos Federal University, SÃ£o Carlos, SP 13565-905, BrazilÂ (2) Institute of Chemistry, Campinas State University, Campinas, SP 13083-970, Brazil*

The water gas-shift (WGS) reaction, which deals with the conversion of CO with steam producing CO_2 and H_2, is an important stage for the production of pure H_2, required for energy generation in fuel cells. Despite been a widely used reaction at industrial scale, with well-established two stage process based on iron (high temperature shift–HTS) and copper (low temperature shift-LTS) catalysts, the WGS reaction has attracted considerable attention in the last years with special interest to develop catalyst based on noble metals targeting one stage, low temperature, operation for portable technologies. In this work, colloidal platinum nanoparticles (Pt-NPs) of ~3 nm were synthesized and encapsulated in mesoporous Al2O3 during the sol-gel synthesis. Different contends of cerium (3-20%) were incorporated on the 2% Pt-Al2O3 catalyst by two methods (during the Al2O3 sol-gel synthesis or by impregnation of the Pt/Al2O3 catalyst) to evaluate the impact of metal-support interaction on the catalyst performances. The samples were probed by *in situ* X ray absorption spectroscopy and *in situ* X ray diffraction during: 1) the calcination step, 2) the activation under H_2 and 3) under WGS conditions. The results clearly showed the impact of the Pt-CeO_x interaction on the catalyst performance where turnover frequencies (TOF) at 250^oC proportionally increased with the Ce-contend but, interestingly, was not highly dependent on the crystallinity/size of the CeO_x phase. Complementary, catalysts with low content of platinum (<1 %) were prepared by impregnation to enhance metal dispersion and sensibility to Pt as studied by *in situ* X ray absorption spectroscopy and *in situ* infrared spectroscopy. In this case, it was clearly demonstrated the important role of the Pt-CeO_x interaction on the stability of the Pt dispersion as well as on the stability of the the Pt-adsorbates (H_2 and CO) under different temperatures.

COLL 671

Development of surface enhanced NMR spectrosopy for the characterization of oxide surfaces

***Lyndon Emsley**, lyndon.emsley@ens-lyon.fr.Center for High Field NMR, Ecole normale supÃ©rieure de Lyon, Villeurbanne, France*

Surface enhanced NMR spectroscopy (SENS) can be achieved by using dynamic nuclear polarization (DNP). In this approach, electron polarization is transferred from an organic radical to the rare nuclei (at natural isotopic abundance) at the surface, yielding more than a hundred-fold signal enhancement for species at the surfaces of oxide materials.

We have made rapid progress with this method since its introduction in 2010, and here we show recent advances towards improving the sensitivity of the technique by designing new stable organic radicals to have long electron relaxation times, thereby acting as much improved sources of polarization. These developments allow us to characterize surface composition and structure in a range of materials with DNP SENS, ranging from semi-conducting nanoparticles through tricalcium silicates to periodic mesoporous organosilicates. These materials have low density of surface sites, have surface areas as low as 1 m2/g, and were previously not accessible to detailed characterization by multi-dimensional NMR methods.

COLL 672

Cancer cell theranostics rapidly detects and destroys drug-resistant tumors in vivo

***Dmitri Lapotko**, dl5@rice.edu.Rice University, Houston, TX 77005, United States*

What does “nanotheranostics” mean for biology and medicine? Since their invention, nanoparticles demonstrated both unique properties and an even more unique ability to manipulate energy at nanoscale. Although research into the biological, and especially the medical, applications of nanoparticles will result in entirely new knowledge and medicine, it is yet at the very beginning. In an effort to develop nanotheranostic medicine into true nanomedicine, our lab engaged at nanoscale, the two major life-supporting phenomena, light and heat. Using a mechanism of plasmon resonance in gold nanoparticles, we developed novel, tunable and stealth type nanoprobes, plasmonic nanobubbles (PNBs), tiny vapor bubbles that are generated around gold nanoparticles with short laser pulses. PNBs will provide molecular and cellular imaging, diagnosis, therapy and theranostics (diagnosis and treatment united in one fast procedure) with the speed, selectivity and precision far beyond the limits of modern medicine. Our interdisciplinary research includes three major avenues: fundamental studies of physics, optics and biology of PNBs, studies of PNB-induced bioeffects in cells and organisms, and the development of PNB technologies for cell level imaging, theranostics, surgery, gene therapy and drug delivery.

COLL 673

Hybrid nanotechnologies for detection and synergistic therapies for breast cancer

***Shiladitya Sengupta**, shiladit@mit.edu.Department of Health Sciences and Technology, Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

Our laboratory is focused on developing engineering solutions for complex disease. Our research lies at the interfaces of fundamental biology, medical applications and nano-scale engineering, where basic understanding of biology inspires the development of novel technology or medical applications. We value interdisciplinary approaches to problem solving. We believe innovation happens only through the seamless integration of scientific fields, and that is why our team includes members from diverse professional backgrounds. The unifying thread is our passion for our work and the fact that we all get excited by challenging problems. In this talk, we will describe our recent efforts in using nanoparticles for imaging and treatment of cancer.

COLL 674

Nanoparticle-mediated chemo-RNAi combination therapy for cancer treatment

***Jinjun Shi**, jinjun.shi@zeus.bwh.harvard.edu.Brigham and Women's Hospital, Harvard Medical School, Boston, Massachusetts 02115, United States*

The emergence of drug resistance has been a critical barrier for effective cancer chemotherapy. RNA interference (RNAi) has recently shown promise in suppressing the overexpression of drug resistance-associated proteins, and in treating drug resistant cancers through combination with chemotherapeutic agents. Nevertheless, the safe and effective delivery of RNAi therapeutics (e.g., siRNA) to target cells remains a major hurdle for their clinical applications, and the co-delivery of RNAi and chemotherapeutic agents in a controlled fashion requires specific delivery vehicles.

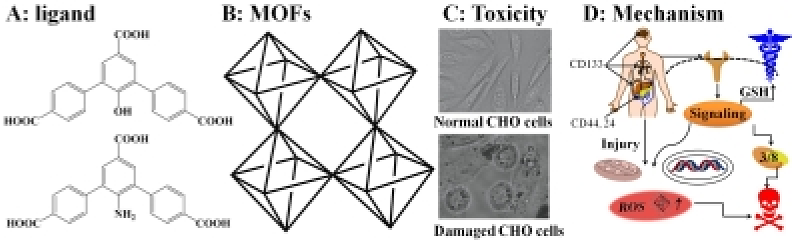
We have developed an innovative nanoparticle (NP) platform to tackle the challenges associated with the delivery of siRNAs and chemotherapeutic drugs, using biodegradable and biocompatible polymers and lipids. The hybrid lipid-polymer NP has a unique hollow core/shell nanostructure which provides the delivery system with three distinct functional features: (i) a positively charged inner hollow core for dense loading of siRNA; (ii) a middle hydrophobic polymer layer for the encapsulation of anti-cancer drugs and the controlled release of both siRNA and drug; and (iii) a polyethylene glycol surface to keep the NP stable and prolong its systematic circulation. The hybrid lipid-polymer NPs show excellent silencing of luciferase (~ 80-95%) at low doses of siRNA. These NPs can also efficiently reduce the expression of drug resistance-associated proteins (e.g., REV1/REV3L and Bcl-2). By co-delivering siREV1/REV3L and cisplatin prodrug, the NPs can effectively inhibit DNA repair activity in LNCaP cancer cells and impair cisplatin-induced mutagenesis, and subsequently dramatically improve the sensitivity of LNCaP cells to concurrent released cisplatin. In vivo results demonstrate that the NPs can sufficiently silence the expression of target genes in tumor tissue after single intratumoral administration, and the NP co-delivery strategy can flat-line the growth of LNCaP xenograft. We expect that the chemo-RNAi nanoparticle co-delivery could be of interest in both fundamental cancer research and clinical applications for cancer treatment.

COLL 675

Functionalized metal-organic frameworks as inhibitor of cell division

Baldemar Martinez[1], *Baldemar.Martinez@students.tamuk.edu, Madhuri Maganti*[1], *Srinath Palakurthi*[2], ***Jingbo Liu***[1], *kfjll00@tamuk.edu, Sajid Bashir*[1]*.Â (1) Department of Chemistry, Texas A&M University-Kingsville, Kingsville, Texas 783638204, United StatesÂ (2) Department of Pharmacy, Texas A&M Health Science Center, Kingsville, Texas 78363, United States*

The purpose of the research was to develop a series of metal-organic frameworks (MOFs), which displayed high potential in delivery drugs and cancer diagnosis. The MOFs were produced via a feasible hydrosolvo-thermal wet-chemistry approach through ligand coordination. Tunable covalent (ligand) coordination frameworks in the fabrication of MOFs allow for high surface area, unique crystal geometry, ultrahigh porosity and controlled particle size. Transition metals centers such as iron (Fe), gold (Au) and platinum (Pt) were used to serve fluorescence platforms whilst the ligands and capping agents served as biocompatibility agents. Several advanced instruments were used to determine the crystalline phase, particle size, distribution, and crystallinity of MOFs. *In-vitro* toxicity data indicated that MOFs IC_{50} (0.02 ppm) is comparable to, or lower than the current first-line drug formulations; at higher doses, the kinetics of action were approximately ten-fold higher. These biological effects may be attributed to the unique tetra-topic carboxylate ligand bridging to a bimeric μ_2-H_2O-centered cluster, in addition to high crystallinity and high aspect ratio.



The latter factors lend themselves to high MOF-cell surface contact, which in turn leads to high degree of catalysis (e.g. depolarization of the mitochondrial membrane from the lactate dehydrogenase assay and inferred anti-topoisomerase I activity by comparison to SN-38 standard). Collectively, our results demonstrate a potentially viable approach in the treatment of solid tumors.

COLL 676

Presenting NuSilico™, a software to predict biodistribution and half life of nanoparticles

***Shalini Ananda**, shalini@crixlabs.com, Jon Stenstrom, Darrin Demchuk.CRIXlabs, Inc., San Francisco, CA 94108, United States*

Nanoparticles as drug delivery systems enable unique approaches for the delivery of active compounds to desired locations in the body. The concept of rationally designed nanoparticles have been expressed throughout the past decade, but the techniques used to approached the problem has seen limited success due to the complexities of trying to create mechanistic models that simulate the body. These simulations have fallen short due to the inability to adequately determine all boundary conditions at a given time.

In this presentation, we describe, NuSilico™, a software that uses predictive analytics to map the spatial and temporal distribution of nanoparticles in the body. We describe a large validation study with 106 experiments comparing observed and predicted results and highlight applications of NuSilico™ for Image Guided Drug Delivery.

COLL 677

Nanoconjugation enhances epidermal growth factor induced apoptosis

***Bjoern Reinhard**, bmr@bu.edu.Department of Chemistry and The Photonics Center, Boston University, Brookline, Massachusetts 02215, United States*

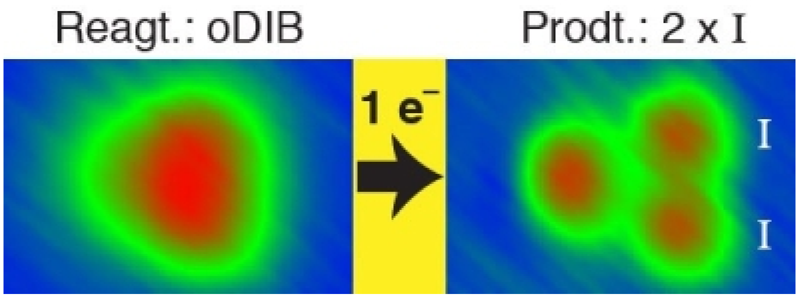
Nanoconjugation, *i.e.* the covalent attachment of a ligand to a nanoparticle, provides new opportunities to influence the cellular processing of the ligand. The ligand of interest in this study is the epidermal growth factor (EGF). EGF receptor (EGFR) signaling is predominantly linked to promoting cell growth and differentiation but has been reported to induce apoptosis in EGFR overexpressing cells. We investigated the impact of EGF nanoconjugation on cellular apoptosis levels, quantified as caspase-3 activity, in two *in vitro* cancer cell lines: A431 and HeLa. The ligand was covalently conjugated to 40 nm diameter gold nanoparticles, which provide large cross-sections in both optical and electron microscopy and, therefore, make the cell-nanoparticle interactions amenable to an experimental characterization. Systematic apoptosis studies of nanoconjugated EGF, nanoparticle controls, and simple mixtures of EGF and nanoparticles revealed that nanoconjugation enhances EGF-induced apoptosis in EGF receptor (EGFR) overexpressing A431 and triggers a quantifiable increase in apoptosis in HeLa cells. The latter have physiological receptor expression levels and do not show apoptosis in response to free EGF. These findings demonstrates that – at least *in vitro* – the apoptotic machinery can be manipulated through ligand nanoconjugation and suggest nanotheranostic strategies aimed at overcoming apoptosis evasion in cancer based on multimodal gold nanoparticles.

COLL 678

How physisorption guides chemisorption: Studied a-molecule-at-a-time by STM

John Polanyi[1]*, jpolanyi@chem.utoronto.ca, Avisek Chatterjee*[1]*, Fang Cheng*[1]*, Kai Huang*[1]*, Stephen J. Jenkins*[2]*, Wei Ji*[3]*, Lydie Leung*[1]*, Tingbin Lim*[1]*, Zhanyu Ning*[1]*, Marco Sacchi*[2]*, Chenguang Wang*[3]*.Â (1) Department of Chemistry, University of Toronto, Toronto, Ontario M5S 3H6, CanadaÂ (2) Department of Chemistry, University of Cambridge, Cambridge, United KingdomÂ (3) Department of Physics, Renmin University of China, Beijing, China*

Electron-induced reactions of aligned physisorbed organic molecules on Si(001) or coinage metals have been characterized by STM of their reagents and products. The configurations intermediate between reagents and products were obtained from a two-electronic-state quantum mechanical model in which the adsorbate was briefly excited to an anti-bonding anionic state and the dynamics were then followed by classical mechanics across the excited and ground potential-energy surfaces. The dynamics were characterized in specific instances by localization of products to the neighbourhood of the physisorbed reagents, directionality of product-recoil dependent on reagent alignment, chiral reaction, bond-selective or multi-bond reaction (see picture for the latter), chain-reaction, or electron-induced long-range migration of reagent prior to surface reaction.



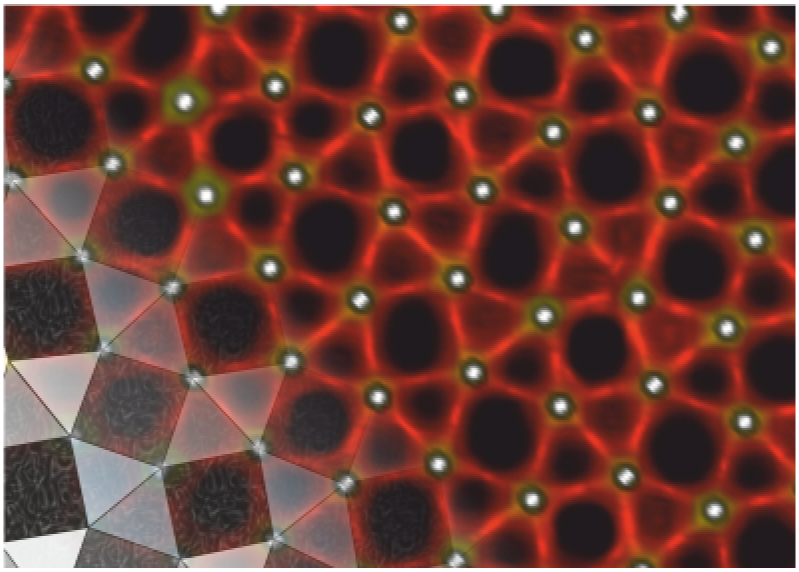
One electron breaks two C-I bonds in o-diiodobenzene physisorbed on Cu(110), to form two chemisorbed I-atoms and an adjacent chemisorbed phenylene.

COLL 679

Nanochemistry at surfaces: From single molecules to complex ensembles and dynamics

Johannes Barth*, jvb@tum.de.Physics, TU MÃ¼nchen, Garching, Bavaria 85748, Germany*

Supramolecular engineering and control of molecular species at interfaces is key to advance molecular science, nanochemistry and the development of novel low-dim materials. The insights gained affect various fields of application, including catalysis, sensing, light-harvesting, nanomagnetism and organic electronics. Here we explore molecular modules, steer their organization and dynamics, and afford novel functions using well-defined surfaces or sp2-nanotemplates as construction platforms. The presented scanning probe real-space observations visualize structural features with atomistic precision, revealing molecular recognition and self-assembly phenomena mediating the expression of genuine nanoarchitectures. Multitechnique studies of flexible species such as metalloporphyrins exemplify the delicate interplay between conformational adaptation, electronic signature and axial ligation of adducts. We describe single-molecule conductance switching via prototropy within a tetrapyrrole macrocycle and stimulate rotational movements of rare-earth porphyrinato sandwich complexes created in vacuo. The devised bottom-up fabrication protocols implement biological and *de novo*synthesized building blocks and exploit error-corrective noncovalent bonding or metal-directed assembly. They yield distinct nanoarchitectures: supramolecular gratings, hierarchic structures, flexible chains and regular or glassy networks. Using porous nanomeshes we demonstrate tunable electron confinement and follow thermal motion of caged units. The developed strategy presents a rationale for the control of adaptive molecular species at interfaces and the design of highly organized molecular nanosystems with complex features, intricate dynamics and tunable functional properties.



Five-vertex Archimedean surface tessellation by lanthanide-directed molecular self-assembly (Proc. Nat. Acad. Sci. 110,6678 (2013))

COLL 680

Chemical reactions in self-assembled organic adlayers

Michael Hietschold[1], *hietschold@physik.tu-chemnitz.de, Nguyen Thi Ngoc Ha*[1]*, Lars Smykalla*[1]*, Thiruvacheril Gopakumar*[3]*, Tobias Rüffer*[2]*, Carola Mende*[2]*, Heinrich Lang*[2]*.Â (1) Department of Physics, Technische UniversitÃ¤t Chemnitz, Chemnitz,* *GermanyÂ (2) Department of Chemistry, Technische UniversitÃ¤t Chemnitz, Chemnitz, GermanyÂ (3) Indian Institute of Technology, Kanpur, India*

Self-assembly of organic molecules on crystalline surfaces may lead to various 2-dimensional patterns of different packing density. At liquid-solid interfaces the appearance of these structures may be controlled by deposition out of a solution playing with the solvent concentration in the solution as a control parameter. We have demonstrated recently this way the appearance of 5 different patterns of trimesic acid out of a solution in octanoic acid on a HOPG (highly-oriented pyrolytic graphite) surface [1].

Moreover enhanced molecular concentration can even result in the induction of a chemical reaction which according to Brown-Le Chatelier's principle saves space for the ordered arrangement of molecules at the substrate surface. We demonstrate this on the example of trimesic acid solved in undecanol. For this system a coadsorption leading to a pattern which contains both kinds of molecules is observed. With increasing concentration of the solvent the packing density of the adsorption pattern increases. However after a threshold value a qualitative change is observed which can be interpreted as a esterification reaction leading to a monoester compound. Interestingly, in the bulk phase the corresponding reaction cannot proceed without a catalyst.

Another kind of chemical reactions in self-assembled molecular adlayers has been discussed earlier by Steinrück et al. after codeposition of a second species in UHV leading to metalation of porphyrins and phthalocyanins [2, 3]. All of these reactions are global (or non-local) in the sense that the whole adlayer is involved.

A second type of chemical reactions can be induced by a STM tip and leads to a local reaction where in the outermost case only a single molecular reaction takes place. We discuss this on a further example: the reversible de-protonation of tetra(p-hydroxyphenyl)prophyrin in a self-assembled monolayer on Ag(111) in UHV. To our best knowledge, this reaction has not yet been observed in a bulk phase.

Finally we discuss the possible induction of other reactions as e.g. a twin-polymerization {4] starting from self-assembled molecular arrays on a crystalline substrate.

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COLL 681

Revealing and manipulating single molecule reactivity in an environmentally controlled liquid-STM

Johannes A.A.W. Elemans[1], *J.Elemans@science.ru.nl, Duncan den Boer*[1]*, Min LI*[2]*, Thomas Habets*[1]*, Patrizia Iavicoli*[3]*, Alan E. Rowan*[1]*, Roeland J.M. Nolte*[1]*, Sylvia Speller*[1]*, David B. Amabilino*[3]*, Steven De Feyter*[2]*.Â (1) Radboud University Nijmegen, Institute for Molecules and Materials, Nijmegen, The NetherlandsÂ (2) Division of Molecular Imaging and Photonics, KU Leuven, Leuven, BelgiumÂ (3) Institut de CiÃ¨ncia de Materials de Barcelona (ICMAB-CSIC), Barcelona, Spain*

Many chemical reactions are catalyzed by metal complexes, and insight in their reaction mechanisms is of fundamental importance for the design of new chemical processes. A wealth of conventional spectroscopic techniques is available to study reaction mechanisms at the ensemble level, but the emergence of scanning probe microscopy has enabled the possibility to obtain information about reactivity at subnanometer scale. I will discuss single molecule studies of the behavior of reactive molecules in an environmentally controlled Scanning Tunneling Microscope (STM). Reactions of manganese(III) porphyrins (Fig. 1A), self-assembled at a solid/liquid interface, with oxygen are investigated in real-space and real-time. Upon exposing these porphyrins to an atmosphere of O_2or to a single oxygen donor, STM revealed a variety of reactions which are detected by clear changes in porphyrin signature in the STM images (Fig. 1B). The signatures can be assigned to the starting compound, reaction products, and intermediates, and their dynamical interchange can be monitored for hours. Furthermore, the reactivity of the porphyrins can be controlled by the applied bias voltage. These studies revealed unique mechanistic insights at the single molecule level that remain hidden in ensemble measurements.

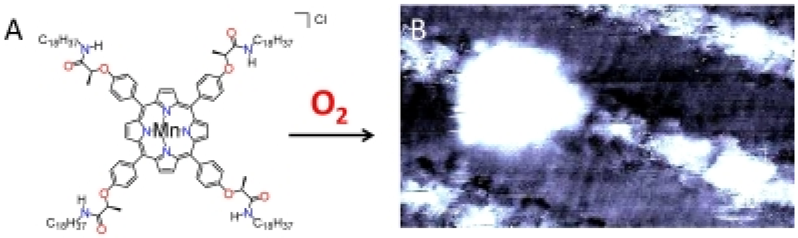

Figure 1 (A) Structure of the Mn(III) porphyrin. (B) STM image (13 × 7 nm^2) of 4 different signatures of the Mn porphyrin at a graphite/liquid interface under an oxygen atmosphere.

COLL 682

Cross-linking and template applications of patterned self-assembled monolayers

***Matthew B Zimmt**, mbz@brown.edu, Jian He, Yan Yang, Yi Xue, Gavyn Ooi.Chemistry, Brown University, Providence, Rhode Island 02912, United States*

Numerous strategies direct self-assembly of patterned monolayers. Efforts to develop functional applications exploiting patterned 2D assemblies will benefit by locking-in monolayer structure. This presentation will describe our recent efforts to develop robust approaches to complex monolayer patterning, to lock-in patterns by post-assembly cross-linking and to apply cross-linked monolayers as templates for patterned deposition.

COLL 683

Steering on-surface polymerization with metal-directed template

***Nian Lin**, phnlin@ust.hk.Department of Physics, The Hong Kong University of Science and Technology, Kowloon, Hong Kong Special Administrative Region of China*

Here we demonstrate a strategy of using metal-directed template to control the on-surface polymerization process. We chose bifunctional porphyrin derivatives with pyridyl and bromine end groups as the model system. Linear template afforded by pyridyl–Cu–pyridyl coordination effectively control the Ullmann coupling of the monomers on a Au(111) surface. Taking advantage of efficient topochemical enhancement owing to the conformation flexibility of the Cu–pyridyl bonds, macromolecular porphyrin structures that exhibit a narrow size distribution were synthesized. We used scanning tunneling microscopy and kinetic Monte Carlo simulation to gain insights into the metal-directed polymerization at the single molecule level. The results reveal that the polymerization process profited from the rich chemistry of Cu which catalyzed the C–C bond formation, controlled the size of the macromolecular products, and organized the macromolecules in a highly ordered manner on the surface.

COLL 684

Multiple dynamical regimes in irreversible surface assembly

***David T Limmer**, dlimmer@gmail.com.Princeton Center for Theoretical Science, Princeton University, Princeton, NJ 08540, United States*

Understanding self-assembly arbitrarily far from equilibrium is complicated by the lack of an underlying free energy surface that determines the properties of the burgeoning material. Such non-equilibrium behavior is particularly ubiquitous at interfaces, where strong surface interactions can promote irreversible processes. Using a simple stochastic model of surface growth, I show how the introduction of irreversible kinetics generically leads to multiple dynamic regimes. These different dynamic regimes are the equivalent of phases in trajectory space and are illuminated by studying rare fluctuations of the dynamical behavior of the system. The possibility of formulating general design principles that exploit this phase behavior are explored using

generalizations of thermodynamics out-of-equilibrium. Specific implications for electrochemical growth are discussed, where the role of applied field and initial surface structure are considered.

COLL 685

Structure transition of alkylthiol monolayer/Au(111) interface during the self-assembly process: Interplay between surface gold atoms and thiol molecules

Kohei Uosaki[1,2]*, uosaki.kohei@nims.go.jp, Toshihiro Kondo*[3]*.Â (1) International Center for Materials Nanoarchitectonics, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, JapanÂ (2) Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo, Hokkaido 060-0810, JapanÂ (3) Division of Chemistry, Ochanomizu University, Tokyo, Japan*

Detailed electrochemical and surface X-ray diffraction measurements shows that the Au(111)-(23x√3) reconstructed structure is converted to the Au(111)-(1x1) structure upon the formation of a self-assembled monolayer (SAM) of hexylthiol but the degree of the lifting of the Au(111) reconstructed structure is not linearly depended on the surface concentration of the thiol SAM, *Γ*. When *Γ* is less than ca. 0.35 nmol cm^{-2}, i.e., ca. 45% of the full coverage, the degree of the reconstruction lifting is almost zero and the thiol seems to adsorb on the reconstructed surface in a lying-down structure. The degree of the reconstruction lifting drastically increases when *G* exceeds this value and the reconstruction is fully lifted to Au(111)-(1x1) structure when *Γ* is 0.77 nmol cm^{-2}, i.e., the full coverage of the thiol SAM in standing-up configuration with the (√3x√3)*R30°* structure. The reconstruction lifting seems to be induced by the formation of the condensed phase of the SAM on the Au(111) surface with (√3x√3)*R30°* structure, which takes place when the surface concentration of the adsorbed thiol on the Au(111)-(23x√3) reconstructed structure reached the full coverage in the lying-down phase.

COLL 686

Multi-compartment magnetic nanoclusters for sequestration of pollutants from marine and fresh water environments

Jeniree A Flores[1]*, jeniree.flores@chem.tamu.edu, Adriana Pavia-Sanders*[1]*, Karen L Wooley*[1,2]*.Â (1) Department of Chemistry, Texas A&M University, College Station, Texas 77840, United StatesÂ (2) Department of Chemical Engineering, Texas A&M University, College Station, Texas 77840, United States*

Water contamination is a severe problem with serious ramifications affecting all levels of our ecosystem. There are several sources of contamination for aquatic environments; however, one of the most devastating causes is associated with the production and extraction of crude oil. Recent developments in our laboratory have resulted in the successful construction of nanomaterials with an added magnetic component for ease of manipulation and recovery. However, a desire to have tailored materials for broader

applications has led us to the development of an enhanced, targeted system. In order to achieve this novel remediation system, we have designed and synthesized multi-compartment magnetic nanoclusters composed of a large magnetic core surrounded by shell crosslinked knedel-like (SCK) nanoparticles. The SCKs, composed of poly(acrylic acid)$_{90}$-*block*-polystyrene$_{140}$ (PAA$_{90}$-*b*-PS$_{140}$) block copolymers, exhibit hydrodynamic diameters of *ca*. 20 nm. Tethering of the SCKs onto a large magnetic core is expected to impart a high magnetic response to the materials. In addition, these multi-compartment nanoclusters are expected to absorb hydrophobic organic pollutants into the satellite SCKs through host-guest interactions. Efforts towards the synthesis of the nanoconstructs *via* covalent attachment of the SCKs onto the magnetic core through azide-alkyne click chemistry will be discussed. Moreover, the novel application of SCKs as solid particle stabilizers of emulsions will be discussed, as well as their utilization in a Pickering emulsion polymerization approach towards the construction of the well-defined multi-compartment magnetic nanoclusters.

COLL 687

Weak magnetic field significantly enhances selenite removal kinetics by zero valent iron

***Xiaohong Guan**, guanxh@tongji.edu.cn, Liping Liang.Department of Municipal Engineering, Tongji University, Shanghai, Shanghai 200092, China*

The effect of weak magnetic field (WMF) on Se(IV) removal by zero valent iron (ZVI) was investigated as functions of pH and initial Se(IV) concentrations. The presence of WMF significantly accelerated Se(IV) removal and extended the working pH range of ZVI from 4.0~6.0 to 4.0~7.2. The WMF induced greater enhancement in Se(IV) removal by ZVI at lower initial Se(IV) concentrations. The influence of WMF on Se(IV) removal by ZVI was associated with a more dramatic drop in ORP and a more rapid release of Fe^{2+} compared to the case without WMF. SEM and XRD analysis revealed that WMF accelerated the corrosion of ZVI and the transformation of amorphous iron (hdyr)oxides to lepidocrocite. XANES analyses showed that WMF expedited the reduction of Se(IV) to Se(0) by ZVI at pH 6.0 when its initial concentration was $\leq$20.0 mg L^{-1}. Se(IV) dosed at 40.0 mg L^{-1} was removed by ZVI via adsorption followed by reduction to Se(0) at pH 7.0 but via adsorption at 7.2 in the presence of WMF. Regardless of WMF, Se(IV) applied at 40.0 mg L^{-1} was removed by reduction at pH 4.0~6.0. The WMF-induced improvement in Se(IV) removal by ZVI may be mainly attributable to the Lorentz force and magnetic field gradient force. Employing WMF to enhance Se(IV) removal by ZVI is a promising and environmental-friendly method since it does not need extra energy and costly reagents.

COLL 688

Implications and application of nano zero-valent iron for anaerobic digestion and wastewater treatment

***Zhiqiang Hu**, huzh@missouri.edu.Civil and Environmental Engineering, University of Missouri, Columbia, MO 65211, United States*

Nano zero valent iron (NZVI), although being increasingly used for environmental remediation, has potential negative effect on anaerobic digestion. NZVI inhibited methanogenic growth and methane production at 1 mM and above. Meanwhile, NZVI dissolution led to rapid production and accumulation of H_2 in anaerobic digestion. The inhibition was due to disruption of cells and coincident with rapid H_2 production from NZVI. For comparison, ZVI powder at the concentration of 30 mM increased methane production because of slow hydrogen production from ZVI dissolution. The highly efficient cell disruption by NZVI opens up new approaches to generate a significant amount of organic substrate for nutrient removal in wastewater treatment. Furthermore, a direct use of functionalized NZVI could be used for sludge bulking control and nutrient removal in wastewater treatment.

COLL 689

Magnetically retrievable nano-catalysts in benign media

***Rajender S Varma**, Varma.Rajender@epa.gov.Sustainable Technology Division, National Risk Management Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268, United States*

Microwave-assisted hydrothermal process has been used to generate nanoferrites[1] and micro-pine structured particles.[2] Sustainable applications of such recyclable and reusable magnetic nanomaterials in catalysis (and organocatalysis) for a wide variety of reactions will be highlighted;[3,4] immobilization of nano Pd, Ni, Ru, Cu etc. on biodegradable and recyclable supports e. g. cellulose and chitosan or on magnetic ferrites via ligands such as dopamine or glutathione will be described,[5] including their use in environmental remediation.

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COLL 690

Investment of the sorption capacity of engineered nanocrystalline magnetic metal oxides for applications in water remediation as environmental sensors

Seung Soo Lee[1], *lees@seas.wustl.edu, Wenlu Li*[1], *Minjung Cho*[2,3], *Paolo Decuzzi*[3], *Vicki L. Colvin*[2], *John D. Fortner*[1]*.Â (1) Energy, Environmental, and Chemical Engineering, Washington University in St. Louis, St. Louis, MO 63130, United StatesÂ (2) Chemistry, Rice University, Houston, TX 77005, United StatesÂ (3) Department of Translational Imaging, The Methodist Hospital Research Institute, Houston, TX 77030, United States*

There have been a lot of interests in use of nanomaterials as environmental sensors for noble, high efficient water treatment processes because of high capacity and sensitivity of uniform nano-scale materials towards metal pollutants, such as, chromium, and arsenic in nature system. In this study, monodisperse magnetic metal oxide nanocrystals (*e.g.* iron oxide (Fe_3O_4), manganese oxide (Mn_xO_y), and manganese ferrite nanocrystals ($Mn_zFe_{3-z}O_4$)) with varying size, shape and composition were synthesized by high temperature metal precursor decomposition. Simple ligand exchange method using various phase transfer agents made the synthesized nanomaterials colloidally stable in aqueous media. Using the phase transferred nanocrystals, the interfacial chemistry of water soluble nanocrystalline magnetic metal oxides including nanocrystal transformation (aggregation and dissolution) were evaluated in the environmental media. Finally, the sorption capacity of the phase transferred nanocrystals toward arsenic and chromium were analyzed for use as environmental sensors. These data suggest that the organic coatings (surface stabilizers) on the nanocrystals do not limit the sorption behavior of the nanocrystals, and that the environmental sensing will be preserved as long as the nanocrystals are colloidally stable.

COLL 691

Preparation and evaluation of titanium dioxide nanoparticles for enhanced lead removal

Zuleyha O Kocabas Ataklı, *ozlemkocabas@sabanciuniv.edu, Yuda Yürüm.Department of Material Science and Engineering, Sabanci University, istanbul, Turkey*

The existence of lead in water supplies is great concern due to its potential effects on human health. This study demonstrates beneficial adsorptive elimination of lead from water using titanium dioxide nanoparticles produced by sol-gel method followed by calcination at 400^oC. The structure of the resulting sample and the surface species of nanoadsorbent were determined using X-ray diffraction (XRD), Raman spectroscopy and X-ray photoelectron spectrometer (XPS). Batch adsorption experiment was carried out to analyze lead removal capacity of the nanoadsorbent. The amount of adsorbed lead by the nanoadsorbent increased with increasing pH. The sorption kinetic data of lead followed the pseudo-second-order model. The equilibrium data were modeled with the help of Langmuir, Freundlich, Redlich-Peterson and Sips equations. Based on the values of correlation coefficients (R^2) and the average percent error (APE), the Langmuir isotherm equation was excellently fitted to the experimental data of the lead adsorption with diminutive error. The maximum experimental adsorption uptakes were 31.25 mg/g for lead. From the thermodynamic calculations the favorable Gibbs energies were entropically controlled during the lead adsorption. This study is valuable for the quality utilization of drinking water that includes lead contamination by using titanium dioxide nanoparticles as a nanoadsorbent.

COLL 692

Size and age dependent surface structure and reactivity of iron oxide nanoparticles

Andrew N Quicksall, *aquicksall@smu.edu, Lindsay S Dietrich, Lael Badakhshanian.Department of Civil and Environmental Engineering, Southern Methodist University, Dallas, TX 75275, United States*

Iron oxides are widespread in nature and are linked to many natural biogeochemical processes; further, they are used as engineered solutions to aqueous contamination problems. Here, we present ongoing work focused on the structure and physiochemical properties of various synthesized nano-scale iron oxide minerals as a function of particle size and age. Crystallinity, surface area, surface hydration and hydroxylation, and phase are constrained by various analytical techniques including XRD, BET, TGA, and TEM. Fe(II) sorption and precipitation with nano-scale ferric oxides is also presented as a function of particle size and age. Surface structure, physiochemical properties, and reactivity all vary with surface area normalized particle size and age. Alteration of nano-scale ferric oxide surfaces occurs over environmentally relevant timescales with impact on environmental processes such as sorption, precipitation, and dissolution. This could have significant ramifications for engineered treatment procedures and interpretation of naturally occurring processes thus far not well explained.

COLL 693

Graphene oxide/zinc oxide nanocomposites as dissolved oxygen sensors

Jameel A. Hasan, *jameelahhasan@gmail.com.Department of Chemistry, Western Michigan University, Kalamazoo, Michigan 49008, United States*

Dissolved oxygen (DO) testing is imperative for variety of applications, which need regulated levels of oxygen to determine the quality and safety of its products and environment. These can involve testing foods, beverages, pharmaceuticals, bloods, and the quality of water. DO in water levels is a very important parameter to regulate its

safety quality. To measure the levels of DO, Clark electrodes and luminescent based optical sensors are normally used. The luminophores used in these special probes detected the DO in samples which operate on the luminescence quenching principles of triplet-triplet annihilation. The problem with turn-off luminescence based probes are their complications with detecting and following minute changes in the DO. In our study, we use newly synthesized Graphene Oxide/Zinc Oxide (GO/ZnO) nanocomposites as turn-on luminescence sensors for DO. The GO/ZnO nanocomposites are sensitive to the oxygen levels in different solvents. Fluorescence luminescence measurements were carried out to observe the trap state luminescence and bande dge luminescence intensities. Luminescence in these nanocomposites arise from the filled and empty oxygen vacancies within the ZnO nanoparticles' systems. The ratiomeric sensing of trap state luminescence over band edge luminescence is observed in different organic solvent environments that further enhanced the sensing ability of the nano composites to DO. Furthermore, ultrafast luminescence studies are carried out to characterize newly synthesized nano composite systems.

COLL 694

Multi-functional nanoparticle coatings on polystyrene spheres by design: Preparation and application to catalysis and sensing

***Brandy Kinkead**, bkinkead@sfu.ca, Abdiwali A Ali, Iris I Guo, John-C. Boyer, Byron D Gates.Department of Chemistry and 4D Labs, Simon Fraser University, Burnaby, British Columbia V5A 1S6, Canada*

Coating nanoparticles (NPs) onto the surfaces of polystyrene (PS) spheres provides the NPs with a support for enhanced stability and improved dispersion. This presentation describes a method to prepare uniform NP coatings that are well distributed over the surfaces of the PS spheres. This method is demonstrated for a number of different types of NPs with varying composition, shape and size. For example, the PS spheres were decorated with Au spheres and rods, ~3-nm diameter Pt NPs and ~40-nm diameter lanthanide upconverting NPs. The number of NPs coating each PS sphere was readily tuned while maintaining a uniform distribution over the surfaces of the PS sphere. This tuning effectively alters the NP parking area (surface area occupied by each NP on a PS sphere), which could have implications on the resulting properties of these NP coatings. Two types of bimetallic NP coatings were also prepared and their composition fine-tuned by controlling the relative ratios of NPs (Figure 1). This well-controlled method was used to prepare uniform NP coatings with a range of interesting catalytic and optical properties. The catalytic decolorization of azo dyes by NP coated PS spheres was demonstrated and the coatings found to be stable for several catalytic cycles. The application of NP coated PS spheres for surface enhanced Raman spectroscopy and biological imaging will also be discussed.

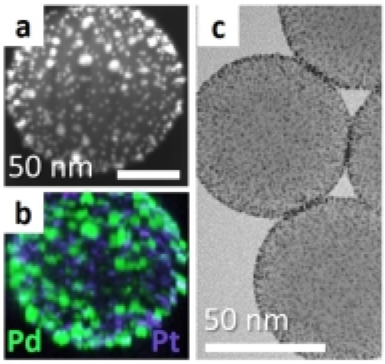

Figure 1. Two types of bimetallic nanoparticle (NP) coatings have been prepared on the surfaces of polystyrene (PS) spheres. (**a**) Scanning transmission electron microscope image and (**b**) elemental map of a Pt and Pd NP coated PS sphere. (**c**) Transmission electron microscope image of FePt NP coated PS spheres.

COLL 695

Water-processable Laponite nanocomposites for energy and environmental applications

Michael E Hagerman, *hagerman@union.edu, Tae Ra Kim, Jared S Mondschein, Isaac A Ramphal, Erin R Waterman.Department of Chemistry, Union College, Schenectady, NY 12308, United States*

Self-assembled nanomaterials offer new routes to rational materials design through inexpensive film growth methods that yield unique, highly functional materials for energy and environmental applications. To this end we have employed the synthetic clay Laponite (Lap) as a structure-directing agent to optimize the inclusion, aggregation, and organization of nanoparticles and conductive polymers in order to improve nanocomposite water processability and film formation. Polyaniline (PANI) nanomaterials have attracted much attention as they offer high conductivity, flexible processability, and versatility for design and fabrication of nanostructures including nanoscale conducting cylinders and lamellar sheets. We have synthesized Lap/PANI and Lap/PANI/graphene nanohybrids through mechanochemical and solution phase polymerization for the development of novel heterojunction solar cells and supercapacitors. In addition, we have fabricated cerium oxide/Lap nanomaterials using solution phase hydrolysis to synthesize microporous nanoflowers that show promise for the removal of arsenic and chromium from contaminated water. Through careful selection of morphosynthetic conditions in these hybrid systems, it is possible to control composite nanomorphologies to realize one-dimensional nanorods, two-dimensional nanosheets, and three-dimensional interpenetrating nanonetworks. SEM, AFM, and FTIR and electronic-absorption spectroscopy studies were completed to probe surface morphology, organic-inorganic interfaces, and expand our understanding of nanostructure-property phenomena that have informed device design strategies.

COLL 696

Cephalopod-inspired tunable infrared camouflage

Long Phan[1], *longp1@uci.edu, Ward G Walkup*[2], *David Ordinario*[1], *Emil Karshalev*[1], *Jonah-Micah Jocson*[1], *Anthony M Burke*[1], ***Alon A Gorodetsky***[1], *alon.gorodetsky@uci.edu.Â (1) Department of Chemical Engineering and Materials Science, University of California, Irvine, Irvine, CA 92697, United StatesÂ (2) Division of Biology, California Institute of Technology, Pasadena, CA 91125, United States*

Cephalopods are known as the chameleons of the sea – they can alter their skin's coloration, pattern, texture, and reflectivity to blend into the surrounding environment. Despite much research effort, there are few known strategies (natural or artificial) for emulating the unique dynamic reflectivity and coloration of cephalopods. We have drawn inspiration from self-assembled structures found in cephalopods to fabricate tunable biomimetic camouflage coatings. The reflectance of these coatings can be dynamically modulated between the visible and infrared regions of the electromagnetic spectrum in situ. Our studies represent a crucial step towards reconfigurable and disposable infrared camouflage for stealth applications.

COLL 697

Surface and interfacial phenomena of hyperbolic metamaterials and metallic films

Yuri A. Barnakov, *ybarnakov@nsu.edu, Srujana Prayakarao, Olivia Penrose-Sadique, Carl E. Bonner.Center for Materials Research, Norfolk State University, Norfolk, VA 23504, United States*

Hyperbolic metamaterials (HMMs) are artificial nanocomposite structures with unique electromagnetic responses, which originated from their dispersion relationship featured opposite signs of dielectric permittivity in orthogonal directions. During the last several years, they are the central subjects of the intensive, competitive research. Metamaterials with hyperbolic dispersion relationship, which experimentally can be realized in two configurations: alternated metal/dielectric multi-nanolayers an array of silver/gold nanowires embedded into the porous alumina membrane, show the number of unusual properties.

They possess broad-band singularity in the density of photonic states and enable imaging with deep sub-wavelength resolution, control of spontaneous emission, and dramatic reduction of reflectance. Particularly intriguing are activeMMs withhyperbolicdispersion, which physical analogies extend to cosmological Big Bang and unusual time-space relations.

Although all these HMMs properties were theoretically predicted and partially experimentally observed, the implication of the surface states of HMMs remains largely unexplored. With the further miniaturization of functional devices, such as MEMS/NEMS (micro-, nano-electromechanical systems), the problem of “stiction”, adhesion between moving parts become a significant one, calling for new ways to combat unwanted interactions. Thus, the ability to engineer the dispersion interactions will play a key role

in surface and interfacial phenomena, such as wetting, adhesion, electrochemistry, sintering, catalysis, and surface sensing.

In the talk, we will show our recent results on the studies of the wetting with gold films and hyperbolic metamaterials, their electrochemical properties and the direct AFM probing of the force and energy landscape (Force-Distance curve) in the system: AFM probe – specimen's surface.

COLL 698

Mechanical properties of EMAA ionomer containing polyelectrolyte multilayers

Hsiu-Chin Huang[1]*, hsiuching.huang@gmail.com, Nicole Zacharia*[2]*.Â (1) Department of Mechanical Engineering, Texas A&M, College Station, texas 77840, United StatesÂ (2) Department of Polymer Engineering, University of Akron, Akron, Ohio 44310, United States*

Copolymers of ethylene and methacrylic acid (EMAA), which are ionomers due to the relatively lesser incorporation of the charged monomer, are known to be tough. In our work we form complexes of these ionomers with oppositely charged polyelectrolytes in order to modify and hopefully improve the properties of EMAA. The research presented here is to employ tensile testing for measuring the mechanical properties of polyelectrolyte multilayers containing EMAA with micro-scale thickness. The thin films are a blend of linear polyethyleneime (LPEI) and EMAA ionomers made using the Layer-by-layer or LbL technique under a water/THF mixed solvent system. The LbL technique is a simple but powerful approach of fabricating films under a molecular level control resulting in film properties that are tunable. EMAA partially neutralized by sodium ions is a commercial polymer widely used in packaging or coatings where high strength or resistance to abrasion is required. Its great mechanical properties are derived from aggregations of the ionic species. We use electrostatic interactions to blend LPEI with EMAA as well as post-complexation annealing. From tensile testing results, we found the effect of ionic complexation on stiffness and toughness of films and different micro-structure on the surface of stretched films. Nano-indentation is another method used to determine the mechanical properties. In addition, this research detected the ionic aggregations in the LPEI/EMAA assemblies by AFM under low oscillation amplitude conditions.

COLL 699

Development and testing of intricate, amphiphilic crosslinked hyperbranched fluoropolymers as anti-icing coatings in aerospace and defense applications

Jennifer N Summerhill[1]*, jennifer.summerhill@mail.chem.tamu.edu, Kevin A Pollack*[1]*, Jeffery E Raymond*[2]*, Karen L Wooley*[1]*.Â (1) Departments of Chemistry and Chemical Engineering, Texas A&M University, College Station, Texas 77842, United StatesÂ (2)*

Laboratory for Synthetic-Biologic Interactions, Texas A&M University, College Station, Texas 77842, United States

This work aims to develop robust, dynamic, anti-icing coatings for aerospace applications through the variation of three main material characteristics including hydrophobicity, low surface energy and thermo-responsive molecular ordering. Aircraft icing is an accumulation of water droplets that freeze in an aircrafts' induction system and/or on the instrumentation that negatively influences performance and efficiency of the aircraft. Current methods of alleviating this issue rely on the application of toxic deicing fluids that are inefficient and expensive as a whole. The research presented focuses on the prevention of icing rather than merely responding to ice after it has already manifested.

We have previously synthesized crosslinked networks comprised of hyperbranched fluoropolymers (HBFP) and poly(ethylene glycol) (PEG), which demonstrated superb anti-biofouling capabilities credited to their amphiphilic morphology, nanoscopic surface topography and dynamic surface reorganization. By extension, this research seeks to expand the application of these materials by exploiting their characteristics for the purpose of inhibiting the organization of water into ice crystals, and subsequently, preventing the formation of ice. Initial differential scanning calorimetry (DSC) data show that the materials presented here exhibit inhibition of ice formation, as determined from reductions in the water melting transition temperatures (freezing point depressions). An array of films was synthesized varying the PEG crosslinker content to study the effect of PEG-to-HBFP ratio on the efficiency of these materials. Based on DSC data obtained from this preliminary study, a second array of films was developed by varying the drop-casting solvent that was used during film preparation. The advances of these materials will be discussed in terms of formulation, the structure-function relationship driving the empirically-derived melting transition temperature and the final effect on the water phase at the surface.

COLL 700

Functional and responsive supramolecular colloids through electrostatic self-assembly: Light-switchable, catalytically active and organic-inorganic assemblies

***Franziska Groehn**, franziska.groehn@fau.de.Chemistry and Pharmacy, University Erlangen-Nuernberg, Erlangen, Germany*

The design of supramolecular composite colloids is of great importance, as self-assembly allows the production of a variety of structures for example for carrier systems, nanotechnology or solar energy conversion. Recently we have introduced an approach to electrostatic self-assembly for the formation of well-defined and responsive supramolecular nano-objects in solution: building blocks are polyelectrolytes and multivalent organic counterions. Colloidal aggregates with varying shape such as spheres, cylinders, vesicles and networks result and pH-responsive assemblies can be built. Key to the structural design is an interplay of electrostatics, p-p interaction and geometric factors. Through isothermal titration calorimetry, we quantify enthalpic and entropic contributions and can relate aggregation number and free energy of the assembly formation.

Next to pH-responsiveness, light is an elegant, non-invasive stimulus: Supramolecular particles can be made the size of which can be triggered by light. Further, the possibility to design functional ionic assemblies in a facile manner is demonstrated by catalysis. New types of catalytically active self-assembled nanostructures in aqueous solution will be presented. For example, polyelectrolyte-porphyrin nanoscale assemblies exhibit up to 8-fold higher catalytic activity than the corresponding porphyrins without polymeric template.

Composite nano-objects with metal and semiconductor nanoparticles as building blocks will also be discussed. Detailed structural characterization by static and dynamic light scattering, AFM, SANS, zeta-potential and spectroscopy yields insight into structural control in the self-assembly process and particle size control.

COLL 701

Hybrid plasmonic-magnetic nanoparticles

Orathai Thumthan, *orathai.thumthan@mavs.uta.edu, Yaowu Hao.Department of materials Science and Engineering, University of Texas at Arlington, Arlington, TX 76019, United States*

We designed and fabricated a new type of magnetic nanoparticles: multilayered magnetic nanodisks. This nanodisk consists of two magnetic layers (Co and NiFe) separated by a non-magnetic Au layer with two anchorage Au layers. Such nanodisks possess near zero remanance, high saturation moment and tunable saturation field. They can potentially replace commonly used superparamagnetic iron oxide nanoparticles for bioapplications. At the same time, such nanoparticles also comprise three Au nanodisks. Au nanodisks, due to their surface plasmon resonance properties, can provide unique optical properties, and potentially can act as optical contrast agents for bioimaging.

For the mass production of such multilayered magnetic nanodisks, electrochemical deposition into nanoscale channels inside anodic alumina membranes was used. First, a simple anodization process to produce anodic alumina membranes with channel diameter less than 100 nm has been developed. A thin layer (~500nm) of Cu film was evaporated to the AAO membrane surface to block the channels and act as working electrode for electrodeposition. Sacrificial Cu was then electrodeposited into the channels followed by electrodeposition of Au and NiFe, respectively. The last bilayer of Co/Au was electrodeposited into the channels from an electrolyte containing both Co and Au ions. By dissolving sacrificial Cu and AAO membrane, nanodisks were released into the solution. Magnetic and optical properties of nanodisks were characterized. It shows that SPR peak of multilayered nanodisks significantly shift towards longer

wavelength comparing to Au nanodisks. Finite difference time domain (FDTD) computer simulation was conducted to explain this phenomenon.

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COLL 702

Optimzation of pollen performance as a filler in poly(vinyl acetate) composites

***Oluwatimilehin Fadiran**, ofadiran3@gatech.edu, J. Carson Meredith.School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States*

Pollen grains have the potential to be effective biorenewable fillers in polymer matrices in part due to the exine shell's high mechanical strength, chemical stability, and unique architectures. In addition, pollen-polymer composites are attractive because they could form the basis for a new class of light-weight, high strength materials with a sustainable plant-based filler. Using pollen as a filler also provides a unique way to study how filler microstructure affects wetting and adhesion between the phases. The effectiveness of pollen as a reinforcing filler in poly(vinyl acetate) (PVAc), a common commercial polymer, is characterized by mechanical properties, interfacial morphology, and glass transition temperature of pollen-polymer composites as a function of pollen loading. We report the optimization of wetting and adhesion of pollen fillers in a polymer matrix via in situ free radical polymerization of vinyl acetate monomer (VAM) versus purely solution processing. As received pollen displayed interfacial voids, degraded mechanical properties, and a decreased glass transition width because of low surface interactions between the native pollen and the polymer matrix. Pollen treated with an acid-base hydrolysis displayed improved interfacial morphology, increasing modulus with increasing pollen loading (29% increase). This is due to increased surface interactions on treated pollen because of exposed polar functional groups. Adhesion was further tuned by functionalizing pollen with an organosilane to enable grafting of polymer chains. Functionalized pollen resulted in simultaneous stiffening and strengthening of composites (80% increase in tensile strength) due to increased stress transfer from interactions of grafted chains with the polymer matrix. Films containing treated and functionalized pollen also displayed a wider glass transition region in the presence of pollen filler.

COLL 703

Interactions of pluonics with supported lipid membranes

*Jinghui Wang, Laura Segatori, **Sibani Lisa Biswal**, biswal@rice.edu.Department of Chemical and Biomolecular Engineering, Rice University, Houston, TX 77005, United States*

The interactions of Pluornics, amphiphilic poly(ethylene oxide) - poly(propylene oxide) - poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymers, and lipid membranes have been characterized. The solubility of these triblock polymers in a lipid membrane can be changed with temperature leading to the ability to create a tunable insertion within the membrane. Here, we present our results when this system is changed from a free standing lipid membrane to a supported lipid membrane, in which one lipid leaflet is confined by a solid support. With the use of microcantilevers and fluorescence recovery after photobleaching (FRAP), we measure the solubility and interactions of triblock copolymers (F68 and F98) within supported lipid bilayers. Two factors are found to affect the lipid polymer interactions: temperature and number of repeating units in hydrophobic PPO block.

COLL 704

Extracellular matrix modulates mechanical characteristics of cell-matrix adhesions

*Harini Sreenivasappa[1,2], Soon-Mi Lim[1], Jerome P Trzeciakowski[1], Michael W Davidson[3], **Andreea Trache**[1,2], trache@tamu.edu.Â (1) Department of Medical Physiology, Texas A&M Health Science Center, College Station, TX 77843-1114, United StatesÂ (2) Department of Biomedical Engineering, Texas A&M University, College Station, TX 77840, United StatesÂ (3) National High Magnetic Laboratory, Florida State University, Tallahassee, FL 32310, United States*

Cellular response to mechanical stimulation is a balance between contractile elements of the cytoskeleton and cell-matrix (focal) adhesions. This study investigates the effect of the extracellular matrix on mechanical signaling through integrins, which controls actin organization and focal adhesion formation. Vascular smooth muscle cells (VSMC) were plated on different matrix proteins used as substrate (fibronectin, collagen IV, collagen I, and laminin), or have been mechanically stimulated by an atomic force microscope (AFM) probe functionalized with matrix proteins. Matrix-induced cellular characteristic morphology and the specific cellular adaptive responses to mechanical stimulation were recorded by total internal reflection fluorescence (TIRF) and confocal microscopy. Adhesion assays and western blot analysis were used as complementary approaches to determine protein expression. In addition, integrin-matrix adhesion force measurements using the AFM were performed on cells in which the pre-existing cytoskeletal tension has been modulated by drugs affecting actomyosin contractility. Our results showed that matrix has an important role in cell spreading, adhesion and morphology with a direct effect on modulating cell response to external mechanical cues. Protein recruitment at focal adhesions as initiated by fibronectin, induced early maturation of these adhesion sites anchoring the cell to the matrix. Fibronectin-functionalized AFM probes sustained long-termed interactions with the VSMC by

inducing a functional focal adhesion. In contrast, laminin-functionalized and uncoated probes detached from the cell surface at very low forces. Taken together, our results show that matrix has an important role in modulating VSMC response to mechanical stimuli inducing key signaling pathways involved in cellular adaptation to the local extracellular microenvironment.

COLL 705

Correlated imaging and force mapping study on living cells

***Shan Zou**, shan.zou@nrc.gc.ca.Measurement Science and Standards, National Research Council Canada, Ottawa, Ontario K1A0R6, Canada*

To study the mechanical properties of living cells at molecular resolution is of the outmost importance in understanding cellular processes and disease.[1] Change in cell membrane elasticity and stiffness is an emerging characteristic of cancer cells that affects the way they spread. An attractive option to sensitively explore the elasticity of cells is to use atomic force microscopy and force spectroscopy, correlated with optical imaging. 15 and 20 µm polymer microwell (SU-8 10) substrates are prepared to confine the accute leukemia NB4 cells on surface for AFM indentation measurements. Viablility tests of drug treated NB4 cells are systemiatically evaluated in order to determine and compare the dosage of different drugs incuded cell membrane elasticity changes. After 24 h treatment with high doseage (50% vialbility), elasticity of NB4 cells increased upto 40%. This indicates that ATO induced apoptosis may introduce increase of osmotic pressure and resulte in the Young's modulus rise.

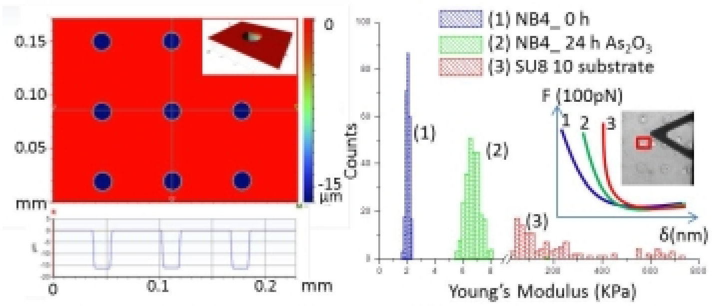


Fig 1. Microwell confined NB4 cells and preliminary mechanical measurements.

1.Force Spectroscopy Measurements Show That Cortical Neurons Exposed to Excitotoxic Agonists Stiffen before Showing Evidence of Bleb Damage

Zou, S.; Chisholm, R.; Tauskela, J. S.; Mealing, G. A.; Johnston, J.L.; Morris, C. E. *PLoS ONE* **2013** , *8,* e73499

COLL 706

Combining CLSM and AFM indentation reveals metastatic cancer cells stiffen during invasion into collagen I matrices

*Jack R. Staunton[1,2], Bryant L. Doss[1,2], **Robert Ros**[1,2], Robert.Ros@asu.edu.Â (1) Center for Biological Physics, Arizona State University, Tempe, AZ 85287, United StatesÂ (2) Department of Physics, Arizona State University, Tempe, AZ 85287, United States*

A critical step in the metastatic cascade is the process wherein a single cell breaks through the basement membrane, leaving the primary tumor and entering the stroma whence it can disseminate. In the case of many solid tumor cancers, increased cell deformability is thought to facilitate this process. To investigate the mechanical interplay between the cell and ECM during this process, we created a simple model of stromal invasion using 80-200 µm thick bovine collagen I hydrogels ranging from 0.1-5 kPa in Young's modulus that were seeded with highly metastatic MDA-MB-231 breast cancer cells. Significant population fractions invaded the matrices either partially or fully. We then combined confocal fluorescence microscopy and AFM indentation to determine the Young's moduli of individual embedded cells and the pericellular matrix using novel analysis methods for heterogeneous samples. In partially embedded cells, we observe a statistically significant correlation between the degree of invasion and the Young's modulus, which was up to an order of magnitude greater than that of the same cells measured in 2D. ROCK inhibition returned the cells' Young's moduli to values similar to 2D and diminished but did not abrogate invasion. This provides evidence that Rho/ROCK-dependent actomyosin contractility is employed for matrix reorganization during initial invasion, and suggests the observed cell stiffening is due to an attendant increase in actin stress fibers.

COLL 707

Controlled distribution of lipids and proteins in a micropatterned model membrane

***Kenichi Morigaki**, morigaki@port.kobe-u.ac.jp.Research Center for Environmental Genomics, Kobe University, Kobe, Hyogo 657-8501, Japan*

Association of membrane-bound molecules to lipid micro-domains (lipid rafts) is believed to play critical roles in the biological membrane, but its roles remain elusive due to their complex and dynamic nature. We describe a methodology to construct an artificial membrane system to study the functional roles of lipid rafts. We developed a micropatterned model biological membrane that could control the distribution of membrane-bound lipid and protein molecules with pre-defined geometries. The model system was composed of polymeric and fluid phospholipid bilayers supported on a glass substrate. By lithographically modulating the densities of polymeric bilayer domains, liquid-ordered (Lo) and liquid-disordered (Ld) bilayer phases in the fluid bilayer were found to preferentially accumulate in the polymer-free region and partially polymerized region, respectively. The compositions of Lo/ Ld phases in each region

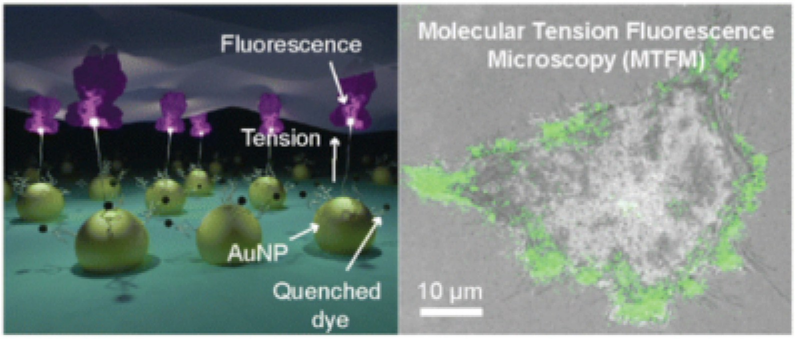
could be controlled by the experimental variables such as pattern geometries and area fractions of polymeric bilayers. We observed that membrane-bound proteins were sorted between the membrane regions according to their affinities to lipid phases. Therefore, we can quantify the affinities of membrane-bound molecules to lipid rafts by measuring their distributions in the micropatterned membrane. This novel possibility should help to elucidate the functional roles of micro-domains in the native biological membranes.

COLL 708

Visualizing and manipulating forces in the membrane of living cells

Khalid Salaita, *k.salaita@emory.edu, Yang Liu, Yun Zhang, Zheng Liu, Carol Jurchenko, Yuan Chang.Department of Chemistry, Emory University, Atlanta, GA 30322, United States*

Forces have a profound role across all living systems, and many processes ranging from development and migration to mitosis and meiosis cannot proceed without precisely tuned mechanical signals. A major challenge to understanding chemo-mechanical couplings in biology pertains to the lack of molecular tools that allow one to image and manipulate forces within cells and especially at the cell membrane. To address this issue, we have developed a set of fluorescent probes and molecular opto-actuators to investigate the role of mechanical forces in biochemical signaling. In this talk, I will first describe the synthesis and characterization of molecular force probes and their application in the area of mechanotransduction. Force probes take advantage of fluorescence quenching to determine the extension of an entropic polymer “spring” to quantify tension using a standard fluorescence microscope (Nat. Methods 2012). I will describe the development of second and third generation force probes that allow one to quantify molecular forces with high spatial and temporal resolution for a range of recombinant proteins. Finally, I will discuss the development of molecular tension actuators and their application to studying Notch and integrin receptor mechano-regulation in living systems.



COLL 709

Water permeation drives tumor cell migration in confined microenvironments

Kimberly M. Stroka[1,2,3], Hongyuan Jiang[4], Shih-Hsun Chen[3], Ziqiu Tong[1,2,3], Denis Wirtz[1,2,3], Sean X Sun[1,2,3,4,5], ***Konstantinos Konstantopoulos**[1,2,3,4,5],* *konstant@jhu.edu.Â (1) Johns Hopkins Institute for NanoBioTechnology,, The Johns Hopkins University, Baltimore, MD 21218, United StatesÂ (2) Johns Hopkins Physical Sciences-Oncology Center, The Johns Hopkins University, Baltimore, MD 21218, United StatesÂ (3) Department of Chemical and Biomolecular Engineering,, The Johns Hopkins University, Baltimore, MD 21218, United StatesÂ (4) Department of Mechanical Engineering, The Johns Hopkins University, Baltimore, MD 21218, United StatesÂ (5) Department of Biomedical Engineering, The Johns Hopkins University, Baltimore, MD 21218, United States*

Cell migration is a critical process for diverse (patho)physiological phenomena. Intriguingly,

cell migration through physically confined spaces can persist even when typical hallmarks of

two-dimensional (2D) planar migration, such as actin polymerization and myosin II-mediated

contractility, are inhibited. Here, we present an integrated experimental and theoretical

approach (“Osmotic Engine Model”) and demonstrate that directed water permeation is a major

mechanism of cell migration in confined microenvironments. Using microfluidic and imaging

techniques along with mathematical modeling, we show that tumor cells confined in a narrow

channel establish a polarized distribution of Na+

which creates a net inflow of water and ions at the cell leading edge and a net outflow of water

and ions at the trailing edge, leading to net cell displacement. Collectively, this study presents an

alternate mechanism of cell migration in confinement that depends on cell volume regulation via

water permeation.

COLL 710

Nonadiabatic dynamics at metal and semiconductor surfaces

***John Tully**, john.tully@yale.edu.Department of Chemistry, Yale University, New Haven, Connecticut 06520, United States*

The adiabatic (Born-Oppenheimer) approximation underlies most of our understanding of chemical reaction dynamics. It has become clear, however, that nonadiabatic electronic transitions can sometimes play an important role, particularly in photo-initiated and highly energetic reactions. It is not as widely known that for reactions at metal surfaces, even at thermal energies, nonadiabatic behavior is the rule rather than the exception. Electron-hole pair transitions, charge transfer and hot-electron-induced motion can be dominant pathways for energy flow and can drastically alter reaction pathways. These processes are likely to be important as well at semiconductor surfaces when the system has been excited above the band gap, such as in solar energy applications. This talk will present progress toward a unified picture of nonadiabatic dynamics at metal and semiconductor surfaces, with application to multi-quantum vibrational-to-electronic energy transfer in the scattering of nitric oxide from a gold surface.

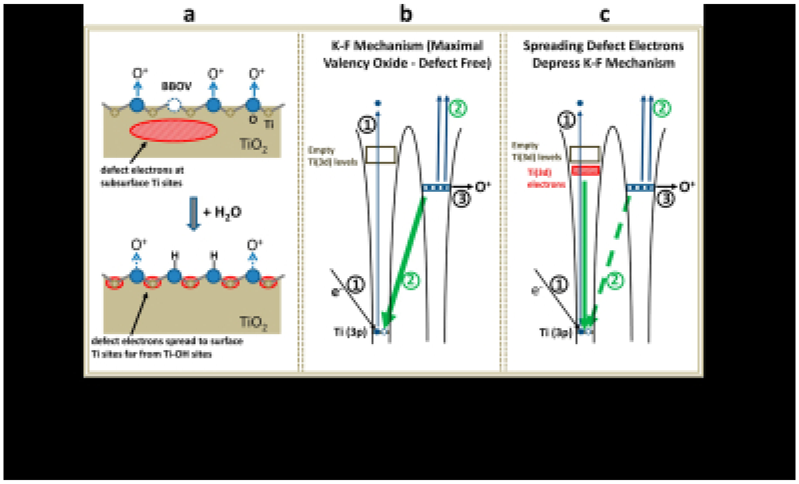
COLL 711

Watching hot carriers in TiO_2 excited by UV radiation

***John T. Yates, Jr.**, johnt@virginia.edu, Zhen Zhang, Ke Cao.Chemistry, University of Virginia, Charlottesville, VA 22904, United States*

The photoproduction of hot electron/hole pairs forms the basis for activating TiO_2-based photovoltaic cells as well as for environmental remediation for removal of toxic materials[1]. We have separated the activation of adsorbed molecular oxygen by holes (causing O_2 desorption) from activation by electrons (causing photooxidation reactions). I will show how controlled band bending can be used to determine which charge carrier is responsible for a carrier-mediated surface process [2].

In addition, we have observed that defect-bound Ti(3d) electrons in the near surface region act to compete with the Knotek-Feibleman (KF) mechanism [3] for O^+ formation during electron stimulated desorption (ESD). One OH group, produced by water adsorption, causes the suppression of ESD-induced ionization to O^+ of about 5 surface bridge-bonded O atoms on TiO_2(110). Here Ti(3d) defect-bound electrons compete with the interatomic Auger process of the KF mechanism leading to O^+ production. It is postulated that this is caused by defect-electron spreading across the surface away from an OH species attached to a surface oxygen vacancy defect site [4].



COLL 712

Dehydrogenation reactions catalyzed by molten halides

*Henrik Kristofferson[1], Chang Huang[1,2], Eric W. McFarland[2], **Horia Metiu**[1], metiu@chem.ucsb.edu.Â (1) Department of Chemistry & Biochemistry, University of California, Santa Barbara, Santa Barbara, CA 93106-9510, United StatesÂ (2) Department of Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA 93106-5080, United States*

The dehydrogenation of alkanes is one of the most important industrial reaction producing important alkenes, such as ethylene, propylene and styrene. In this talk we present results of density functional theory calculations that examine aspects of the oxidative dehydrogenation catalyzed by molten LiCl and molten LiI.

COLL 713

First principles quantum simulations of (photo)electrocatalysis at semiconductor surfaces

***Emily A. Carter**, eac@princeton.edu.Department of Mechanical and Aerospace Engineering, Program in Applied and Computational Mathematics, Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ 08544-5263, United States*

Efficient (photo-)electrochemical production of fuels is one of the great technological challenges of our time. Such processes offer the possibility of renewable fuel sources based on either solar or wind energy rather than biomass. However, despite periodic media reports to the contrary, no efficient catalysts exist yet. Over the past few years, we have been applying first principles quantum mechanics techniques to help identify

robust, efficient, and inexpensive materials for photo-catalytic electrodes that could convert sunlight, carbon dioxide, and water into fuels. In the spirit of this symposium honoring Melissa Hines, we focus on the surface chemistry of semiconductors, in particular those that have been used as anodes (e.g., hematite) or cathodes (e.g., gallium phosphide) in photo-electrochemical cells to either split water or to convert carbon dioxide into methanol. Given the inherent experimental difficulties with probing molecular species at the semiconductor electrodes immersed in water, our calculations offer the means to fill the knowledge gap regarding, e.g., the relative stability of various electrochemical intermediates, both in solution and at the semiconductor-liquid junction. Armed with such knowledge, it has been possible, for example, to exclude certain mechanisms for the production of methanol at the cathode and to suggest surface additives to enhance water oxidation at the anode.

COLL 714

Novel directions for modeling of surface processes in nanotechnology: Hot atom kinetic Monte Carlo for hyperthermal trajectory determination

Alain Estève[1]*, aesteve@laas.Fr, Anne Hemeryck*[1]*, Darius Djafari-Rouhani*[1]*, Cloé Lanthony*[1]*, Jean-Marie Ducéré*[1]*, Mehdi Djafari-Rouhani*[1]*, Carole Rossi*[1]*, Yves J Chabal*[2]*.Â (1) LAAS-CNRS, Toulouse, FranceÂ (2) Department of Materials Science and Engineering, UTD, Dallas, Texas 75080, United States*

Predictive simulations of chemical processes at surfaces is a major step in developing new materials and systems for which surfaces and interfaces control the most important properties. Multi-scale modelling, i.e. development of multi-model strategies, is one of the ways to address complexity, ranging from atomic and molecular interactions to the mesoscale organization atoms in nanostructures. We have developed and present a Density Functional (DFT) – Kinetic Monte Carlo (KMC) coupled approach aimed at dealing with *reactive* materials (i.e. involving large energies), which introduces severe difficulties for conventional modelling, particularly at the KMC level. Along this line, local exothermic mechanisms are treated differently to allow determination and specific inclusion of hot atom hyperthermal trajectories in conventional Kinetic Monte Carlo where kinetics alone are considered. This approach is illustrated by considering the fabrication of Al/CuO nanothermite nanolaminate films for applications of nanoenergetic materials. Preliminary results of the “hot atom” modified KMC technique will be highlighted on O, O_2 and CuO molecules interacting with the Al(111) surface and associated hyperthermal trajectories will be discussed. Overall, we will show that Al penetrated deeply into CuO, forming an interface layer characterized by severely reduced Cu. In contrast, the deposition of CuO molecules onto Al(111) surfaces indicates that oxygen does not penetrate Al and highlights the critical role of Cu and the coverage of oxygen. These examples underscore the complexity introduced at interfaces of energetic materials and the need for advanced modeling tools to deal with energetic atoms.

We acknowledge the support of both ANR and NSF agencies (NSF-DMR-1312525), the PUF program MOMA and CALMIP/IDRIS computer resources.

COLL 715

Transparent metal oxide interlayers for charge selective contacts in organic electronics

*Philip Schulz, James Endres, **Antoine Kahn**, kahn@princeton.edu.Electrical Engineering, Princeton University, Princeton, NJ 08544, United States*

Thin films of transparent metal oxides (TCO) have become important components in a range of organic electronics applications. In particular, promising results are achieved for efficient charge carrier collection in high-performance organic solar cells. The large band gap of these materials, coupled with their definite doping characteristics (p-type for NiO_x, n-type for ZnO or TiO_2) makes these materials excellent candidates for carrier-selective, i.e. electron or hole blocking, contact interlayers. Investigations of the electronic structure of these materials and of the energetics of their interfaces with organic semiconductors are therefore timely and important. We present here an overview of the work done in our group over the past three years on TCOs such as NiOx, ZnO and TiO_2, and their interfaces with organic materials and active blends. Valence and conduction band positions and work function are investigated as a function of deposition method (e.g. vacuum evaporation, plasma enhanced atomic layer deposition, solution-based deposition, etc..), and interface molecular level alignments are measured. The modification of the work function of TCO surfaces with self-assembled monolayers of phosphonate molecules with different molecular dipoles is discussed. Finally, we report on recent work on the combination of TCOs, e.g. NiO_x as electron-blocker and MoO_3 as very high work function material, to improve hole-collection in bulk-heterojunction solar cells.

COLL 716

Atomically precise gold nanoclusters: Synthesis and catalytic application

***Rongchao Jin**, rongchao@andrew.cmu.edu.Carnegie Mellon University, Pittsburgh, PA 15213, United States*

The pursuit of well-defined nanoparticles has attracted much attention in recent research. The attainment of atomically precise nanoparticles is of major importance for both fundamental studies and development of applications. This talk will present the synthesis and catalytic application of size-specific $Au_n(SR)_m$ nanoparticles with n ranging from a few dozens to several hundreds of atoms (often called nanoclusters). Such ultrasmall nanoparticles exhibit distinct quantum size effects and interesting electronic and optical properties, which are fundamentally different from their larger counterparts — *plasmonic* nanoparticles. New types of atom-packing structures have been discovered in $Au_n(SR)_m$ nanoclusters. The catalytic properties of nanoclusters can

be truly tuned on an atom-by-atom basis. Correlation of the catalytic properties with structures will ultimately offer fundamental understanding on nanogold catalysis.

COLL 717

Combined optical and electrochemical methods for studying electrochemistry of single plasmonic nanoparticles

Shanlin Pan, *span12@as.ua.edu, Caleb Hill, Jia Liu.Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama 35478, United States*

Interfacial charge transfer activities at single plasmonic nanoparticles are studied using the combined methods of traditional electrochemistry and optical spectroscopy (e.g., fluorescence, dark field light scattering, and electrogenerated chemiluminescence (ECL)). Our results show that these optical methods enable the exploration of electrochemical events with improved temporal and spatial resolution which are usually obstructed by the ensemble averaging inherent in conventional electrochemical methods. Particularly, dark field scattering microscopy is employed to study the electrochemical synthesis of individual plasmonic nanostructures in situ. Using this technique, scattering-time curves describing the deposition of hundreds of individual Ag nanostructures can be obtained simultaneously, yielding a direct insight into the heterogeneity inherent in the deposition of such metallic nanostructures on transparent oxide electrodes. Theoretical calculations of the scattering intensity as a function of particle size (here through Mie theory, making the rough assumption of spherical particles) combined with the electron microscopy analysis allows for an estimation of particle size to be obtained from the scattering intensity. By having an estimate of a particle's size at every stage of its growth, the estimation of the current-potential (I-V) curve depicting the faradaic current associated with particle formation follows directly.

COLL 718

Electrochemistry of functionalized

Joe JP Roberts, *jjpr@unc.edu, Royce W Murray.Chemistry, University of North Carolina, Chapel Hill, NC 27599, United States*

Nanoparticles of all sizes and compositions have been used for a variety of biological, medicinal, and technological applications. Small (<10 nm) metal oxide nanoparticles synthesized by a high temperature, non-aqueous route provide excellent reproducibility and size dispersion but leave the nanoparticles capped in a fatty surfactant. In an effort to better understand nanoparticle surface chemistry, these surfactants have been replaced with silanes and phosphates then functionalized with a redox tag. This redox tag for allows quantitative analysis via many electrochemical methods to determine the extent of surface modification. This was originally shown with 6 nm indium tin oxide nanoparticles (ITO) covalently modified with aminosilanes and reacted with a ferrocenyl chloride to provide our redox tag. We then began modifying the surface of 2 nm zirconium oxid. These nanoparticles were modified using a phosphate azide to undergo a “click” reaction with ethynylferrocene to provide the redox tag. Additional work has also shown that magnetite (Fe_3O_4) nanoparticles modified with citric acid undergoes an electrochemical exchange between Fe^{2+} and Fe^{3+}. These nanoparticles maintain some of their magnetism which can be used to alter the currents in electrochemical experiments.

COLL 719

Single electron transfer reaction of atomically precise gold nanoclusters with the organic compound

***Manzhou Zhu**, zmz@ahu.edu.cn.Department of Chemistry, Anhui University, Hefei, Anhui 230601, China*

The deep study for atomically precise gold nanoclusters has revealed the relationship between frontier molecular orbital of clusters and its physical and chemical properties in terms of quantum chemistry. Based on the recognition of structure of nanoclusters, we can further understand the catalytic performance of nanoclusters, which will be help for us to discuss the mechanism of catalytic reaction at the molecular and atom level. Consequently, we can design a new type of catalyst with high selectivity and activity. Recently, we have systematacially studied the natural performance of the gold nanocluster in catalytic organic reactions. Firstly, we found the single electron transfer reaction between $Au_{25}(SCH_2CH_2Ph)_{18}^{-}TOA^{+}$ and organic oxidizer, such as 2,2,6,6-tetramethylpiperidin-1-oxoammonium tetrafluoroborate, PTZ–TCBQ complex. Furthermore, as the electron transfer catalyst, the Au_{25}^{-} also can turn the 2-nitrobenzene nitrile into azoxybenzene through intramolecular series reactions. Last, the ultrasmall gold nanoclusters, which are supported on mesoporous CeO_2nanospheres, showed efficient catalytic performance in transforming nitrobenzene into azoxybenzene. In these works, we have made some discussion on the reaction mechanism by means of CV、ESR、UV-vis、NMR and so on.

COLL 720

Size-dependent charge separation and photocatalytic activity of ZnO-metal nanoparticle composites

***Dongil Lee**, dongil@yonsei.ac.kr, Jaehyun Kim, Dukhan Kim.Department of Chemistry, Yonsei University, Seoul, Republic of Korea*

Recent advances in the synthesis of ultra-small metal nanoparticles have opened the possibility to synthesize stable, molecule-like metal nanoparticles. Much progress has been made toward understanding their structures and fundamental properties. However, the technological application of such nanoparticles is still scarce. We present size-controlled photocatalytic activity of ZnO nanoparticles coated with thiolate-protected gold nanoparticles with diameters of 1.1, 1.6 and 2.8 nm. The photocatalytic activity of the ZnO-Au composites was found to increase with increasing gold size for both oxidative and reductive catalytic reactions. Photoluminescence decay dynamics of the composites showed that electron transfer rate from the photoexcited ZnO to gold nanoparticle also increased as the gold size increased. These results demonstrate that the photogenerated electron transfer and the resulting catalytic activity of the composites can be controlled by the size of the mediating gold capacitors.

COLL 721

Stability and electrochemical activities of di- and mono- thiolates stabilized metal nanoclusters and their precursors

***Tanyu Wang**, tzw0001@tigermail.auburn.edu, Jie Jiang, Cecil V Conroy, Tarushee Ahuja, Jonathan W Padelford, Gangli Wang.Department of Chemistry, Georgia State University, Atlanta, GA 30302, United States*

Metal nanoclusters with molecular compositions have attracted significant attention from fundamental scientific perspectives and technological applications in energy and biomedical fields. Proper design and synthesis of Au nanoclusters stabilized by multidentate dithiolates exhibit novel physicochemical properties distinct from their monothiolate counterparts. Furthermore, surprising stability and redox activities are frequently observed in recent reports of Au, Ag, and bimetallic nanoclusters. Limited mechanistic insights have been gained regarding how the newly-developed synthetic routes and the materials nature being adopted generate the novel nanoclusters that display fascinating properties. Herein, we will discuss the redox activities of reaction intermediates and final metal nanoclusters, composed of gold and/or silver as metal core stabilized by monothiolates and/or dithiolates as ligand monolayer. The voltammetry features directly reveal their energetics and shine light on the synthesis mechanism and the redox activities. The discussion will be focused on multi-dentate dithiolate systems established by our group that is proven effective to tailor the electrochemical and some optical properties. The distinct electrochemical features of reaction intermediates and final nanoclusters explain the advantages and limitations of multidentate and monodentate approaches respectively. The factors that could further improve fundamental properties will be addressed aiming at bioimaging, cellular transport and delivery, and energy and catalysis applications.

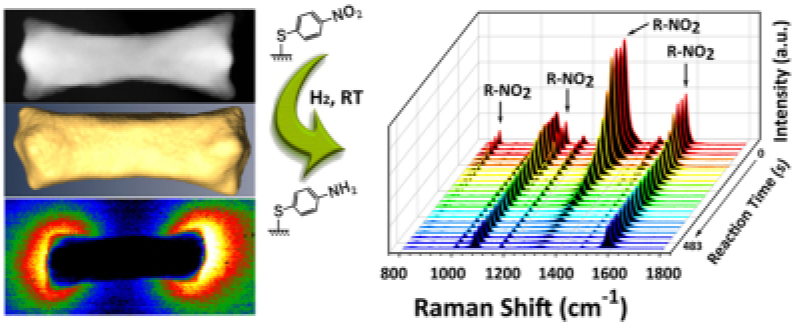
COLL 722

Highly sensitive monitoring of catalytic reactions by surface enhancement Raman spectroscopy using Au-Pd nanorods

***Yu Han**, yu.han@kaust.edu.sa.Physical Science and Engineering Division, KAUST, Thuwal, Saudi Arabia*

Surface-enhanced Raman scattering (SERS) is a highly sensitive probe for molecular detection. The aim of this study was to develop an efficient platform for investigating the

kinetics of catalytic reactions with SERS. To achieve this, we synthesized a novel Au-Pd bimetallic nanostructure (HIF-AuNR@AuPd) through site-specific epitaxial growth of Au-Pd alloy horns as catalytic sites at the ends of Au nanorods. Using high-resolution electron microscopy and tomography, we successfully reconstructed the complex three-dimensional morphology of HIF-AuNR@AuPd and identified that the horns are bound with high-index $\{11l\}$ $(0.25 < l < 0.43)$ facets. With an electron beam probe, we visualized the distribution of surface plasmon over the HIF-AuNR@AuPd nanorods, finding that strong longitudinal surface plasmon resonance concentrated at the rod ends. This unique crystal morphology led to the coupling of high catalytic activity with a strong SERS effect at the rod ends, making HIF-AuNR@AuPd an excellent bifunctional platform for *in-situ* monitoring of surface catalytic reactions. Using the hydrogenation of 4-nitrothiophenol as a model reaction, we demonstrated that its first-order reaction kinetics could be accurately determined from this platform. Moreover, we clearly identified the superior catalytic activity of the rod ends relative to that of the rod bodies, owing to the different SERS activities at the two positions. In comparison with other reported Au-Pd bimetallic nanostructures, HIF-AuNR@AuPd offered both higher catalytic activity and greater detection sensitivity



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COLL 723

From aggregation-induced emission of gold(I)-thiolate complexes to highly luminescent thiolate-protected gold nanoclusters

***Zhentao Luo**, zhentaoluo@nus.edu.sg, Jianping Xie.Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore, Singapore 120415, Singapore*

The understanding of the fundamental aspects of the luminescence of thiolate-protected gold nanoclusters (or Au-thiolate NCs), such as the source of emission, size and structure effects on the luminescence, and the critical factors that affects the quantum yield (QY), is pivotal to the development of efficient synthesis routes for highly luminescent Au-thiolate NCs. We recently found that Au(I)–thiolate complexes can emit strong luminescence by the mechanism of aggregation-induced emission (AIE). On the basis of this finding, we developed a simple one-pot synthesis of Au(0)@Au(I)–thiolate

core–shell NCs with strong luminescence (QY ~15%) that was generated by the AIE of Au(I)–thiolate complexes on the NCs. We further developed some similar synthetic approaches to fabricate Au-thiolate NCs with AIE and study their luminescence properties. The findings of this study can contribute significantly to the fundamental understanding, development of efficient syntheses, and applications of these new luminescent probes.

COLL 724

Theranostic nanomedicine for imaging-guided treatment of cancer

***Prakash Rai**, prakash_rai@uml.edu.Department of Chemical Engineering, University of Massachusetts, Lowell, Lowell, MA 01854, United States*

According to the American Cancer Society a total of 232,340 new cases and 39,620 deaths from breast cancer are projected to occur in the United States by the end of 2013. There is a dire need for better strategies to prevent, diagnose and treat this deadly disease. The research efforts in the Rai lab are focused on the use of biodegradable and biocompatible nanoparticles for the prevention and treatment of breast cancer. In this talk we will present work on using nanoconstructs for both the prevention and treatment of breast cancer. Nanochemoprevention, which involves use of nanoparticles for delivery of chemopreventive agents, is an emerging field that has shown some promise for cancer prevention by improving the bioavailability and reducing toxicity associated with these drugs. We have developed nanometer-sized constructs that encapsulate multiple promising chemopreventive agents and tested their efficacy in cell culture and animal models of breast cancer. From a treatment perspective, theranostic nanoconstructs have also been synthesized, purified, characterized and are being evaluated in cell culture models of breast cancer. Our results from these studies will be presented.

COLL 725

Impact of nanoparticle size on photothermal therapy efficacy in triple negative breast cancer

*Ciceron Ayala[2], Cordula Urban[1], Naomi Halas[2], **Amit Joshi**[1], amitj@bcm.edu.Â (1) Department of Radiology, Baylor College of Medicine, Houston, TX 77030, United StatesÂ (2) Department of Electrical and Computer Engineering, Rice University, Houston, TX 77030, United States*

Gold nanoparticles that absorb near-infrared (NIR) photons are known to efficiently convert light into heat for applications in photothermal therapy of cancer. Development of highly efficient near-infrared photothermal transducers is critical for treatment of highly aggressive cancers and/or large tumors where the penetration of light can be substantially reduced in the innermost part of the tissue. Herein, we report gold nanomatryoshkas (Au/SiO_2/Au) as highly efficient photothermal transducers that

improve the therapeutic efficacy in highly aggressive triple negative breast cancer (TNBC) tumors *in vivo* by benchmarking against gold nanoshells.A single dose of intravenous injection of gold nannomatryoshka in combination with a single NIR light laser dose of 2 W/cm^2 for 3 min doubles the survival time of mice bearing large (~1000 mm^3) TNBC tumors with respect to the control without nanoparticles. We show that gold nanomatryoshkas with a diameter of ~90 nm exhibit a higher absorption cross-section than the benchmark SiO_2/Au nanoshells of ~150 nm. The higher absorption cross-section of a nanomatryoshka results in a higher efficiency of photonic to thermal energy conversion. Theoretical calculations of the optical spectrum explain that gold nanomatryoshkas are strong light absorbers with 77% absorption efficiency, but weak scatterers with 23% scattering efficiency. However, nanoshells are weak absorbers with 15% absorption efficiency, but strong scatterers with 85% scattering efficiency. In addition, we show that the accumulation of nanomatryoshkas in tumors is enhanced with respect to nanoshells due to their sub-100 nm diameter. Therefore, these nanomatryoshkas show a double enhancement effect in photothermal therapy by: 1) increasing accumulation of particles in the tumor and 2) the larger light-to-heat conversion efficiency due to the higher absorption efficiency.

COLL 726

Pulsed magnetic field induced fast drug release from magneto liposomes

George V Podaru[1]*, gvp@ksu.edu, Raj K Dani*[1]*, Saralyn Ogden*[1]*, Amanda Baxter*[1]*, Hongwang Wang*[1]*, Matthew T Basel*[1]*, Shenqiang Ren*[2]*, Stefan H Bossmann*[1]*, Viktor Chikan*[1]*.Â (1) Department of Chemistry, Kansas State University, Manhattan, KS 66506, United StatesÂ (2) Department of Chemistry, University of Kansas, Lawrence, KS 66045, United States*

Here a method developed for the fast release of the liposomes' payload without a significant increase in (local) temperatures is described. This goal is achieved by using the mechanical disruption of the liposomes loaded with magnetic nanoparticles. The mechanical motion of the magnetic nanoparticles locally destabilizes the lipid bilayer resulting in the release of liposomes' payload. The drug release has been tested by two independent assays. The first assay relies on the AC impedance measurements of $MgSO_4$ released from the magnetic liposomes. The second standard permeability assay is based on the increase of the fluorescence signal from 5(6)-Carboxyfluorescein dye when it the dye is released from the magneto liposomes.

COLL 727

Immunoselective cellulose nanospheres by antibody conjugation

Christopher Carrick[1]*, Lars Wågberg*[1]*,* ***Per Larsson***[1,2]*, per.larsson@polymer.kth.se.Â (1) Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Stockholm 100 44, SwedenÂ (2) BiMaC Innovation, KTH Royal Institute of Technology, Stockholm, Stockholm 100 44, Sweden*

Cellulose inhibits both excellent biocompatibility and low toxicity to organisms or environment, and is therefore an interesting material to use in biomedical and therapeutical applications. This work demonstrates the fabrication of cellulose nanospheres, about 100 nm in diameter, prepared by precipitation of cellulose dissolved in a lithium chloride-dimethylacetamide system using a microporous membrane. After capsule fabrication, an antibody with affinity to Epidermal Growth Factor receptor (EGFR) proteins, i.e. a protein often being overexpressed in cancer cells, was covalently conjugated to the spheres. This resulted in spheres that could bind specifically to a surface coated with EGFR protein, shown experimentally by quartz crystal microbalance and scanning electron microscopy. The spheres may be used for localised extended release and contrast enhancement to locate tumours.

COLL 728

CD44 mediated transcytosis for enhancement of drug delivery by hyaluronan coated nanoparticles

Xuefei Huang[1]*, xuefei@chemistry.msu.edu, Mohammad H El-Dakdouki*[1,2]*.Â (1) Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, United StatesÂ (2) Department of Chemistry, Beirut Arab University, Beirut, Lebanon*

Nanoparticles are being extensively studied as carriers for drug delivery, but they often have limited penetration inside tumor. In this presentation, we report that transcytosis mediated by CD44 can be utilized to facilitate tumor penetration and drug delivery by nanoparticles. We synthesized hyaluronan coated silica nanoparticles and magnetic nanoparticles to target CD44 over-expressed on cancer cell surface. Although prior studies have primarily focused on CD44 mediated endocytosis to facilitate cellular uptake of hyaluronan nanoparticles, we discovered that once internalized, the hyaluronan coated nanoparticles could be transported out of the cells with its cargo. The exported nanoparticles could be taken up by neighboring cells. This enabled the nanoparticles to penetrate deeper inside tumor and reach much greater number of cells in 3D tumor models, presumably through tandem cycles of CD44 mediated endocytosis and exocytosis. When doxorubicin was loaded onto the nanoparticles, better penetration of multilayered tumor cells was observed with much improved cytotoxicites against both drug sensitive and drug resistant cancer spheroids compared to free doxorubicin. Furthermore, *in vivo* studies were performed using an ovarian cancer xenograft model. Hyaluronan coated nanoparticles penetrated deep into tumor enabling imaging of tumor by magnetic resonance imaging as well as enhanced toxicity of doxorubicin delivered. Thus, receptor mediated transcytosis can become a general strategy to enhance tumor penetration by nanoparticles and their theranostic potential.

COLL 729

NIR pH activatable nanoprobes for real-time imaging-guided tumor resection

Tian Zhao, *tian.zhao@utsouthwestern.edu, Gang Huang, Lee-Chun Su, Yiguang Wang, Xinpeng Ma, Joel Sun, Zhiqun Zeng, Baran Sumer, Jinming Gao.Harold C. Simmons Comprehensive Cancer Center, UT Southwestern Medical Center at Dallas, Dallas, TX 75390, United States*

Surgical preservation strategy has been able to achieve great oncologic results and preserving function as well as improving the quality of life for patients with head and neck cancer. However, the surgical success depends greatly on the ability of the surgeon to identify tumor margin and normal tissue. A complete removal of tumor is especially difficult for the patients with invasive infiltrating tumors. Herein, we reported a NIR pH activatable nanoprobe that stays silent in blood but ultra-pH sensitive (UPS) to the acidic tumor microenvironment, providing high resolution delineation of primary and residual tumors to achieve complete resections during surgery.

We conjugated FDA-approved NIR dye, ICG onto the UPSe nanoprobes as we reported before. The pH transition point of the nanoprobe is 6.92 with a pH responsive sharpness of only 0.15 pH unit. The probes kept silent in blood, and showed a 20 fold fluorescence increase once activated in the acidic tumor interstitial space. The probes illuminated different tumor modals with high contrasts *in vivo* by a SPY Elite® System which is specially designed for real-time ICG imaging in OR and clinics. *Ex vivo* results revealed a 30 fold tumor to muscle ratio which demonstrated the viability for complete tumor resection and maximum normal tissue preservation.

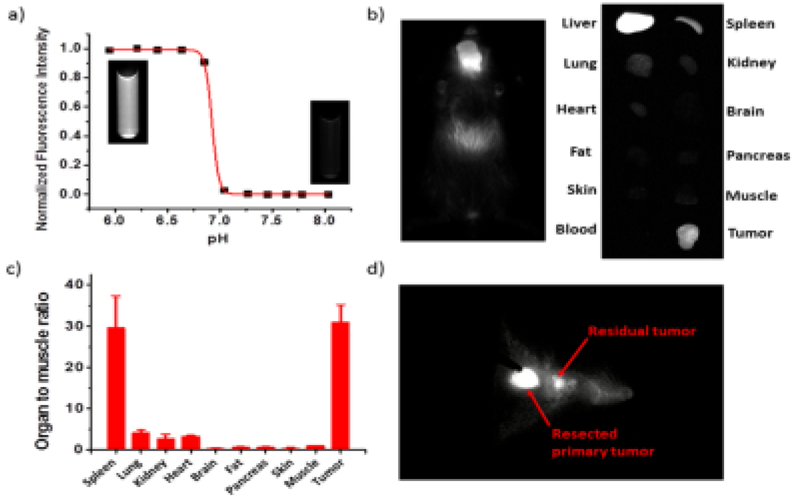

Figure 1. a) Normalized fluorescence intensity as a function of pH for UPSe-ICG. At high pH, probes stay silent. At pH below transitional pH (6.92), the nanoprobes can be activated as a result of micelle dissociation. **b)** UPSe-ICG nanoprobes illuminate orthotopic HN5 head-neck tumors with high imaging contrast *in vivo* and *ex vivo*. **c)** Organ to muscle ratios of fluorescence intensity at 24 h post-injection of nanoprobes. Data are presented as mean ± s.d. (n= 3). Liver was not calculated due to saturation. **d)** Representative real-time imaging from UPSe-ICG-guided surgery. The residual tumor was also illuminated which could not be identified under white light by the otolaryngological surgeon.

A double blind tumor resection experiment on head and neck tumor bearing mice (orthotopic modal) showed improved tumor-free survival compared to the non-imaging-guided group.

COLL 730

Construction of hybrid nanostructures as multimodal contrast agents for cancer imaging

***Kai Cheng**, kaicheng@stanford.edu, Jesse V Jokerst, Hongguang Liu, Sri R Kothapalli, Han Jiang, Meng Yang, Xinhui Su, Shuxian Ming, Xiang Hu, Jinbo Li, Yang Liu, Jelena Levi, Sanjiv Sam Gambhir, Zhen Cheng.MIPS, Department of Radiology and Bio-X Program, Stanford University, Stanford, CA 94305, United States*

To take advantage of each modality during multimodality imaging and provide complementary information of diseases, we have designed and tested multifunctional gold nanotripods (Au-tripods) for positron emission tomography (PET)/photoacoustic imaging (PAI)/Raman triple-modality imaging of tumors in living subjects. The Affibody modification on the PEGylated surface of Au-tripods was used to specifically target the epidermal growth factor receptor EGFR-positive tumor. The resultant Au-tripod-Affibody probes showed significantly enhanced PA and Raman contrast effects in both phantom and small animal imaging experiments. Compared to the Affibody blocking controls, the tumor accumulation was significantly high (more than 8% ID/g after 24 hr). The PA images correlated well with the corresponding PET quantification. Such plasmonic gold nanostructures as multimodal contrast agents were successfully prepared, and it could allow us to specifically image tumors in an accurate and quantitative manner.

COLL 731

Maximizing polymer multilayer film growth and gas barrier performance by adjusting exposure time while depositing layers

***David A Hagen**[1], david_hagen@tamu.edu, Brendan Foster[1], Stephen M Greenlee[1], **Jaime C Grunlan**[1,2], jgrunlan@tamu.edu.Â (1) Department of Mechanical Engineering, Texas A&M University, College Station, Texas 77843, United StatesÂ (2) Department of Chemical Engineering, Texas A&M University, College Station, Texas 77834, United States*

Thin film assemblies of branched polyethylenimine (PEI) and poly(acrylic acid) (PAA) were deposited using the layer by layer deposition process. These unique all-polymer thin films have low oxygen permeability after a small number of bilayers. It is shown that varying exposure time to polymer solutions (i.e., dip time) significantly alters the growth rate of the thin films. The PEI/PAA system grows linearly when employing 1 second dip times, but exponentially for longer times. To optimize film thickness, films were deposited using 1 second dips for the first 4 bilayers, and then 1 minute for subsequent dips. This change in deposition time mid-growth increased the growth rate of the 1 minute exposure film, as shown in Figure 1. The thickness of an 8BL film (650 nm) prepared with 1 min dips was achieved with only 6 BL (550 nm) by changing the dip time (both films exhibit OTR below the detection limit of commercial testing equipment). This adjustment in dip time, now dubbed 'shift time', is a major breakthrough for those considering commercial application of layer-by-layer assembly due to the opportunity to deposit fewer layers in a shorter time to achieve the same thickness and performance.

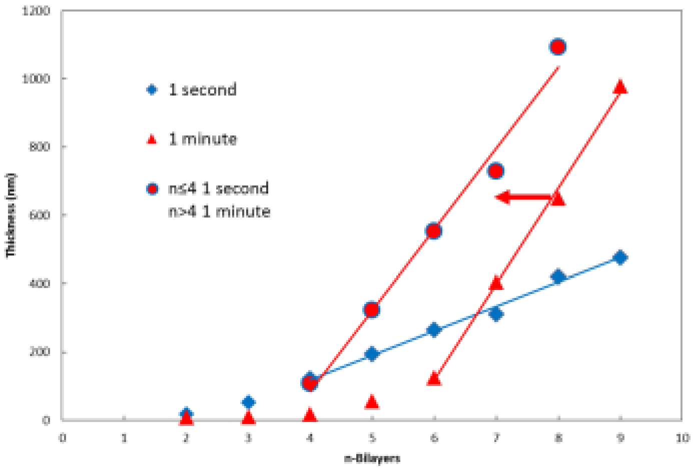

Figure 1. Ellipsometric thickness for PEI/PAA BLs at different exposure times, including a combination of 1 second for the first 4 BL and 1 minute subsequent bilayers.

COLL 732

Layer-by-Layer self-assembled films of polyallylamine and hyaluronic acid with superadhesive properties

Andrew Marais[1]*, marais@kth.se, Samuel Pendergraph*[1]*, Lars Wågberg*[1,2]*.Â (1) Department of Fiber and Polymer Technology, KTH Royal Institute of Technology, Stockholm, SwedenÂ (2) The Wallenberg Wood Science Centre, KTH Royal Institute of Technology, Stockholm, Sweden*

The Layer-by-Layer technique (LbL)[1] was used to build multilayer thin films of polyallylamine (PAH) and hyaluronic acid (HA) and the subsequent adhesive properties of these films were investigated. Model surfaces of flat silicon wafers and polydimethylsiloxane (PDMS) spheres were used as substrates for the adsorption of the polyelectrolyte multilayers. Adhesion measurements were performed using a specially designed Micro Adhesion Measurement Apparatus (MAMA), approaching the two treated surfaces in contact and pulling them apart. The results show that a coating of PAH/HA as thin as 3 bilayers (~12 nm thick) exhibits astonishingly high adhesive properties. The contact between the two coated surfaces was formed in the wet state to provide the highest area of contact and chain mobility and thus higher adhesion. These observations were consistent and substantiated previous results on the nanoscale, which were measured using atomic force microscopy[2]. In order to highlight the higher adhesive forces, similar measurements were performed using another LbL polymeric system composed of PAH and polyacrylic acid (PAA) (Figure 1).

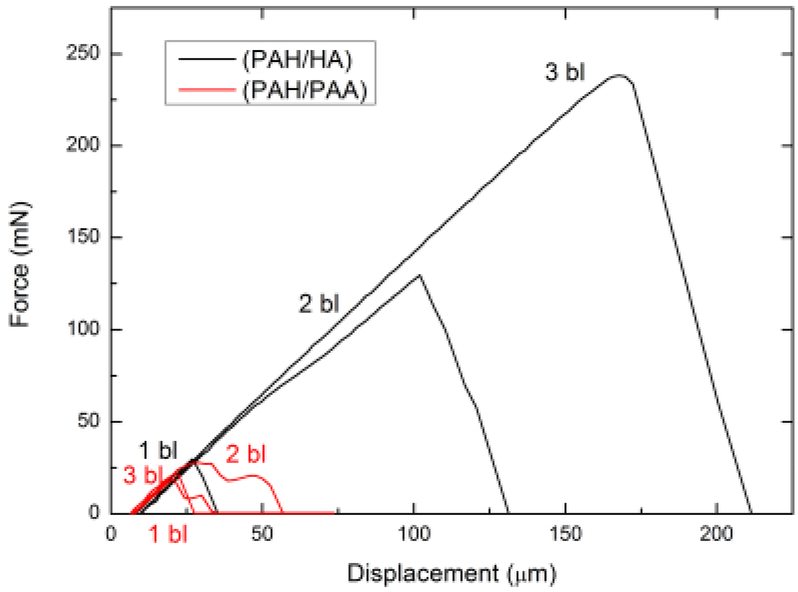

Figure 1: Force/displacement curves for systems with increasing number of bilayers of (PAH/HA) (black) and (PAH/PAA) (red).

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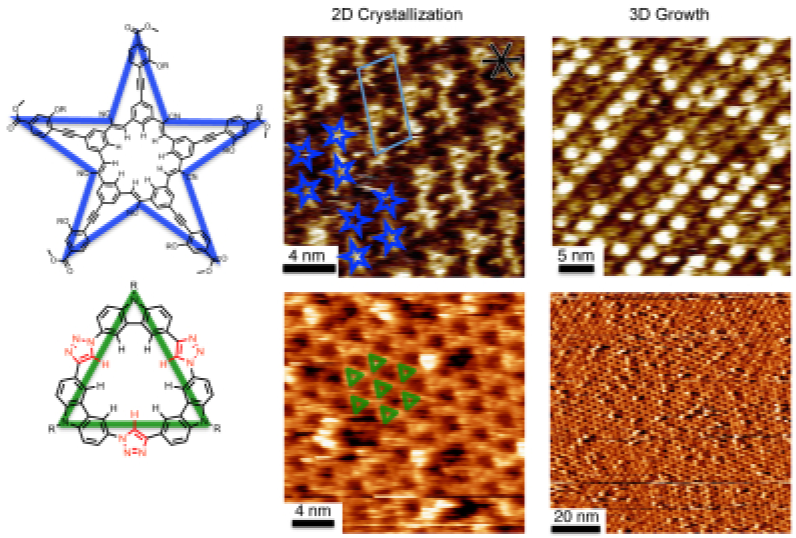
COLL 733

Assembly and stacking of novel macrocycles on surfaces

Brandon E. Hirsch, *behirsch@indiana.edu, Semin Lee, Kevin P. McDonald, Amar H. Flood, Steven L. Tait.Department of Chemistry, Indiana University, Bloomington, IN 47405, United States*



Self-assembly has long been demonstrated as the authoritative strategy to engineer complex, organic nanostructures at surfaces with high fidelity. The formation of these arrays using components with solution phase host-guest recognition properties can result in stimuli-responsive and dynamic self-assemblies that extend growth away from the surface into the third dimension. We demonstrate the two-dimensional crystallization and three-dimensional stacking of novel organic macrocycles that self-assemble from solution on surfaces. The 5-fold symmetric cyanostar assembles into antiparallel rows of molecules. Anions appear to drive sandwich formation on the surface as observed with scanning tunneling microscopy (STM). Dimer stacking can also be shown *without* guest anions in the 3-fold symmetric tricarbazolo triazolophane, which is believed to stack on the basis of favorable electrostatic matching of the π surfaces. This work demonstrates characteristics of supramolecular self-assemblies required for extending order and function beyond the two-dimensional surface plane.

COLL 734

Flexibility and stacking in linear and cyclic polymers on a gold surface

Peter Beton[1], *peter.beton@nottingham.ac.uk, Maria Wieland*[1]*, Alex Summerfield*[1]*, Simon Svatek*[1]*, Ayad Esmail*[1]*, Luis Perdigao*[1]*, Andrew Stannard*[1]*, Dmitry Kondratuk*[2]*, Harry Anderson*[2]*, James O'Shea*[1]*.Â (1) School of Physics & Astronomy, Nottingham University, Nottingham, United KingdomÂ (2) Department of Chemistry, Oxford University, Oxford, United Kingdom*

The properties of porphyrin oligomers, polymers and nanorings deposited on Au(111) and graphite has been investigated using scanning tunneling microscopy (STM). Oligomers and linear polymers pack with chains in a parallel alignment. For oligomers this leads to a regular periodic arrangement, but the polymers are highly flexible and show hairpin bends and we show that it is possible to define a 2D correlation length characterizing this bending. Cyclic polymers have also been deposited and are found to diffuse on the surface with step edges acting as preferential adsorption sites. STM is used to confirm the structure of rings with respectively 12 (cP12) and 24 (cP24) porphyrin units. The cP24 nanorings display much greater distortion from a circular shape than the shorter cP12. In addition we observe an unexpected stacking of cP24 rings which is induced by changing the solvent used in electrospray. The rings stack into columns which are up to 4 layers in height, and we also find that the shape distortion of the stacked rings is greatly reduced as the stack height increases. In more recent work we have studied the deposition of the nanorings from solution and find on gold that a similar solvent-controlled stacking occurs, while on graphite extended regular arrays of nanorings are observed. We also discuss the co-deposition of other materials with the nanorings and show that C60 is selectively captured within the nanorings. We analyse the configuration of the nanorings using Monte Carlo simulations and show that the bending rigidity increases linearly with height for stacked rings and discuss the interplay between flexibility and and packing in arrays of rings.

COLL 735

Interfacial systems chemistry: Surface-templated assembly of 3D functional frameworks

Christof Woell, *christof.woell@kit.edu.Insittue of Functional Interfaces (IFG), Karlsruhe Institute of Technology, Karlsrue, Germany*

Supramolecular chemistry holds unique prospects for the fabrication of novel functional materials. Molecularly precisely defined, nanometer-sized subunits which may already be rather complex self-assemble to form even more complex structures which exhibit functionalities not provided by the individual building blocks. In two dimensions, the understanding of a surface-templated assembly of organic molecules (ligands) interacting through hydrogen bonds or ionic interactions has been significantly advanced in recent years.[1]

Here we extend the fabrication of surface-anchored networks beyond the formation of planar, two-dimensional adlayers by demonstrating the synthesis of highly-ordered, three-dimensional porous metal-organic frameworks (MOFs) nucleated on organic surfaces using liquid phase epitaxy [2]. The availability of porous frameworks rigidly anchored to solid surfaces opens the prospect of adding additional functionality to these ultrathin surface coatings [4] by placing nanoobjects inside the pores within the MOFs, e.g. metal clusters or dye molecules [3]. We will demonstrate the potential of this approach by loading the three-dimensional porous scaffolds with metal-containing molecules such as ferrocene and then characterizing their properties using electrochemistry.[5]

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[4] MOF thin films: existing and future applications, O.Shekhah, J.Liu, R.A.Fischer, Ch.Wöll Chem.Soc.Rev. **40** , 1081 (2011)

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COLL 736

Nanopatterning of graphite and graphene at the liquid/solid interface via molecular self-assembly: From fundamentals to applications

Steven De Feyter, *steven.defeyter@chem.kuleuven.be.Department of Chemistry, KU Leuven - University of Leuven, Leuven, Belgium*

Monolayers of molecules can be formed at a variety of interfaces, and over the years many techniques have been developed to construct them and to study the resulting organisation of the molecules. At a liquid-solid interface, 2D assemblies can be created by depositing a solution of the compound of interest on top of the substrate. Depending on the nature of the solvent, the substrate, and the dissolved molecules, the latter might form an ordered monolayer or multilayer at the liquid-solid interface. When the interactions remain relatively weak, the process is called physisorption. Advanced interface specific methods such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM) are needed to study the interface at the nanoscopic level.

We focus on several aspects of self-assembly at the liquid-solid interface, ranging from the fundamentals to applications. We will discuss the concept of 2D crystal engineering and the effect of solvent, solute concentration and temperature, bringing insight into thermodynamic and kinetics aspects of the self-assembly process at the liquid-solid interface.Based on these insights, we demonstrate the self-assembly of several molecular systems at the liquid-solid interface for the formation of functional (nanoporous) networks and the functionalization of surfaces, including graphene. Applications range from surface-assisted enantioselective adsorption and separation of enantiomers, to tunable doping of graphene based field effect transistors.

COLL 737

Scanning probe microscopies beyond imaging: Unraveling the dynamic properties of the supramolecular world

***Paolo Samorì**, samori@unistra.fr.ISIS, University of Strasbourg & CNRS, Strasbourg, France*

My lecture will review our recent results on the use of different Scanning Probe Microscopy approaches, relying on STM, C-AFM and KPFM methods, to unveil physical and chemical processes in complex supramolecular systems. Particular emphasis will be given to the sub-molecularly resolved STM mapping of the activity of light-responsive physisorbed and chemisorbed self-assembled monolayers as well as to the on-surface reaction for the unique case of dynamic covalent chemistry. On the other hand, examples of C-AFM explorations of low-dimensional architectures will be given, with a particular focus on the fabrication of nanoscopic supramolecularly engineered 3-terminal devices (OFETs) and on the possibility of changing the electrical properties of nanostructures by photochemical generation of charge carriers.

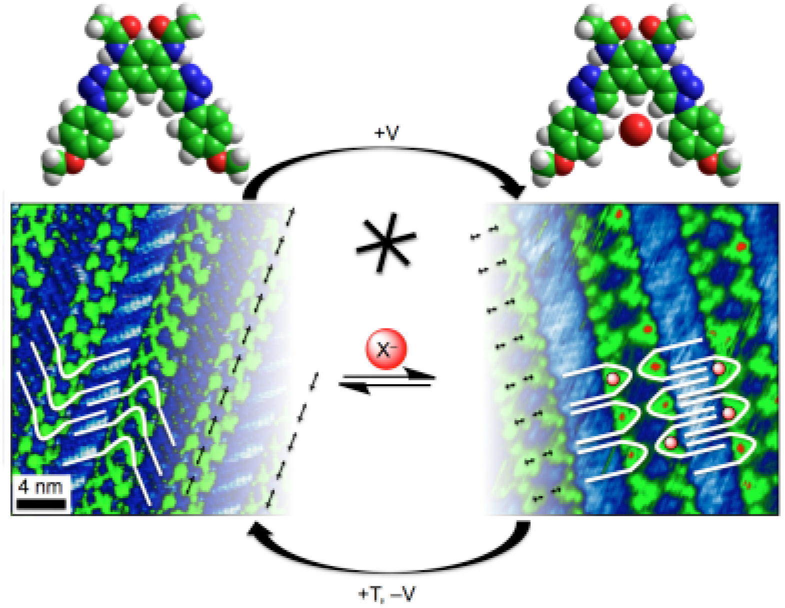
Our findings will open new avenues towards the development of multifunctional materials and devices.

COLL 738

Anion-triggered switching of supramolecular architectures at the liquid-solid interface

***Amar Flood**, aflood@indiana.edu, Brandon Hirsch, Kevin McDonald, Steven Tait.Department of Chemistry, Indiana University, United States*

Two-dimensional crystals of organic adsorbates that self-assemble from solution onto surfaces can be switched using a variety of different stimuli. We demonstrate how binding of anions (X = Cl^-, Br^-, I^-) inside pre-programmed cavities of adsorbed aryl-triazole based receptors drives switching of the surface morphology, as observed using scanning tunneling microscopy (STM). Indicative of the adsorption of the anion-receptor complex, bright spots in the binding pockets are observed. Consistently, the STM surface bias can be used to locally switch the structure by ejecting or attracting anions to the surface. We have formulated a model of packing that rationalizes the anion-induced switching, as well as the bias and tip dependences. This work demonstrates the hierarchical and dynamic character of supramolecular self-assemblies.



COLL 739

Carbon fiber fabric treated with polyaniline for hexavalent chromium removal

*Bin Qiu[1,2], Cuixia Xu[1], Dezhi Sun[2], Xi Zhang[1], Qiang Wang[2], **Suying Wei**[1,3], zhanhu.guo@lamar.edu, **Zhanhu Guo**[1], zhanhu.guo@lamar.edu.Â (1) Department of Chemical Engineering, Lamar University, Beaumont,, TX 77710, United StatesÂ (2) College of Environmental Science and Engineering, Beijing Forestry University, Beijing, ChinaÂ (3) Department of Chemistry and Biochemistry, Lamar University, Beaumont, TX 77710, United States*

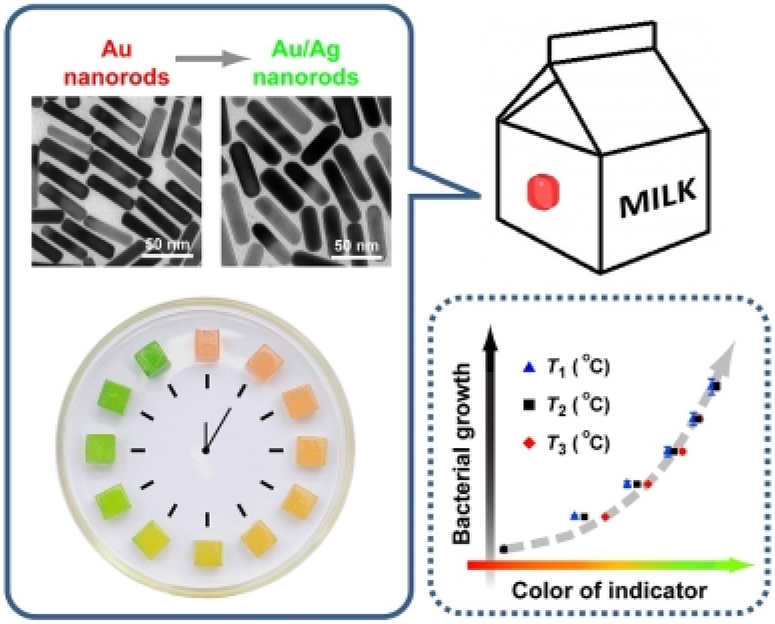
Carbon fiber fabric-supported polyaniline (PANI/CF) with 5, 10, 15 and 20 wt % of PANI loadings were synthesized by dropping 1.0 wt % of PANI solution in m-cresol on the surface of CF. The PANI/CF with a PANI loading of 10 wt % displayed a good performance for hexavalent chromium (Cr(VI)) adsorption from polluted solution. PANI/CF can completely remove Cr(VI) with an initial concentration of 1 mg/L within 15 min, which is faster than the conventional active carbon (6 h) and carbon fibers (1 h). It exhibited better Cr(VI) removal efficiency with low pH. The PANI/CF follows the pseudo-second-order behavior and exhibits a much higher removal rate (0.06 g/(mg·min)) as compared with the ~0.03 g/(mg·min) of active carbon. The adsorption isotherm justified the Langmuir model for this novel adsorbents with a calculated maximum adsorption capacity of 18.1 mg/g for the 10 wt % PANI/CF. The mechanisms of Cr(VI) removal based on the results from FT-IR and XPS involve the reduction of Cr(VI) to Cr(III) by the reduction of PANI. The PANI/CF adsorbents have demonstrated easy recycling capability for upto five cycles with a Cr(VI) removal rate at above 91%.

COLL 740

Self-evolving color-changing smart tags capable of quality indication for perishable products

Chao Zhang[1,2]*, august.pmo@gmail.com, Jianfang Wang*[2]*, Ling-Dong Sun*[1]*, Chun-Hua Yan*[1]*.Â (1) College of Chemistry and Molecular Engineering, Peking University, Beijing, Beijing 100871, ChinaÂ (2) Department of Physics, The Chinese University of Hong Kong, Hong Kong, Hong Kong 999077, Hong Kong Special Administrative Region of China*

The quality of perishable products (such as foods, beverages, pharmaceuticals and cosmetics) strongly depends on their temperature history. Temperature abuses during the custody chain may lead to significant quality degradation, which, however, is usually not directly visible to customers. Here we developed a self-evolving color-changing smart tag to track, mimic and indicate the deteriorative processes in common perishables. The smart tag exploits the chronochromic behaviors during the Ag overgrowth on Au nanorods in aqueous solution. Under given conditions, the smart tag spontaneously changes its appearance from an initial red to a final green color, exhibiting sharp visual contrast. At room temperature, the temporal duration for this red-to-green self-evolution can be adjusted from minutes to months, and the apparent activation energy can be widely tuned from 50 to 190 kJ/mol, covering the kinetic features of almost all ambient-temperature deteriorative processes found in foods. Using *E. coli*growth in milk as a model, we successfully synchronized, at multiple temperatures, the chemical evolution process in the smart tag with the microbial growth processes, implying that the “bio-chemo” correlation is temperature-independent. The smart tag is also cost-effective and eco-friendly, and well meets the ASSURED criteria (Affordable, Sensitive, Specific, User-friendly, Robust and rapid, Equipment-free, and Deliverable to end-users) proposed by WHO. We believe that this smart tag holds the promise to be further developed into a standardized protocol for the current food/beverage/pharmaceutical industries.



COLL 741

Cylindrospermopsis raciborskii (Cyanobacteria) exudates: Chemical characterization and complexation capacity for Cu, Zn, Cd and Pb

Alessandra Emanuele Tonietto[1]*, aletonietto@gmail.com, Ana Teresa Lombardi*[1]*, Armando Augusto Henriques Vieira*[1]*, Christopher C. Parrish*[2]*, Rodrigo Brasil Choueri*[3]*.Â (1) Department of Botany, Federal University of SÃ£o Carlos, SÃ£o Carlos, SÃ£o Paulo, BrazilÂ (2) Department of Ocean Sciences, Memorial University of Newfoundland, St John's, NL, CanadaÂ (3) Departament of Marine Sciences, Federal University of SÃ£o Paulo, Santos, SÃ£o Paulo, Brazil*

Cylindrospermopsis raciborskii is a cosmopolitan and potentially toxic planktonic Cyanobacteria that produces and exudes copious amounts of dissolved organic materials. This organism dominates the eutrophic reservoir Barra Bonita (Brazil), where it normally blooms throughout the year. This investigation focused on the characterization of such exudates analyzing their capacity to complex copper, zinc, lead and cadmium through the determination of ligand concentration (C_L) and conditional stability constant ($\log K'_{ML}$), as well as elemental composition (C, H, N and S), the content of carbohydrates, proteins, lipids and dissolved organic carbon (DOC). The dissolved organic material was fractionated into 3 molecular weights (>30 kDa; 30-10 kDa; 10-3 kDa) and each fraction was analyzed. The results showed that in the > 30 kDa and 30-10 kDa fractions carbohydrates dominate over proteins and lipids. Different C_L and $\log K'_{ML}$ were obtained for the different molecular weight fractions of the excreted organic materials, suggesting high diversity of ligands. In the > 30 kDa, there were more complexing sites (C_L) for Cu, but higher affinity (K') for Zn. In the 30-10 kDa fraction, the

higher C_L was for Cd, but the greatest affinities were for Cu and Zn. In the 10-3 kDa fraction, higher $C_L$was obtained for Cd and Zn, while Cu and Cd had the highest strengths of association. In the environment, such diversity of ligands and strengths of association can result in a displacement of metals weakly bound to the EOM, and increase metal buffering capacity of the environment, supporting higher metal inputs before toxic effects are detected in the biota.

COLL 742

Toxicity assessment of Ag and TiO_2 nanoparticles using zebrafish embryos in the presence of environmental contaminants

***Rajasekhar Balasubramanian**, ceerbala@nus.edu.sg, Shruti Pavagadhi.Department of Civil and Environmental Engineering, National University of Singapore, Singapore, Singapore 117576, Singapore*

Engineered Nanoparticles (ENPs) have gained tremendous attention in recent times due to their great potential to address consumer and industrial needs. Their extensive use in various processes and in consumer products is likely to result in releases into the environment. Following environmental release, ENPs are likely to deposit in aquatic systems and represent a possible risk to aquatic life. Upon their release, they interact with a host of other environmental pollutants present in these aquatic systems which would finally determine their fate and transport and consequently their toxic potencies. In order to understand the toxic effects of ENPs released in the environment, it is important to study their relationship with other environmental pollutants. In the present study, attempts were made to get an overview of the possible interactions of ENPs with a range of environmental pollutants. Silver (Ag) and titanium dioxide (TiO_2) NPs were used as model ENPs as these NPs not only find a variety of applications in water treatment and water purification technologies, but are also used in a wide range of consumer products. To assess the toxicity and uptake kinetics, zebrafish embryos were used. The environmental implications of the study will be discussed.

COLL 743

Nanoparticles for environmental pollution removal

***Xiaobo Chen**, chenxiaobo@umkc.edu.Department of Chemistry, University of Missouri - Kansas City, Kansas City, MO 64110, United States*

TiO_2 has proven to be the most promising photocatalyst for environmental pollution removal. Normally, TiO_2 nanoparticles are put into the water to photodecompose the aqueous pollutants under sunlight. The photocatalytic decomposition process includes surface adsorption and photodecomposition. Here we demonstrate that new nanoparticles can be used to efficiently remove environmental pollutions, i.e. from aqueous solution. This would expand the practical application of nanophotocatalyst for environmental applications.

COLL 744

Highly efficient nano-adsorbents for the removal of arsenic (III, V) from water

Li Qi*, qili@imr.ac.cn.Department of Environment Functional Materials, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, Liaoning 110016, China*

Arsenic (As) contamination is of serious concern to the human health due to its toxicity and carcinogenicity. Long-term exposure to As contaminated water causes cancers in skin and lung,; as well pigmentation changes, hyperkeratosis, and neurological disorders. It could also induce cardiovascular and cerebrovascular diseases. To minimize these risks, the World Health Organization suggested a low guideline limit of 0.01 mg/L standard in drinking water. Implementing this strict guideline limit requires to develop simple and cost effective approaches for As-removal. Adsorption is the most promising technology at low concentration due to its simplicity, cost-effectiveness, potential for regeneration, and sludge free operation. In the natural water, As occurs in two predominant species, arsenate (As(V)) and arsenite (As(III)). The As(III), existing as nonionic H_3AsO_3at various pH values is reported to have a lower affinity to various adsorbents compared to As(V). To enhance As removal, a pretreatment (oxidation and pH justifiction) is needed before the coprecipitation/adsorption. This requires a post-adjustment of pH, which causes operation cost increase and secondary pollution. Thus, to develop adsorbents with enhanced adsorption effect on both As (III) and As (V) without pre-treatment becomes desirable.

The development of a series of highly efficient As adsorbents composed of nano-sized metal oxides will be presented in this talk. A single step adsorption treatment could be available to remove As from water without the pre-/post-treatment for industrialization. To address the issue of the difficult separation of nanoadsorbents from treated water bodies, superparamagnetic magnesium ferrite nanoadsorbents were developed to achieve high dispersion and high contact efficiency when there was no external magnetic field applied. It is feasible for magnetic separation from treated water bodies when the external magnetic field was applied after the water treatment. Additionally, highly porous, nanostructured zirconium oxide spheres and its adsportive performance will be presented.

COLL 745

Carbon nanostructure adsorption, ordering, and displacement at metal surfaces

Qian Shao*, qshao@umd.edu.University of Maryland, MD 20742, United States*

Functionalized C_{60} and C_{70} fullerenes are employed as active components in organic electronic devices and have spurred interest in improved methods for controlled materials deposition from the liquid state. The structure of C 60 and C 70 -PCBM-electrode interfaces is expected to strongly impact charge transfer processes in photovoltaic devices. We report a molecularly detailed study of the growth of C 60 and

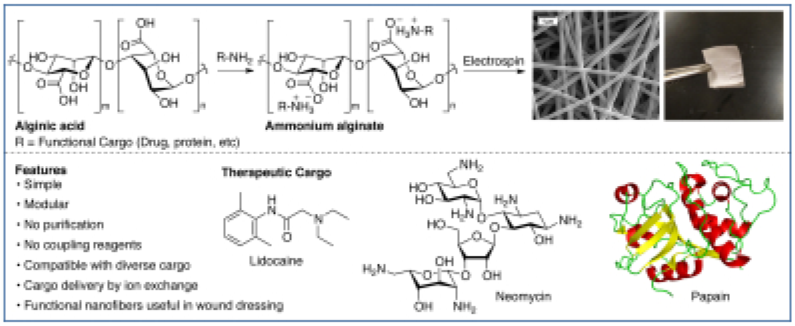
C 70 -PCBM on Au (111) and Ag (111) metal surfaces using UHV-STM. Thin films are grown on atomically clean substrates with a custom-build pulsed aerosol molecular beam deposition source. The directed deposition of aerosols offers materials versatility, low cost, large-scale manufacturing capacity and advantages to the environment through reduced. Structure is tracked from the sub-monolayer to multilayer regime under thermally driven conditions. C 60 and C 70 -PCBM films on the (23 × √3)-Au (111) surface undergo transformation from disordered films to semicrystalline films with islands of hcp- packed fullerenes upon annealing to 250 ℃ .
Bilayer C 70 -PCBM films undergo thermal transformation, with 2-D hcp-packed domains evident
for both the 2 nd -layer and 1 st -layer fullerenes. We propose structural models with hydrogen-bonding interactions between the fullerenes, accounting for the observed hcp packing
and registry-shift between 1 st -layer and 2 nd -layer C 70 -PCBM molecules. Solvation effects in nanoparticle adsorption and ordering are additionally explored for these PCBM model systems. This work was supported by the NSF-Division of Chemistry (MSN) under CHE-CHE1310380.

COLL 746

Facile preparation of ammonium alginate-derived nanofibers carrying therapeutic payloads

*Caitlin E. Pegg, Gregory H. Jones, Thushara J. Athauda, Ruya R. Ozer, **Justin M. Chalker**, justin-chalker@utulsa.edu.Department of Chemistry and Biochemistry, The University of Tulsa, Tulsa, OK 74104, United States*

Alginic acid can be converted into a variety of ammonium alginate derivatives that carry medically relevant cargo such as analgesics, antibiotics, and enzymes. These modified polymers can then be fashioned into nanofibers by electrostatic spinning. These fibrous mats were shown to carry functional therapeutics through a variety of biological assays. Since these materials dissolve slowly in water and release the cargo through ion-exchange, we envision their application as next-generation, biodegradable wound dressings. In addition to our interest in the biomedical applications of these fibrous materials, we discuss ammonium alginates as general precursors to functional nanofibers. The straightforward preparation is key: the cargo need only contain a basic functional group such as an amine for ligation to alginate through an ionic linkage, neither coupling reagents nor purification are required, and cargo can be used in its native state.



COLL 747

Effctive decontamination of microbial pathogens via hybrid nanoscale materials

Sherine O. Obare, *sherine.obare@wmich.edu, Setare Tahmasebi Nick, Michael J. Fish.Chemistry, Western Michigan University, Kalamazoo, MI 49008, United States*

Engineered nanomaterials (ENMs) possess unique size and shape dependent chemical and physical properties. As a result of their properties, ENMs have been effective in several important applications including catalysis, sensor design, photonics, electronics, medicine, and the environmental remediation of toxic pollutants. Recently, our group has investigated the effect of various metallic and semiconductor nanomaterials, with well-defined size and shape, on the various strains of microbial pathogens. We have also investigated the effects of small molecules anchored on the surface of nanoparticles and their influence on the decontamination of microbial pathogens. This presentation will demonstrate our ability to control of the particle size and shape in one-step synthetic procedures. Monodisperse metallic nanoparticles were synthesized and characterized using spectroscopic, microscopic and x-ray techniques. The chemical composition, surface reactivity, solubility, and aggregation tendency of ENMs were studied under various environmental conditions. We will also discuss how ENMs interact with various components in the environment with an emphasis of their interaction with Gram-negative and Gram-positive bacteria. The results provide insights on design strategies for new materials to safely decontaminate microbial pathogens.

COLL 748

Functional coatings based on polymers doped with clay nanotubes

Yuri Lvov, *ylvov@latech.edu.Engineering Dep., Louisiana Tech University, IfM, Ruston, Louisiana 71272, United States*

Halloysite clay nanotubes are a naturally occurring, biocompatible alumosilicate material with a length of 1 μm, outer diameter of 50 nm and lumen size 15 nm. We developed polymeric composites doped at 5-7 wt. % with halloysite that release application - specific inhibitors in a sustained fashion (anticorrosion, flame-retardant, and antimicrobial). Doping loaded clay nanotubes into a polymeric paint provides a kind of ceramic “skeleton” within the coating layer, and these “skeleton bones” are loaded with functional chemicals (like real bones are loaded with marrow). This “skeleton” also improves on 30-50 % the coating strength and adhesivity. Sustained corrosion protection was achieved by leaking of inhibitors (such as benzotriazole and hydroxyquinoline) from the nanotubes in the coating defects which heals metal surface and prevents further corrosion. Halloysite loading efficiency was optimized by its treatment with sulfuric acid. Tunable controlled release of corrosion and antifouling agents has been achieved by synthesis of tube end stoppers. Halloysite is “green” nanomaterial which is not hazardous for the environment, and these clay nanotubes are available in the thousands of tons from natural deposits.

COLL 749

Smart elastomeric opal films

Daniel Scheid, *m.gallei@mc.tu-darmstadt.de, Christian G. Schäfer,* ***Markus Gallei****,*
m.gallei@mc.tu-darmstadt.de.Department of Chemistry, Technische UniversitÃ¤t
Darmstadt, Darmstadt, Hessen 64287, Germany

Monodisperse core-interlayer-shell (CIS) particles obtained by convenient semicontinuous emulsion polymerization were used to obtain elastomeric opal films. By taking advantage of the so-called melt shear technique it is possible to gain highly ordered and reversibly stretch-tunable elastomeric polymer opal films after subsequent thermal or UV cross-linking reactions.[1-3] Resulting opal films revealed distinct angle-dependent reflection colors due to Bragg's law. The responsiveness of the matrix-forming polymers used makes these opal films excellent candidates for solvatochromic and mechanochromic sensing due to the change of the distances of the (111) planes after stimulation. Embedding the opal films into porous paper substrates permits the rapid absorption of different analytes accompanied with a fast and reversible optical response.[4]Incorporated functional monomers with e.g. redox-active ferrocenes, fluorescent dyes or pH-responsive moieties could be used to change the optical properties of the opal films suitable for a plethora of sensing materials. Hence, in the presence of different analytes, a selective response can be achieved for a variety of polymer-based soft sensor devices. The multi-stimuli-responsiveness of herein investigated opal films turns them unambiguously to very attractive materials with a wide range of applications in fields of optical sensing, rewriteable photonics and actuation systems. Recent efforts have resorted to synthesize functional CIS particles based on inorganic magnetic nanoparticles, which extend the range of potential applications of the opal films towards nanophotonics, nanoelectronics, plasmonics and metamaterials.

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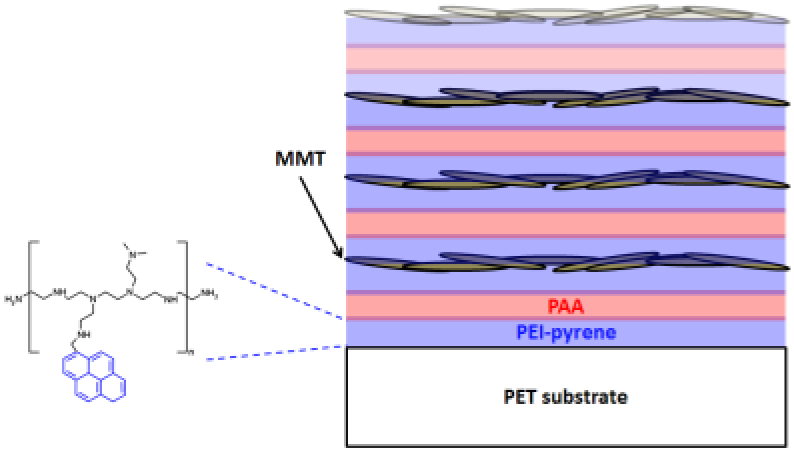
COLL 750

Increasing hydrophobic interactions in a polyelectrolyte for improved oxygen barrier in multilayer nanocomposite thin films

Bart Stevens[1]*, bartstevens@tamu.edu, Patrick K Odenborg*[1]*,* ***Jaime C Grunlan***[1,2]*, jgrunlan@tamu.edu.Â (1) Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843-3123, United StatesÂ (2) Department of Materials Science, Texas A&M University, College Station, TX 77843-3123, United States*

The influence of attaching hydrophobic side groups to a polyelectrolyte used for thin film deposition of oxygen gas barriers was investigated. Polyethyleneimine (PEI) was labeled with pyrene and deposited in 'quadlayers' of PEI, poly(acrylic acid), and sodium montmorillonite clay using layer-by-layer assembly. Thin films made of four repeating quadlayers using unmodified PEI-based films deposited much thinner (51 nm) compared to pyrene-labeled PEI-based films (92 nm), which is believed to be the result of greater chain coiling from the increased hydrophobicity of pendant pyrene groups. This increased thickness in pyrene-labeled PEI layers produced greater clay spacing that allowed three quadlayers to match the oxygen transmission rate of a four quadlayer film made with unmodified PEI.



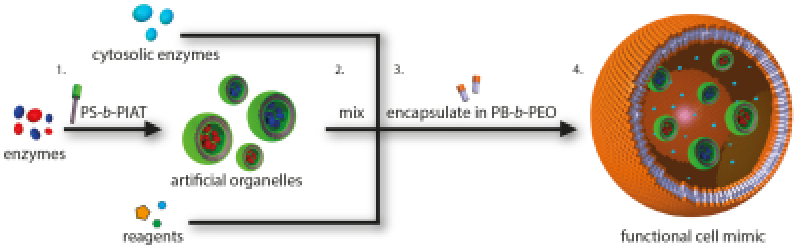
COLL 751

Enzymatic cascade reactions in multicompartmentalized polymersomes

Ruud J.R.W. Peters[1], *ruud.peters@science.ru.nl, Maïté Marguet*[2]*, Sebastien Lecommandoux*[2]*, Jan C.M. van Hest*[1]*.Â (1) Department of Bio-organic Chemistry, Radboud University Nijmegen, Nijmegen, Gelderland 6525 AJ, The NetherlandsÂ (2) Department of Polymer Chemistry, UniversitÃ© de Bordeaux, Bordeaux, France*

Eukaryotic cells possess a multicompartmentalized structure, via which the cell gains spatiotemporal control over its processes, allowing it to physically separate incompatible reaction components and pathways from each other by confining them to different compartments.

In order to construct a model system that will allow the effects of compartmentalization on multi-step processes to be studied, we have developed a functional and structural cell mimic via a self-assembly approach. Enzyme-filled semipermeable polymeric nanoreactors were used to mimic organelle compartments. These nanoreactors are only porous to small molecules, like substrates and cofactors. The multicompartment, cell-like architecture was then established by encapsulating the nanoreactors, together with other required reagents, in a larger PB-*b*-PEG polymer vesicle that acts as the artificial cell membrane.



To introduce function to the system, a three-enzyme cascade reaction, requiring the presence of natural cofactors, was used as a model reaction pathway. The enzymes were confined to both the cytosol and different organelle subcompartments to demonstrate multicompartment catalysis. Subsequently, enzyme confinement was also shown to allow incompatible enzymes to function together more efficiently compared to non-compartmentalized systems. The cascade reactions were subsequently monitored in single cell mimics by fluorescence microscopy, which demonstrated that the reaction only takes place inside the cell mimics, and that multi-step cascade reactions can be performed across different compartments.

COLL 752

Tannic acid based natural particle for versatile use

Nurettin Sahiner[1,2]*, sahiner71@gmail.com, Selin Sagbas*[1]*,* ***Nahit Aktas***[3]*, cinar49@gmail.com.Â (1) Department of Chemistry, Canakkale Onsekiz Mart*

University, Canakkale, Canakkale 17100, TurkeyÂ (2) Nanoscience and Technology Research and Application Center (NANORAC), Canakkale Onsekiz Mart University, Canakkale, Canakkale 17100, TurkeyÂ (3) Department of Chemical Engineering, Yuzuncu Yil University, Van, Van 65080, Turkey

We prepared natural polymeric particles based on Tannic Acid (TA) in nano and micron dimensions using water oil micro emulsion polymerization/crosslinking method.[1,2] The prepared poly(tannic acid) (p(TA)) particles were chemically modified for desired physical chemical and properties and morphologies. The abundant number of -OH functional groups in the structure of TA provided the opportunity for particle formation and post modification reactions for new functional groups. The polyphenolic structure of TA present many inherently superior characteristics such as a high antioxidant nature, and high amounts of active agents (drug, protein, growth hormones etc) loading and release characteristics. Moreover, metal ions such as Fe(II/III), Co(II), Ni(II), Cu(II) can be readily uptaked by p(TA) particles and reduced by the phenol groups in situ or by the use of reducing agents such as $NaBH_4$.[3] In this investigation, we also report the multiple use of p(TA) particles in biomedical and environment applications. Gallic acid (GA) is used as model drug, and used for loading and release studies from p(TA) particles. In addition to the use of p(TA) particles for metal ion absorption for environmental applications, metal nano particle prepared within p(TA) particles as composite were also used in catalytic applications such the reduction of 4 or 2-nitro phenols to 4 or 2-amino phenols. Various parameters affecting the biomedical and environmental application of p(TA) particles were investigated.

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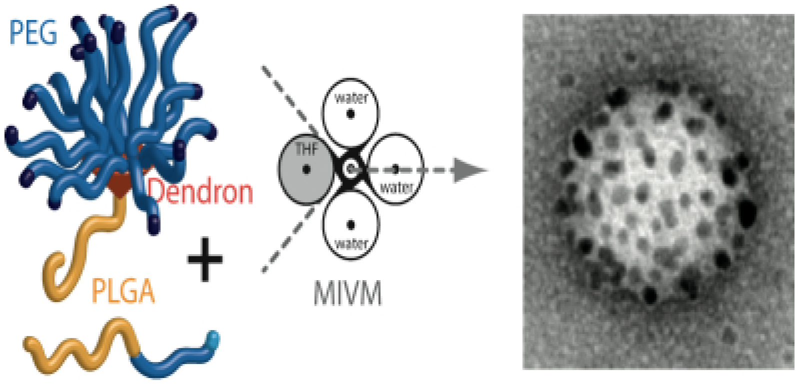
COLL 753

Kinetically arrested assemblies of architecturally distinct block copolymers: Effect of amphiphile on protein-micelles interactions

***Jose Luis Santos**, jlsantos@jhu.edu, Margarita Herrera Alonso.Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, MD 21218, United States*

There has been increasing interest in the development of hybrid systems with readily tunable properties to afford a myriad of materials with unique physiochemical features.

For instance mixed polymeric micelles –hybrid systems prepared from the coassembly of polymer amphiphiles exhibiting distinct chemical properties- find multiple applications in the field of drug delivery and targeting. Here we report on the formation of hybrid nanoparticles from architecturally distinct block copolymer amphiphiles by controlling the molar composition of a blend and the kinetic features of the assembly process. Specifically, we examined and contrasted the co-assembly of linear and linear-dendritic amphiphiles under equilibrium and non-equilibrium conditions. Through careful manipulation of the amphiphile architecture, blend composition and final solvent content, hybrid nanoparticles of controllable size and patchiness could be readily achieved. The stability of hybrid nanoparticles towards protein solutions/serum and red blood cells is subsequently assessed *in vitro* using FRET, DLS and isothermal titration calorimetry techniques. The results shows that amphiphile architecture plays a significant role on the protein-nanoparticle interactions.



COLL 754

Targeted delivery of Ru to cancer cells via polymeric nanoparticles

Ronaldo Cavazos, Alesha N Harris, Amanda Phelps, ***Robby A Petros****,*
petros@unt.edu.Department of Chemistry, University of North Texas, Denton, TX 76203, United States

The field of targeted drug delivery focuses primarily on delivering small organics or biologics as therapeutics and has largely ignored the potential for delivering transition metals other than platinum. Thus, there is a need for delivery vectors for transition metal complexes because metal-based therapeutics, like their small molecule organic counterparts, routinely exhibit low solubility, off-target toxicity, poor pharmacokinetics, and short circulation half-lives. We have utilized azole chemistry to attach metal complexes to nanoparticles. To this end, we have designed two approaches to encapsulating Ru in nanoparticles. In the first, we have synthesized phosphate-functionalized nanoparticles by including a phosphate containing monomer in the free radical polymerization used in particle synthesis. For the second, we synthesized an imidazole containing acrylate monomer that can then be polymerized to form nanoparticles. After purification, either particle formulation can be loaded with a variety of metal species, some of which exhibit interesting luminescent or pharmacological properties. Details of the synthesis, characterization, *in vitro* activity, and potential for clinical translation will be discussed.

COLL 755

Lung cancer diagnostics by measuring protease signatures in blood serum

Pamela Maynez[1]*, pmaynez@k-state.edu, Dinusha N. Udukala*[1]*, Hongwang Wang*[1]*, Thilani N. Samarakoon*[1]*, Deryl L. Troyer*[2]*, Stefan H. Bossmann*[1]*.Â (1) Department of Chemistry, Kansas State University, Manhattan, Kansas 66506, United StatesÂ (2) Department of Anatomy & Physiology, Kansas State University, Manhattan, Kansas 66506, United States*

Developing cancer diagnostics for recognizing lung cancer at the localized stage would be very advantageous, because most lung cancer mortalities occur after the cancer has metastasized.

In 2013, the American Cancer Society's estimates for lung cancer in the United States are approx. 228,000 new cases and about 160,000 deaths (small and non-small cell lung cancer combined). Lung cancer mortalities account for about 27% of all cancer deaths in the US.

Numerous proteases that can be found in the blood and urine of lungcancer patients are of proven diagnostic value. Compared to immunoassays, luminescence assays have the potential to be two orders of magnitude more sensitive and very importantly they are able to detect only chemically active proteases, whereas immunoassays detect always mixture of active proteases and zymogens. Fluorescent nanoplatforms that have been developed and validated in the Bossmann group have been used to determine the protease concentrations of a series of cancer-related proteases (urokinase plasminogen activator, matrix metalloproteinases 2,7,9,11,13 and cathepsins B,D,L,K). 25% of the samples (36 in total) have come from healthy control subjects. The results indicate that early detection of non-small cell lung cancer is possible in stage I.

COLL 756

Dimethyldiethoxysilane emulsion droplets-mediated synthesis and loading of monodispersed polymer nanocapsules for biomedical applications

Yajun Wang[1]*, yajunwang@fudan.edu.cn, Shanshan Bian*[2]*, Wuli Yang*[2]*.Â (1) Department of Chemistry, Fudan University, Shanghai, ChinaÂ (2) State Key Laboratory of Molecular Engineering of Polymers and Department of Macromolecular Science, Fudan University, Shanghai 200433, China*

In the past decade, polymer capsule-based therapeutic delivery systems have attracted considerable interest because capsules engineered with various nanotechnologies can provide unparalleled advantages in many aspects of biomedical applications. Various methods, including polymerization, phase separation, self-assembly, and templating synthesis, have been developed to prepare a range of polymer capsules. Among these techniques, the templating synthesis approach is versatile and general, allowing the morphology, size, composition, and properties of the capsules to be finely tuned, which are particularly important for drug delivery.

Here, we will focus on the talk of our recent progress in the preparation of monodispersed, biodegradable polymer capsules through a novel interfacial polymerization technique onto dimethyldiethoxysilane (DMDES) emulsion droplets and facile removal of the DMDES templates with ethanol after the polymerization step. Encapsulating of various functional substances, such as magnetic nanoparticles, quantum dots, and hydrophobic drugs, in the polymer capsules is achieved through preloading these substances in the emulsion droplets. All of the unloaded and loaded polymer capsules were monodisperse and did not aggregate in aqueous media. Furthermore, biodegradability of the capsules in reducing environment is also discussed. This work provides new avenues for the preparation of a suite of polymeric capsules with defined size and properties and for the encapsulation of a range of substances. Such materials are expected to find application in biosensing, diagnostics, and controlled drug delivery.

COLL 757

Biomolecular recognition principles for bionanocombinatorics: An integrated approach to elucidate enthalpic and entropic factors

Zhenghua Tang[1]*, z.tang@miami.edu, Pablo J. Palafox-Hernandez*[2]*, Wing-Cheung Law*[3]*, Zak Hughes*[2]*, Mark T. Swihart*[4]*, Paras N. Prasad*[3,5]*, Marc R. Knecht*[1]*, Tiffany R. Walsh*[2]*.Â (1) Department of Chemistry, University of Miami, Coral Gables, FL 33146, United StatesÂ (2) Institute for Frontier Materials, Deakin University, Geelong, Vic. 3216, AustraliaÂ (3) Department of Chemistry and Institute for Laser Photonics and Biophotonics, University at Buffalo (SUNY), Buffalo, NY 14260, United StatesÂ (4) Department of Chemical and Biological Engineering, University at Buffalo (SUNY), Buffalo, NY 14260, United StatesÂ (5) Department of Chemistry, Korea University, Seoul, Republic of Korea*

Bionanocombinatorics represents a new avenue to organize multiple nanomaterials into 3D architectures with emergent properties and functionalities. In an effort to realize the full potential of this approach, non-covalent binding between inorganic materials and biomolecules has been widely employed. For instance, materials-binding peptides have been extensively studied, because their binding specificity could play an important role in bionanocombinatorics; however, the basis for this binding affinity and selectivity remains unclear. To address this issue, an integrative approach that combines experimental measurement with advanced molecular simulation has been developed to probe the fundamental basis of peptide-inorganic surface interactions for Au. From this analysis, the significance of entropy-driven binding has been quantitatively demonstrated, in combination with enthalpic considerations. Furthermore, the general criteria for designing either entropy or enthalpy driven peptide sequences is formulated. This approach could pave the pathway to establishing bionanocombinatorics principles based upon specific material recognition by peptides.

COLL 758

Mechanistic investigation of DNA sequence-dependent morphological evolution of silver nanoparticles and optical and biorecognition properties

Jiangjiexing Wu[1,2]*, wujiangjiexing2007@126.com, Kevin Hwang*[2]*, Li Huey Tan*[2]*, Peiwen Wu*[3]*, Wei Li*[1]*, Yi Lu*[2,3]*.Â (1) Key Laboratory for Green Chemical Technology MOE, Tianjin University, Tianjin, Tianjin 300072, ChinaÂ (2) Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United StatesÂ (3) Department of Biochemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States*

The effects of different DNA sequences on the morphologies of Ag nanocubes during synthesis are investigated. It is observed that different DNA sequences can result in different morphologies: 10-mer poly C induces the formation of triangular bipyramid nanoparticles Ag_C10. 10-mer poly A and 10-mer poly T induce the formation of two types of slightly different octahedron-shaped Ag nanoparticles, Ag_A10 and Ag_T10, respectively, with Ag_T10 being smaller in size and more truncated compared with Ag_A10. Ag nanoparticles generated from incubation with G10 remain cubic (Ag_G10). Detailed mechanistic studies indicate that the difference in DNA affinity to the Ag nanoparticle and the formed secondary structure are playing the major role in controlling the different morphologies. The DNA adsorbed on the Ag nanocube surface act as a template to mediate the formation of different Ag nanoparticles, which can induce selective deposition of the reduced Ag metal on Ag nanocube. DNA mediated synthesized Ag nanoparticles show not only sequence-dependent shapes but also optical properties. The as-prepared octahedron-shaped Ag_T10 and Ag_A10 give SERS signals that are approximately 8 and 3 times stronger, respectively, than that of the conventional octahedrons with a similar size. Furthermore, we show that the DNA-functionalized Ag nanoparticles are more stable than the SH-DNA functionalized ones, and that DNA functionalization can be realized *in situ* during the one-step synthesis while retaining their biorecognition ability, which allows for programmable assembly of new nanostructures.

COLL 759

Quantitative study of the catalytic activity and stability of horse radish peroxidase on gold nanoparticles

***Charles B Nettles**, cbn15@msstate.edu, Dongmao Zhang.Department of Chemistry, Mississippi State University, Mississippi State, MS 39762-9573, United States*

Protein interactions with gold nanoparticles (AuNPs) have broad implications for AuNP biological and biomedical applications. Probing protein structure, conformation, and biological activities are challenging due to a host of experimental limitations. Presented in this work is a systematic quantative study of the effect of AuNP binding on horse radish peroxidase (HRP). The most important finding is that AuNP reduces HRP catalytic activities but enhances its stability. Different experimental strategies are explored to improve the HRP catalytic activity on the AuNPs. This research is important for fundamental understanding of protein and AuNP interactions and for AuNP biological applications.

COLL 760

Polypeptide composite particles by click chemistry: Preparation, characterization, and applications

***Cornelia Rosu**[1,2], crosu1@tigers.lsu.edu, Rafael Cueto[1,2], Lu Zou[3], Chanjoong Kim[3], Paul S Russo[1,2].Â (1) Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, United StatesÂ (2) Macromolecular Studies Group, Louisiana State University, Baton Rouge, Louisiana 70803, United StatesÂ (3) Liquid Crystal Institute, Kent State University, Kent, OH 44242, United States*

Polypeptide composite particles, PCPs, with a magnetic core and an α-helical homopolypeptide shell have been produced by combining ring-opening polymerization and Huisgen's 1,3-dipolar cycloadition also known as click chemistry. The desired sparse coverage with polypeptide was confirmed by TGA analysis. Shell molecular weights were measured by GPC and MALDI-TOF and their conformation was investigated by FTIR. Other techniques such as XRD, TEM, XPS, DLS and SQUID were used to investigate the nature of the composite particles.

PSLG-click hybrid was found to be a good support for lipase from *Candida Rugosa* immobilization. Suspension of the PSLG-click hybrid particles in a liquid crystal, LC, rodlike PSLG matrix enabled a good control of the clustering under applied magnetic field. Under stress, PCBL-click particles showed shear thinning tendency and behaved as a non-Newtonian stiff material.

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COLL 761

Understanding protein-nanoparticle interactions at a molecular level

***Wayne Lin**, wlin19@illinois.edu, Catherine Murphy, Chad Rienstra, Deborah Berthold.Department of Chemistry, University of Illinois at Urbana Champaign, Urbana, IL 61801, United States*

Understanding the nanoparticle-biological interface is important for both biomedical applications and environmental implications of these materials. Molecular-level understanding of this interface requires molecular-level techniques. We present the use of nuclear magnetic resonance spectroscopy to examine the interaction of 15N-labeled α-synuclein, a protein whose secondary structure is correlated with neurodegenerative disease, with a standard set of gold nanoparticles. α-synuclein is known to exist as a random coil in solution, adopt alpha helical conformations upon binding to phospholipid vesicles, but form beta sheet structures when aggregating to form cytotoxic fibrils. Understanding how α-synuclein interacts with gold nanoparticles might lead to control of its shape and aggregation, and further enhance knowledge of neurodegenerative disease pathways.

COLL 762

Membrane structure from surface enhanced Raman spectroscopy

***James R Matthews**[1], jrm18@rice.edu, Courtney M Payne[2], Jason H Hafner[1,2].Â (1) Department of Physics and Astronomy, Rice University, Houston, Texas 77005, United StatesÂ (2) Department of Chemistry, Rice University, Houston, Texas 77005, United States*

Membrane structure is inherently complex, and understanding the structure of peptide chains inserted in membranes is vitally important for the development of effective diagnosis and treatments of diseases. We present progress toward applying Surface Enhanced Raman Spectroscopy (SERS) as a tool for studying lipid membrane structure. Optical excitation of gold nanoparticles at their size and shape-dependent plasmon resonant frequency induces strong oscillations of the nanoparticle's free electron gas, leading to SERS – an enhancement of Raman scattering signals in a distance dependent manner at the molecular scale. This project utilizes gold nanorods, tuned to an excitation laser wavelength of 785 nm, as a substrate for lipid membranes so that their structure can be analyzed by SERS. This project aims to displace the surfactant cetyltrimethylammonium bromide (CTAB) that stabilizes nanorods with the biologically relevant lipid dioleoylphosphatidylcholine (DOPC), and to observe the insertion of the peptide melitin into the lipid membrane using SERS for confirmation. Gold nanorods were incubated in solutions of DOPC much higher than CTAB to cause direct molecular substitution. SERS spectra clearly indicate a complete substitution based on the reduction and absence of the 760 cm^{-1} peak of the CTAB headgroup and the introduction of the 719 cm^{-1} peak of the DOPC headgroup. The continued presence of a peak at $180cm^{-1}$ indicates that the bromide ions remain bound to the nanorod surface, serving as the intermediary between the chemically similar DOPC choline group and the CTAB trimethylammonium group. Upon addition of melittin to the lipid coated nanorods, SERS spectra show the introduction of the amide I peak at $1650cm^{-1}$

indicating the presence of the peptide. Initial observations give us confidence that a complete and well formed lipid bilayer is present at the surface of the nanorods and the peptide melittin is close enough to provide a SERS signal.

COLL 763

Lipid bilayer energetics, deformations, and interaction with carbon nanoparticles studied by molecular dynamics simulations

Steven O Nielsen[1]*, steven.nielsen@utdallas.edu, Wataru Shinoda*[2]*.Â (1) Department of Chemistry, The University of Texas at Dallas, Richardson, TX 75080, United StatesÂ (2) Health Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka 563-8577, Japan*

The properties of lipid bilayers, such as their mechanical strength and bending rigidity, are of critical importance for biological function.
We will present new methodology for measuring these properties using molecular simulation. Also, aggregation of carbon nanoparticles in lipid membranes is assessed because of the strong link between aggregation and toxicity.

COLL 764

Behaviour of a recombinant protein G at the air/water interface

Louise Deschênes[2]*, louise.deschenes@agr.gc.ca, Habib Horchani*[1]*, Christian Salesse*[2]*.Â (1) Agriculture & Agri-Food Canada, Food Research and Development Centre, Saint-Hyacinthe, QuÃ©bec J2S 8E3, CanadaÂ (2) HÃ´pital du St-Sacrement, UniversitÃ© Laval,, QuÃ©bec, Quebec, Canada*

Recombinant proteins are of great importance in several biological key processes. On the engineer point of view, their specific binding properties are of great interest and are widely used in biosensing. Since their bioactivity and efficiency are related to their conformation, a better understanding of their behaviour and organization at interfaces is needed in optimizing their use for such purposes. The present study was undertaken in order to get a better knowledge of recombinant Protein G molecular organization using the air/water interface as a model system. Surface pressure isotherms, PM-IRRAS and circular dichroism were used to monitor the impact of surface concentration on the molecular organization of the recombinant Protein G. Its maximal insertion pressure (MIP) in a self-assembled monolayer of PS-PEO block copolymer was determined. Such a system presents the advantages of combining bioactivity and reduction of non-specific interactions.

COLL 765

Ion distributions in electrolyte confined by multiple dielectric interfaces

***Yufei Jing**, yufeijing2011@u.northwestern.edu, Jos W. Zwanikken, Vikram Jadhao, Monica Olvera de la Cruz.Department of Material Science, Northwestern University, Evanston, IL 60208, United States*

Coarse-grained models of biological and synthetic materials such as cell membranes, colloids and oil-water emulsions often involve ions in medium characterized by different dielectric permittivities, separated by sharp interfaces. Knowing the distribution of ions near interfaces is crucial in understanding the physical properties of these systems. The knowledge of ionic structure of these systems is also exploited in several industrial applications such as double-layer supercapacitors for energy storage and electro-assisted solvent extraction of metal ions from wastewater. The presence of multiple dielectric interfaces often complicates computing the desired ionic distributions via simulations or theory. Here, we compute the ionic distributions in a system of electrolyte confined by two planar dielectric interfaces using Car-Parrinello molecular dynamics simulations and liquid state theory. We compute the density profiles for various electrolyte concentrations, stoichiometric ratios and dielectric contrasts. We also provide the explanations for the trends in these profiles and discuss their effects on the behavior of the confined charged fluid.

COLL 766

Electrostatic and hydrophobic interactions between chitosans and Langmuir monolayers mimicking cell membranes

***Osvaldo N. Oliveira**, chu@ifsc.usp.br.Sao Carlos Institute of Physics, University of Sao Paulo, Sao Carlos, SP 13560-970, Brazil*

In this presentation, an overview will be provided of the relative importance of electrostatic and hydrophobic interactions in cell membrane models represented by phospholipid Langmuir monolayers, for the specific case of chitosans. These polysaccharides have many biological applications that depend on the interaction with the cell membrane. In various pieces of work, our group found that the positively charged chitosan interacts more strongly with negatively charged phospholipids [1], including selectivity in removal of some proteins from the air/water interface [2]. However, the chitosan action is not based solely on electrostatic interactions, which was clearly demonstrated in a comparison with a synthetic cationic polyelectrolyte whose charged groups are the same as in chitosan, but affected Langmuir monolayers to a much lower extent [3]. Of particular importance in the effects on monolayers is the change in elasticity which is maximized for low molecular weight chitosans [4] owing to a combination of hydrophobic interactions and ease with which chitosan chains can penetrate the hydrophobic region of the phospholipid monolayers. Taken together, these results may serve for assisting the design of chitosan derivatives with tailored physicochemical properties leading to optimized bactericide and antimicrobial activity.

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COLL 767

Comparative study of protein-polymer interaction through the diffusion behavior between PEG and PolySBMA hydrogel

***Jiang Wu**, woody870402@hotmail.com, Shengfu Chen.Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou, Zhejiang 310027, China*

The knowledge of the interaction behavior of protein between the super-low fouling materials such as poly(ethylene glycol) (PEG)- and zwitterionic poly(sulfobetaine methacrylate) (pSBMA) has a great effect in their implications in drug-delivery systems such as controlled release protein-base drug delivery devices. In this paper, we investigate the protein-polymer interaction behavior through the diffusion behavior of the labeled protein in the PEG and pSBMA hydrogel. For the first time, this newly fluorescence spectroscopy method of labeled protein-hydrogel method was employed to study the diffusion of protein (bovine serum albumin (BSA) and lysozyme) in the different kinds of polymer hydrogel to study the polymer-protein interaction. It was observed that the movement of protein diffused inside and outside the PEG hydrogel is much smaller than in the pSBMA hydrogel, indicating the interaction between the protein-PEG is much stronger than protein-pSBMA and also the diffusion efficiency of lysozyme is much higher than BSA because of the smaller size and positive charge of lysozyme in PBS solution. Also the mesh-size and the physical property of the hydrogel were determined in this study.This work provides new insights into the fundamental understanding of protein-polymer interactions as well as the application of the hydrogel in the fundamental study.

COLL 768

Designing nonagglomerating polylactide particles with various interaction forces by covalent photografting

***Torbjörn Pettersson**, torbj@kth.se, Robertus Wahyu N. Nugroho, Karin Odelius, Anders Hoglund, Ann-Christine Albertsson.Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm, Stockholm SE-10044, Sweden*

One key aspect in many applications of polymer particles is to avoid agglomeration. We have used Polylactide (PLA) particles to investigate the effect of polymer grafting on the

interaction between PLA and PLA grafted particles. The PLA particles were surface grafted with hydrophilic poly(acrylic acid) (PAA) or poly(acrylamide) (PAAm), the force interactions were evaluated with colloidal probe atomic force microscopy (AFM). AFM imaging were also performed both dry and in salt solutions of different concentrations and changes in surface roughness of the grafted surfaces are addressed as conformational changes induced by altered Debye screening length in the different salt concentrations. For the particle interactions attractive interactions were observed in the hydrophobic PLA/PLA system as expected. However, in contrast to the PLA/PLA system long-range repulsive interactions were detected in the hydrophilic/hydrophilic systems and in the mixed hydrophobic/hydrophilic PLA/PLA-g-PAAm system. To evaluate the origin of these observed repulsive forces, the AFM force profiles were compared to DLVO and Alexander de Gennes models. The steric repulsion provided by the different hydrophilic polymers grafted to the particles was useful to hinder agglomeration of polymeric particles.

COLL 769

Selective CO_2 capture in an imine and benzothiazole based porous polymer

Venkata Neti*, pawanchem@gmail.com, Luis Echegoyen.Department of Chemistry, University of Texas at El Paso, El Paso, Texas 79902, United States*

A new imine and benzothiazole linked mesoporous polymer, IBTP (imine benzothiazole polymer), has been synthesized under solvothermal conditions. The IBTP showed high CO_2 capture (7.8 wt% at 273 K/1 bar) and very good selectivity for CO_2/CH_4 adsorption (6.3) at 1.0 bar and 273K, and exhibited BET surface area of 831 m^2 g^{-1} with high thermal stability (up to 400°C), thus showing good potential for CO_2 capture. The IBTP also exhibits a CH_4 capacity of 0.9 wt% at 273K, 1bar and an adsorption capacity of 0.78 wt% for H_2 at 77K/1bar. The chemical connectivity and composition of the IBTP were characterized by several methods such as BET surface area measurements, infrared spectroscopy, powder X-ray diffraction (PXRD), solid-state ^{13}C CP-MAS NMR, solid-state UV-Vis, and thermogravimetric and elemental analysis.

COLL 770

Designing polymeric nanoparticles for hydrocarbon detection in oil fields

Gedeng Ruan*[1], gedeng.ruan@rice.edu, Yinhong Cheng[2], Jason A. Mann[1], Alexander Rodríguez[1], Michael Wong[1,2], James M. Tour[1,2,3,4].Â (1) Department of Chemistry, Rice University, Houston, Texas 77005, United StatesÂ (2) Department of Chemical and Biomolecular Engineering, Rice University, Houston, TX 77005, United StatesÂ (3) The Richard E. Smalley Institute for Nanoscale Science and Technology, Rice University, Houston, TX 77005, United StatesÂ (4) The Department of Mechanical Engineering and Materials Science, Rice University, Houston, TX 77005, United States*

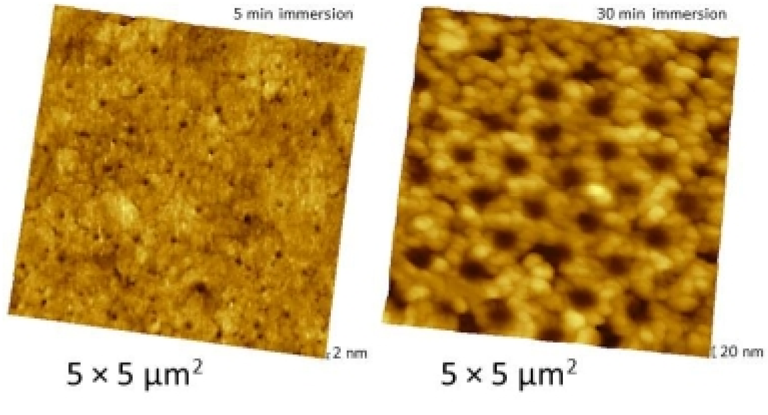
Detection and quantification of residual oil in reservoirs to determine viability for additional oil recovery remains a challenge. We have developed polymeric nanoparticles capable of controlled release of oil soluble small molecule indicators. These nanoparticles are synthesized by cross-linking micelles and are stable and soluble at the high temperatures and salinities present downhole and show low adsorption on relevant sandstone rocks. Here we demonstrate that upon contact with oil, these nanoparticles release indicators at a constant rate, allowing us to determine the amount and type (i.e. aromatic or aliphatic) of oil encountered. In addition, the rate of release can be tuned by varying the degree of cross-linking as well as the type of cross-linker used.

COLL 771

Polyphenylene nanostructures prepared on Au(111) using photoredox catalysis and immersion particle lithography

Susan D. Verberne-Sutton, *sverbe2@lsu.edu, Rashanique Quarles, Xianglin Zhai, Justin R Ragains, Jayne C. Garno.Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, United States*

Photoredox catalysis using visible light was combined with particle lithography to successfully prepare nanostructures of polyphenylene on Au(111). We are developing particle lithography methods to prepare nanopatterns with designed interfacial chemistry. Our strategy uses particle lithography with surface masks of silica mesospheres to protect small, discrete regions of the surface from reaction. Surfaces masked with mesospheres were immersed in solutions of *p*-nitrobenzenediazonium tetrafluoroborate and irradiated in the presence of the photoredox catalyst $Ru(bpy)_3(PF_6)_2$ to produce *p*-nitrophenyl radicals that graft onto gold. As the reaction proceeds, successive attachment of aryl radicals results in oligomerization to form polyphenylene structures. The resulting film thickness depends on the initial concentration of diazonium salt and the duration of immersion of substrates to generate multilayers ranging from 2 to 50 nm in thickness.



Photoredox catalysis with visible light provides mild, user-friendly conditions for generating carbon-centered radicals. Compared to chemisorbed attachment of *n*-alkylthiol self-assembled monolayers through S-Au bonds which readily oxidize, the films grafted with photoredox catalysis form robust carbon-gold linkages to the surface which are reported to be covalent. Experiments are in progress to evaluate the stability of polyphenylene films. Images acquired with atomic force microscopy disclose the long range order and periodicity of the polyphenylene nanostructures. Surface platforms of polyphenylene nanostructures provide a well-defined foundation for further chemical reactions to enable spatially selective binding of small molecules, nanoparticles or proteins.

COLL 772

What is the major structural aspect to determine the blood circulation time for polymeric micelles

Yusuke Sanada[1]*, y-sanada@kitakyu-u.ac.jp, Kouichi Shiraishi*[2]*, Masayuki Yokoyama*[2]*, Kazuo Sakurai*[1]*.Â (1) Department of Chemistry and Biochemistry, The University of Kitakyushu, 1-1 Hibikino, Wakamatsu-ku, Kitakyushu, Fukuoka 808-0135, JapanÂ (2) Research Center for Medical Science, Jikei University School of Medicine, 3-25-8 Nishi-shinbashi, Minato-ku, Tokyo 105-8461, Japan*

Polymeric micelles, consisting of hydrophilic shell and hydrophobic core, are used as a drug delivery system (DDS), because the core can encapsulate hydrophilic drugs and the shell can provide bio-compatibility, such as prolonged circulation time in blood. We prepared a series of block copolymers comprising poly(ethylene glycol) (PEG) block with the fixed chain length (M_w = 5200, and 12000) and partially benzyl esterified polyaspartic acid with changing its chain length and benzyl esterification ratio. By use of synchrotron small-angle X-ray scattering (SAXS) and field-flow fractionation combined with light scattering (FFF-LS), we determined the core and shell sizes, and the aggregation numbers. For the same sample, we measured the blood circulation time in mice. We found that the PEG chain density of the water/shell interface is the major structural factor to determine the prolonged circulation time in blood.

COLL 773

Flash nanoprecipitation as a route to produce polymer nanoparticles

Chris Sosa, Chuan Zhang, Vikram J. Pansare, Rui Liu, Robert K. Prud'homme, ***Rodney D. Priestley****, rpriestl@princeton.edu.Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey 08544, United States*

Aside from polymerization techniques, polymer nanoparticles can be generated through the displacement of a solvent with a nonsolvent, *i.e.*, nanoprecipitation. In this talk, we present a facile process termed Flash NanoPrecipitation (FNP) to generate pure polystyrene (PS) nanoparticles and heterogeneous polymer nanoparticles. As compared to PS nanoparticles synthesized by surfactant free emulsion polymerization, nanoparticles prepared by FNP show comparable size distributions when the diameter is less than 150 nm. Furthermore, we illustrate that the sizes of PS nanoparticles prepared by FNP can be fine-tuned by changing the polymer and/or electrolyte concentration. The stabilized nanoparticles contain only the radically polymerized polymer chains, which have sulfate anions at the chain termini and no additional external stabilizers. Calculations of the mechanism of particle formation and stabilization show that the size-dependent electrostatic repulsions between nanoparticles and nanoparticles versus single collapsed polymer chains control assembly and monodispersity. We conclude the talk discussing recent developments in heterogeneous nanoparticle formation using the FNP platform.

COLL 774

Novel patterned hydrogels using “breath figure” polymer structures as templates

Jaspreet S Arora*, jarora@tulane.edu, Thiruselvam Ponnusamy, Vijay T John.Department of Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana 70118, United States*

Breath Figures are a morphological class of polymers with highly ordered pore structures. They can be made in a simple one-step procedure in which a polymer solution in an organic solvent is evaporated under humid conditions. The cooling effect produced by the solvent evaporation causes water droplets to condense on the surface of the polymer solution. These arrays of droplets do not coalesce but further penetrate into the polymer solution subsequently condensing more water droplets around which a polymer film forms leading to pore formation upon eventual droplet removal. We hypothesized that breath figures could be used as a template to pattern hydrogels. Poly(2-hydroxyethyl methacrylate) (pHEMA) hydrogels were used for patterning as they are easy to fabricate and have long been accepted as safe materials.

We have synthesized breath figures by spin coating PLGA (poly lactic-co-glycolic acid)-PEG (Poly Ethylene Glycol) polymer films (pore size 2 microns) and used them as a reverse template to create thin films of pHEMA hydrogels with a highly ordered surface protruding pattern. High resolution scanning electron microscopy images show that the fidelity of the breath figure template is maintained in the inverse morphology of protrusions on the hydrogel. Magnetically responsive hydrogels were fabricated by incorporation of iron particles in these hydrogels to create structures with spatially selective field response characteristics. The versatility of the technique allows placement of biomolecules precisely on the tip of the ordered film protrusions. Applications of the breath figure structure and its inverse template as scaffolds for cell and tissue engineering and for controlled drug delivery will be presented.

COLL 775

Investigating pH dependent layer-by-layer assembly on nanoparticles: A universal tool for engineering surface properties for enhanced stability

Ashvin Nagaraja[1]*, ashvin.nagaraja@gmail.com, Yilhwan You*[2]*, Kennith Meissner*[1,2]*, Mike McShane*[1,2]*.Â (1) Department of Biomedical Engineering, Texas A&M University, United StatesÂ (2) Department of Material Science, Texas A&M University, College Station, Texas 77843, United States*

Colloids exist as a variety of different core and core/shell materials with a variety of surface coatings that require individual optimization and specific chemical modification for further use; thus, a generic surface modification approach is highly desired. Layer-by-Layer (LbL) modification is a powerful for the engineering of planar and colloidal surfaces based on the adsorption of alternating layers of charged polyelectrolytes. LbL on colloids below 10nm in size has been limited because of steric limitation of rigid polyelectrolytes wrapping highly curved nanoparticle surfaces which under improper conditions leads to irreversible aggregation. Using mercaptoundecanoic acid (MUA) modified gold nanoparticles (~5nm) as a template and the polyelectrolytes poly(allylamine hydrochloride) (PAH), poly(acrylic acid) (PAA), and poly(4-styrenesulfonic acid-co-maleic acid) (PSS-co-MA), the conditions for coating nanoparticles without aggregation were rapidly optimized by characterizing the plasmon peak location, zeta potential, and percent recovery after the addition of each polymer layer. We found a key feature of success in this process is understanding the charge density interplay between the polyelectrolytes and nanoparticles by separating the process into two distinct phases of adsorption and centrifugation, wherein solution pH is carefully chosen. The pH dependent charge density was characterized (Figure 1) for different nanomaterial templates and after coating with polyelectrolytes. This information is crucial for understanding pH dependent colloidal stability and for generalizing the process for other nanomaterials.

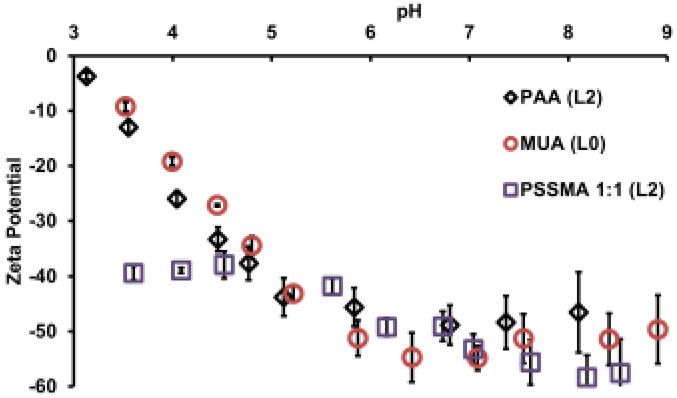


Figure 1: The pH dependent Zeta potential titrations for (A) MUA-AuNPs (red ○) (B) PAH/PAA (black ◊) (C) PAH/PSS-co-MA 1:1 (green Δ) (D) PAH/PSS-co-MA 3:1 (purple □)

COLL 776

Stochastic, quantum-based approach to molecular modeling of zeolites

***Adam Donato**, adonato@vt.edu, Rangarajan Pitchumani.Department of Mechanical Engineering, Virginia Tech, Blacksburg, Virginia 24060, United States*

Zeolites are the most widely used adsorbent for commercial separation, catalysis, and gas storage, and many performance properties of zeolites are driven by the nanoscale locations of aluminum atoms within the crystalline framework. For many zeolites, the location of aluminum atoms can only be described stochastically, and thus require a stochastic molecular modeling approach. Conventional molecular modeling methodologies for zeolites, which are based on a deterministic framework and experiment-based force fields, cannot accurately address the variable aluminum locations. In an effort to address this challenge, this paper presents a stochastic molecular modeling methodology, based on ab initio force fields, and validates the methodology by comparison with a diverse range of published experimental data.

COLL 777

Electronic structure studies of molecular-like plasmonic nanoparticles

***George C Schatz**, schatz@chem.northwestern.edu.Department of Chemistry, Northwestern University, Evanston, IL 60208, United States*

This talk describes the use of time dependent density functional theory to describe the optical properties of few nm silver and gold nanoparticles. Included will be studies of electronic spectra that transition from molecular to plasmonic properties, and studies of the influence of ligands on these spectra. Also of interest are the use of continuum electrodynamics to describe these spectra, the use of these particles to understand chemical effects in SERS, and studies of the time-evolution of excitation in these nanoparticles.

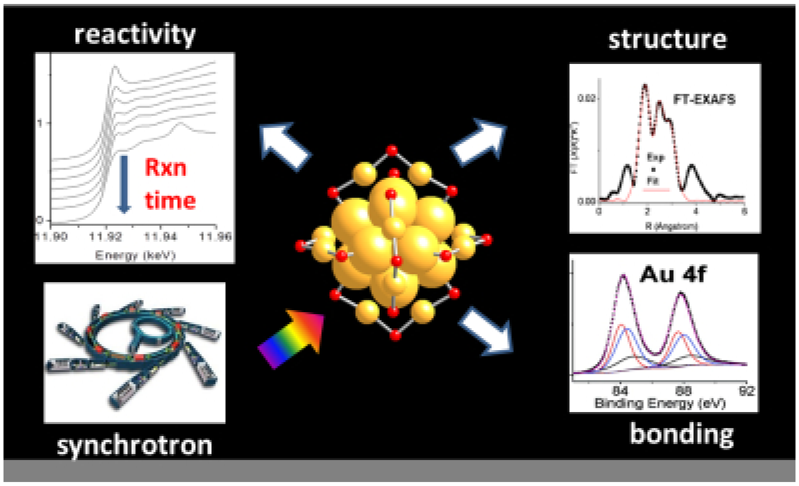
COLL 778

Structure and properties of metal nanoclusters from synchrotron X-ray spectroscopy

***Peng Zhang**, peng.zhang@dal.ca.Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H4R2, Canada*

Noble metal nanoclusters are unique materials given their unexpected structure-property relationships. To elucidate the properties of metal nanoclusters, synchrotron-based X-ray spectroscopy techniques can provide valuable information from an element-specific perspective. In particular, X-ray absorption spectroscopy (XAS) can provide structural details on the bond length and coordination number of various neighboring atoms while X-ray photoelectron spectroscopy (XPS) mainly offers electronic structure information. Together, XAS and XPS can reveal important findings on the properties of metal nanoclusters from both the protecting ligand and different metal atom environments. This work will demonstrate the usefulness of synchrotron-

based X-ray spectroscopy techniques, along with complimentary methods, towards an understanding of metal nanocluster structure and properties. X-ray meausrements in various experimental conditions such as liquid-phase, low temperature, and time-dependent are easily performed, which lends to the diversity of our X-ray studies on metal nanocluster systems.



COLL 779

Structure-property relationships in thiolate-stabilized nanoparticles studied by DFT

Christine M. Aikens, *cmaikens@ksu.edu.Department of Chemistry, Kansas State University, Manhattan, KS 66506, United States*

Density functional theory (DFT) investigations of monolayer-protected noble metal nanoparticles play an important role in determining the origins of the unique chemical and physical properties of these systems that lead to applications in photonics, sensing, catalysis, etc. Time-dependent density functional theory (TDDFT) calculations are employed to elucidate the excitation spectrum of $Au_{25}(SR)_{18}^-$ and related nanoparticles. Recent work on the luminescence of these systems will be presented. Silver atoms have recently been introduced experimentally into the $Au_{25}(SR)_{18}^-$ nanoparticle, and this work investigates the effect of silver doping by studying $Au_{25-n}Ag_n(SH)_{18}^-$ (n = 1, 2, 4, 6, 8, 10, 12)systems. Silver doping lowers the energy of ligand-based orbitals and facilitates the transitions between the superatom orbitals. Silver-doped systems show broader excitation spectra due to a breaking of the symmetry of the superatom orbitals.

COLL 780

WITHDRAWN

COLL 781

Structure determination of nanoparticles using stem diffraction

Miguel Jose Yacaman, *miguel.yacaman@utsa.edu.Physics & Astronomy, University Of Texas at san Antonio, San Antonio, Texas 78249, United States*

A very limiting factor of the use of electron diffraction for structure determination is the fact that spot intensity I_{hkl} is not simple equal to the / $F_{hkl/}{}^{2}$ ($F_{khl=}$ Structure Factor). This is the result of “dynamical effects” occurring in electron diffraction. One particular important case on modern nanotechnology is the determination of the structure of ligend covered metal nanoparticles with a well defined number of atoms. The structure determination by x-ray can only be achieved after crystallizing the sample. So far using this method, researchers have been able to determine the structure of Au_{36}, Au_{28} and Au_{102}. However the crystallization is not easy to achieve and a more general method is needed.

In a recent paper (1) we described a method using STEM-Diffraction, combined with image and diffraction patterns calculations and ab initio computations that allow the full determination of the thiol covered Au_{144}. This method sample involves single particle diffraction and is much broader in application.

In this talk we will present a discussion of this technique and show a number of applications. Including the extension to Au130 clusters.

(1) D. Bahena, N. Bhattarai, U. Santiago, A. Tlahuice, A. Ponce, S. B. H. Bach, B. Yoon, R. L. Whetten, U. Landman, and M. Jose Yacaman, STEM Electron Diffraction and High Resolution Images Used in the Full Determination of the Crystal Structure of $Au_{144}(SR)_{60}$ Cluster. *The Journal of Physical Chemistry Letters, 4* (**2013**), 975-981

COLL 782

Structure prediction for molecule-like metal clusters

De-en Jiang, *jiangd@ornl.gov.Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6201, United States*

Compositions of nanoclusters are nowadays readily available from mass spectrometry. However, to predict their structures remain a great challenge, due to the notoriously hard problem of global minimization. In this talk, I will present strategies we have tried in the past six years to predict structures for thiolated gold nanoclusters, binary clusters, and ligand-free metal clusters. Several examples of success will be shown together with further challenges and solutions.

COLL 783

Gold and silver dispersed by ligands: Electronic, optical, and bioconjugate properties

Hannu Hakkinen, *hannu.hakkinen@jyu.fi.Departments of Chemistry and Physics, University of Jyvaskyla, Jyvaskyla, Finland*

The electronic structure of gold and silver nanoclusters stabilized by organic ligands can be understood quite well from the simple superatom model that accounts for the delocalized sp-electrons in the metal core. Forming in most cases the frontier orbitals of the nanoparticle, these electrons are responsible for low-energy optical transitions and much of the chemistry. Recent progress in understanding the structure as well as physical and chemical properties of this class of superatoms is reviewed, and a novel application of using atomically precise, functionalized thiol-stabilized gold nanoclusters for site-specific conjugation to enteroviruses is discussed.

COLL 784

Key structure-property relationships in CO_2 capture by supported alkanolamines

Samuel A Tenney[1], *stenney@bnl.gov, Deyu Lu*[1], *Feng He*[2], *Niv Levy*[1], *Gayani Perera*[1], *David E Starr*[1], *Kathrin Muller*[1], *Hendrik Bluhm*[3], *Peter Sutter*[1]*.Â (1) Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973, United StatesÂ (2) Department of Materials Science and Engineering, Stony Brook University, Stony Brook, NY 11794, United StatesÂ (3) Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States*

We have studied titania-supported 3-amino-1-propanol (3AP) and monoethanolamine (MEA) as a potential CO_2 capture material using synchrotron-based ambient pressure X-ray photoelectron spectroscopy (AP-XPS), scanning tunneling microscopy (STM), and ab-initio calcualtions. STM and AP-XPS of C(1s) and N(1s) core levels demonstrate the successful adsorption of 3AP molecules along the Ti rows of the rutile TiO_2(110) surface, a process that self-terminates with the completion of the 1st layer at 300 K. Calculations give an optimized structure in which both terminal groups of 3AP form donor-acceptor bonds with 5-fold coordinated surface Ti atoms. In stark contrast to the facile CO_2 capture by 3AP/TiO_2(110), MEA on the same support is shown to be inactive towards CO_2 capture. Calculations show that the vanishing activity is due to strong binding of the amine functional group in MEA to surface Ti atoms of the support, which is facilitated by a close correspondence between the separation of reactive end groups of the molecule and the binding sites of the substrate. Exposing 3AP/TiO_2(110) to near-ambient pressures of CO_2 (up to 2 Torr) gives rise to additional C(1s) peaks, which are attributed to captured CO_2 and gas phase CO_2 respectively. The peak attributed to captured CO_2 is consistent with a carbamate (-NHCOO) species on the surface, but its lineshape is consistent with a minority contribution from a carbonate species as well. Our results illustrate the importance of structure-property relationships between the adsorbed amine capture species and the support, which govern amine-based solid-

supported CO_2 capture. This talk will discuss the broader implications of our studies on this model system towards solid-state CO_2 capture.

COLL 785

Atomic structure of the anatase TiO_2(001) surface

Yaobiao Xia[1], *Yaobiao_Xia@baylor.edu, Ke Zhu*[1], *Tiffany C. Kaspar*[2], *Blake Birmingham*[1], *Kenneth T. Park*[1], *Zhenrong Zhang*[1]*.Â (1) Department of Physics, Baylor University, Waco, Texas 76798, United StatesÂ (2) Fundamental and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, Washington 99352, United States*

Understand the structure of well-defined anatase TiO_2(001) surfaces is critical for deciphering site-specific thermal and photo-reaction mechanisms on anatase TiO_2. We have studied the atomic structure of anatase TiO_2(001) epitaxial thin films grown by oxygen plasma assisted molecular beam epitaxy. In situ reflection high-energy electron diffraction, X-ray photoelectron spectroscopy and ex situ high resolution scanning tunneling microscopy (STM) were used to characterize the anatase TiO_2(001). Both (1x4) and (4x1) reconstructed terraces are observed. High resolution STM images show that the atomic corrugation of the bright row on the surface is not uniform and highly bias voltage dependent. The bright row can be resolved as three types of features which are originated from two different building blocks. We propose a modified added molecule model for the anatase TiO_2(001) surface structure.

COLL 786

Interactions of phenol with ZnO(10-10) surface: UPS and EELS studies

Chad A Thibodeaux[1], *cthib19@tigers.lsu.edu, Matthew C Patterson*[2], *Mark F DiTusa*[2], *Orhan Kizilkaya*[3], *Richard L Kurtz*[2], *Phillip T Sprunger*[2], *Erwin D Poliakoff*[1]*.Â (1) Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, United StatesÂ (2) Department of Physics and Astronomy, Louisiana State University, Baton Rouge, LA 70803, United StatesÂ (3) Center for Advanced Microstructures and Devices, Baton Rouge, LA 70803, United States*

We report on the adsorption of phenol on ZnO(10-10) single crystal surface in an effort to understand how environmentally persistent free radicals (EPFRs) are formed. EPFRs persist for orders of magnitude longer than typical radicals and have significant public health consequences. Transition metal oxides are known to catalyze the formation of hazardous materials such as dioxins and furans, and a proposed model for this catalytic reaction involves the formation of EPFRs as an intermediate. To date, EPFR formation has been studied on powders. We are extending these studies to single crystal substrates because they are amenable to more unambiguous spectroscopic methods that cannot be applied to insulating powder samples. Ultraviolet photoelectron spectroscopy (UPS) and electron energy loss spectroscopy (EELS) were used to gain

insights on the electron transfer process during chemisorption. UPS data of ZnO(10-10) exposed to phenol at room temperature, 220°C, and 350°C dosing showed clear indications of chemisorption. The indication of charge transfer is observed by a shift of 0.6 eV to lower binding energy (i.e., band bending). Work function measurements also show a relative shift of 1 eV to higher kinetic energy. This indicates a charge transfer from the molecule to the metal oxide surface upon chemisorption. EELS spectra were also obtained for the same temperatures. EELS spectra show features assignable to phenol. The EELS spectra for physisorbed phenol at -177°C shows energy loss features at 6.5 eV, which is attributed to the $\pi\rightarrow\pi^*$ transition of phenol. These features shift to lower energy as the dosing temperature increases. Thus giving the indication that the HOMO-LUMO gap is decreasing as the dosing temperature increases. These data combined with the UPS spectra give a clear picture of the electronic structure changes that occur during chemisorption of phenol.

COLL 787

Molecular studies of thermal transformations of acetone on ZnO powder

Jia Gao, *gaoj@udel.edu, Andrew V. Teplyakov.Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716, United States*

Acetone adsorption and reactions on ZnO powder were investigated by Fourier-transform infrared spectroscopy (FTIR) complemented by density functional theory (DFT) calculations. This approach took advantage of the previous studies of this system by X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) and explored the nature of surface species formed during thermal transformations directly. Consistent with the previously proposed reaction mechanisms, the first step in acetone chemistry on ZnO is the dissociation accompanied by a formation of an enolate, which is predicted by DFT calculations to happen quite easily on ZnO (10$\underline{1}$0) surface, the most common surface in powder sample. The reaction barrier for this process is predicted to be only 29.5 kJ/mol (DFT at the B3LYP/Lanl2dz level of theory). The reaction of acetone at room temperature along with the thermal treatment was repeated multiple times and monitored by FTIR to get insight into the chemistry of this system at realistic catalytic conditions. Thermal transformation leads to the formation of several surface species including mesityl oxide intermediate, identified based on the comparison of the experimentally recorded vibrational spectrum with computational prediction. This reaction pathway may be very important in designing catalytic processes that produce commodity chemicals with multiple functionalities in one step.

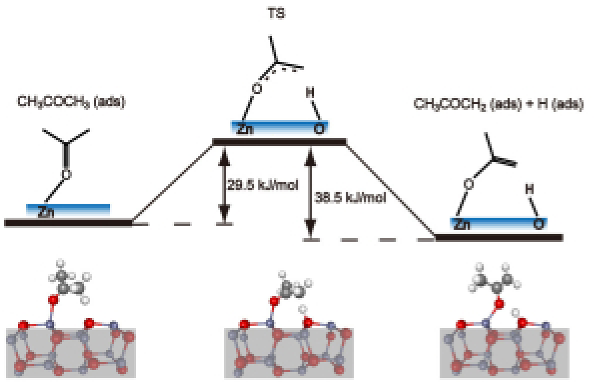


Figure1: Enolization reaction diagram of acetone adsorbed on ZnO(10$\bar{1}$0) surface

COLL 788

Structure and properties of well-ordered Mn-doped ceria thin films

Jing Zhou, *jzhou2@uwyo.edu, Elfrida Ginting, Erik W. Peterson.Department of Chemistry, University of Wyoming, Laramie, WY 82071, United States*

Ceria has been widely studied as an oxidation-reduction catalyst due to its unique redox properties and oxygen storage capacity. To improve the thermal stability and redox properties of ceria, suitable metal elements can be incorporated into it and form mixed metal dopant-Ce-O interfaces or mixed solid ceria-based oxides. We present our study on the growth of Mn-doped ceria thin films and the understanding of their structures using X-ray photoelectron spectroscopy, low-energy electron diffraction, as well as scanning tunneling microscopy. Mn-doped ceria can be prepared by physical vapor evaporation of Mn onto well-ordered reducible $CeO_2(111)$ thin films under ultrahigh vacuum conditions. Upon deposition of submonolayer coverage of Mn at 300 K, Mn is oxidized to Mn^{2+} at the cost of Ce^{4+} reduction which is a thermodynamically favorable process. The degree of Ce^{4+} reduction correlates with the coverage of Mn. With the increase of Mn coverage above one monolayer, metallic Mn was observed. Deposition of Mn on ceria maintains the ceria lattice and produces small clusters with an average height of 0.2 nm and a diameter of 1.8 nm. Nucleation of Mn at the O hollow sites on $CeO_2(111)$ is suggested. Upon heating, the clusters coalesce to form triangular domains. In the talk, the structure of MnO on ceria will be compared to that grown on Ru(0001). The interfacial structure of Mn-doped CeO_2 will be further compared to that of Ce-Mn-O mixed solid solutions. The research is sponsored by the National Science Foundation (Award Number: CHE1151846).

COLL 789

Density-functional studies of dimethyl peroxide adsorption and dissociation on $MoO_3(100)$ and $H_{0.33}MoO_3(100)$ surfaces

Ahmad R. Soufiani[1], *razzagh@okstate.edu, Evgueni B. Kadossov*[2], *Allen W. Apblett*[1], *Nicholas F. Materer*[1]*.Â (1) Chemistry, Oklahoma State University, Stillwater, OK 74078, United StatesÂ (2) XploSafe LLC, Stillwater, OK 74074, United States*

Adsorption and dissociation of dimethyl peroxide on the (100) face of molybdenum trioxide (MoO_3) and the bronze ($H_{0.33}MoO_3$) were studied by means of Density-Functional computations. Dimethyl peroxide adsorbs molecularly on the (100) face of both the oxide and bronze and dissociation can occur through either O-O or C-O bond cleavage. No dissociation products resulting from O-O bond were found on the oxide surface. A stable structure was found for products formed by C-O bond cleavage on the oxide. However, the adsorption energy is positive and is not energetically favorable with respect to desorption. The dissociation of dimethyl peroxide on the bronze surface is possible due to the presence of electron density on the bronze surface. Two stable products were identified for dissociations via O-O and C-O bonds cleavage. These products from O-O bond cleavage can interconvert through stable intermediates. Although C-O bond cleavage dissociation products are stable, the transition states between the molecularly adsorbed species and these structures are larger than the desorption energy. Thus, the decomposition of dimethyl peroxide occurs only on the bronze surface through an O-O bond cleavage pathway.

COLL 790

Support morphology-dependent metal-support interaction, structure, and catalytic performance of supported catalysts

Weixin Huang, *huangwx@ustc.edu.cn.Department of Chemical Physics, University of Science and Technology of China, Hefei, China*

Metal-support interaction plays a decisive role in the structure and catalytic performance of supported catalysts and the structure of oxide support is of great influence. Employing well-defined CeO_2 nanocrystals as supports, we have comprehensively studied the morphology effect of CeO_2 on the metal-CeO_2 interaction, structure and catalytic performance in Ag/CeO_2, Pt/CeO_2 and Cu/CeO_2 catalysts. CeO_2 nanocrystals with different morphologies exhibit different structures and concentrations of oxygen vacancies and thus different metal-CeO_2 interaction. Metal-CeO_2 interaction not only decides the structure of supported metal but also changes the structure and concentration of oxygen vacancy in CeO_2 that cooperatively determin the catalytic performance of resulted catalyst. Metal nanoparticles-CeO_2 ensemble is more active than metal cation-CeO_2 ensemble in catalyzing CO oxidation whereas metal cation-CeO_2 ensemble is more active than metal-CeO_2 ensemble in catalyzing H2-assisted CO oxidation.

COLL 791

Hyaluronic acid-modified multiwalled carbon nanotubes as drug delivery carrier for targeted cancer therapy

***Xueyan Cao**, caoxy_116@dhu.edu.cn, Lei Tao, Shihui Wen, Wenxiu Hou, Xiangyang Shi.Department of Bioengineering, College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai, Shanghai 201620, China*

Development of drug carrier for tumor-targeted therapy with high efficiency and specificity is of paramount importance and has been one of the major topics in current nanomedicine. Here we report a general approach to using multifunctional multi-walled carbon nanotubes-based platform to encapsulate an anticancer drug doxorubicin (DOX) for targeted cancer therapy. In this approach, multiwalled carbon nanotubes modified with polyethyleneimine (PEI), fluorescein isothiocyanate (FITC) and hyaluronic acid (HA) (MWCNT/PEI-FI-HA) were used as a new anticancer drug carrier for target delivery to cancer cell overexpressing CD44 receptors. We show that the formed MWCNT/PEI-FI-HA/DOX complexes with 72% drug loading percentage are water soluble and stable. *In vitro* release studies show that the drug release rate under acidic conditions (pH 5.8, tumor cell environment) is significantly higher than that under physiological condition (pH 7.4). Cell viability assay in conjunction with cell morphology observation demonstrates that the carrier material has good biocompatibility, and the MWCNT/PEI-FI-HA/DOX complexes can specifically target to cancer cell overexpressing CD44 receptors and exert inhibition effect to the cancer cells. The developed hyaluronic acid-modified multiwalled carbon nanotubes hold great promise to be used as an efficient anticancer drug carrier for tumor-targeted chemotherapy.

COLL 792

X-ray scatter imaging of hepatocellular carcinoma using nanoparticle contrast agents

***Danielle Rand**[1], danielle_rand@brown.edu, Zoltan Derdak[2,3], Jack R Wands[2,3], Christoph Rose-Petruck[1].Â (1) Department of Chemistry, Brown University, Providence, RI 02912, United StatesÂ (2) Warren Alpert Medical School, Brown University, Providence, RI 02903, United StatesÂ (3) Rhode Island Hospital, Providence, RI 02903, United States*

Hepatocellular Carcinoma (HCC) is one of the most common malignant tumors worldwide and is almost uniformly fatal. Current methods of detection include ultrasound examination and imaging by CT scan or MRI; however, these techniques are problematic in terms of sensitivity and specificity, and the detection of early tumors has proven elusive. Innovations that improve sensitivity and specificity while also reducing cost are therefore of paramount importance in the diagnostic imaging of HCC. An example of such an innovation is Spatial Frequency Heterodyne Imaging (SFHI), a novel x-ray scatter imaging technique that uses nanoparticles as contrast agents. We present data on the development of this new imaging technique and show that a variety of different types of nanoparticles including gold nanoparticles (AuNPs) and superparamagnetic iron oxide nanoparticles (SPIONs) are suitable for use as SFHI contrast agents. We have determined that SFHI can differentiate between AuNP-labeled and unlabeled cancerous tissue both *in vitro* and *in vivo.* We have also

compared SFHI to both traditional absorption-based x-ray imaging and MRI using SPIONs. Our results indicate that the sensitivity of SFHI is an order of magnitude greater than that of absorption-based x-ray imaging, while it approaches that of MRI when used for biomedical imaging applications. The high contrast provided by SPIONs in SFHI suggests that SFHI could be combined with MRI to provide a dual-modality imaging technique using a single contrast agent. Overall, our results indicate that the novel approach described here could enable the *in vivo* detection of tumors as small as a few millimeters in size. The modality is also applicable to other diseases and can be combined with drug delivery or tumor ablation strategies. Studies currently underway involve targeted imaging of HCC tumors in a mouse model using nanoparticle contrast agents conjugated to HCC-specific antibodies.

COLL 793

Photosensitizer-modified phage bionanowires for selective cancer cell killing

***Chuanbin Mao**, cbmao@ou.edu.Department of Chemistry & Biochemistry, University of Oklahoma, Norman, OK 73019, United States*

Fd-tet filamentous phage is a biological nanowire (~900 nm long and 7 nm wide) non-toxic to human beings and made up of ordered protein shell encasing ssDNA core. Its major protein shell (side wall) is composed of ~3900 copies of a major coat protein (called pVIII) to which cancer targeting peptides can be genetically fused. Here, we describe a novel nanocomposite wire, which is formed by chemically conjugating the phage bionanowire and photosensitizer, and employ the resultant complex bionanowire for selective cancer cell killing through the generation of cytotoxic singlet oxygen via a mechanism of photodynamic therapy (PDT). PDT is an established noninvasive medical treatment procedure which integrates oxygen, photosensitizer and light to generate singlet oxygen for tumor destruction. We first conjugated a porphyrin, pyropheophorbid-a (PPa), to the surface of SKBR-3 breast cancer cell-specific fd-tet phage to form a novel bionanowire called PPa-phage complex. We studied the morphological and spectroscopic changes of the complex as well as the production of singlet oxygen, and demonstrated its use in *in vitro* targeted cancer cell destruction.We believe that the formation of photosensitizer-phage nanowires is a versatile approach to nanotherapeutics since any filamentous bacteriophage, specific to a given organ or tissue, can be first selected by using the phage display technique, and then conjugated with a photosensitizer of interest to form a novel target-specific phage-photosensitizer nanowire. This work opens up new avenues for the development of next generation target specific photosensitizers that can be used for clinical applications in PDT.

COLL 794

Iron nanoparticle-based drug delivery system for effective cancer treatments

***Harshi C Manawadu**[1], harshi@ksu.edu, Hongwang Wang[1], Tej B Shrestha[2], Deryl L Troyer[2], Stefan H Bossmann[1].Â (1) Department of Chemistry, Kansas State University,* *Manhattan, Kansas 66502, United StatesÂ (2) College of Veterinary Medicine, Kansas State University, Manhattan, Kansas 66506, United States*

During tumor propagation, tumor-surrounding areas are highly vascularized in order to provide sufficient nutrients and oxygen supply for the rapid growth of tumor cells. Therefore, rapid formation of tumor blood vessels through angiogenesis causes deficient blood vessels with leaky irregular endothelial cells, which are absent in healthy tissues. As a result, the tumor vasculature becomes more permeable for macromolecular transportation through the gaps formed between the endothelial cells.

With the advancement of nanotechnology, novel drug delivery systems based on nanomaterials as vehicles have been introduced, having the potential of delivering conventional chemotherapeutic agents selectively to the targeted cancer sites following macromolecular transportation through tumor blood vessels. In this particular research, a Fe/Fe_3O_4 based nanoparticle system is constructed by tethering a chemotherapeutic prodrug of doxorubicin and tumor-homing/uptake peptide sequences to dopamine units that are located at the Fe_3O_4-interface of the nanoparticle. Once the nanoparticles are selectively introduced to the targeted areas, the prodrug is activated due to the acidic environments in the interstitium and (after uptake) the endosome, which causes corrosion of the nanoparticle and release of the drugs and peptide sequences from the nanoparticle's surface. The optimization of the drug delivery system and its therapeutic effects was carried out using a statistical analysis method known as response surface methodology.

COLL 795

Modification of hyaluronic acid onto hydrothermally synthesized iron oxide nanoparticles for targeted tumor MR imaging

*Jingchao Li[1], Yao He[2], Wenjie Sun[1], Mingwu Shen[1], Jindong Xia[2], **Xiangyang Shi**[1], xshi@dhu.edu.cn.Â (1) Department of Bioengineering, College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai, Shanghai 201620, ChinaÂ (2) Department of Radiology, Shanghai Songjiang District Central Hospital, Shanghai, Shanghai 201600, China*

We report a polyethyleneimine (PEI)-mediated approach to synthesizing hyaluronic acid (HA)-targeted magnetic iron oxide nanoparticles (Fe_3O_4 NPs) for *in vivo* targeted tumor magnetic resonance (MR) imaging applications. In this work, Fe_3O_4 NPs stabilized by PEI were first synthesized via a one-pot hydrothermal method. The formed PEI-stabilized Fe_3O_4 NPs were then modified with fluorescein isothiocyanate (FI) and HA with two different molecular weights to obtain two different Fe_3O_4 NPs (Fe_3O_4-PEI-FI-HA_{6K} and Fe_3O_4-PEI-FI-HA_{31K} NPs) with a size of 15-16 nm. The formed HA-modified multifunctional Fe_3O_4 NPs were characterized via different techniques. We show that the multifunctional Fe_3O_4 NPs are water-dispersible and colloidal stable in different aqueous media. *In vitro* cell viability and hemolysis studies reveal that the particles are quite cytocompatible and hemocompatible in the given concentration range.

Furthermore, confocal microscopy and flow cytometry data demonstrate that HA-targeted Fe_3O_4 NPs are able to be uptaken specifically by cancer cells overexpressing CD44 receptors, and be used as efficient probes for targeted MR imaging of cancer cells *in vitro* and xenografted tumor models *in vivo*. With the tunable amine-based conjugation chemistry, the PEI-stabilized Fe_3O_4 NPs may be functionalized with other biological ligands or drugs for diagnosis and therapy of different biological systems.

COLL 796

Environmentally responsive theranostic carrier systems for oral delivery of chemotherapeutic agents

Mary Caldorera-Moore[1]*, mcmoore@latech.edu, Nicholas A Peppas*[2]*.Â (1) Department of Biomedical Engineering, Louisiana Tech University, Ruston, LA 71272, United StatesÂ (2) Department of Chemical Engineering, Biomedical Engineering and Pharmaceutics, University of Texas at Austin, Austin, TX 78712, United States*

The emergence of nanotechnology has spawned new opportunities for novel drug delivery vehicles capable of simultaneous detection, monitoring, and localized treatment of specific disease sites. Recent developments in polymeric drug delivery systems allow for targeted delivery of a wide variety of traditional hydrophobic chemotherapeutic drugs, proteins, and diagnostic gold nanoparticles. In the Peppas group we have developed a new class of micro- and nanocarriers composed of pH- or temperature-responsive grafted hydrogel networks that can be tailored to deliver drugs to a targeted site, efficiently. We have demonstrated the ability to load a variety of chemotherapeutic agents and/or gold nanoparticles, into the synthesized particles for the development of theranostic carrier systems. Using these particles, the biophysical mechanisms controlling biodistribution of the hydrophobic chemotherapeutic drug doxorubicin, protein based chemotherapeutic agent Interferon alpha, and imaging modalities like gold nanoparticles, are under investigation for the treatment of colon and pancreatic cancer.

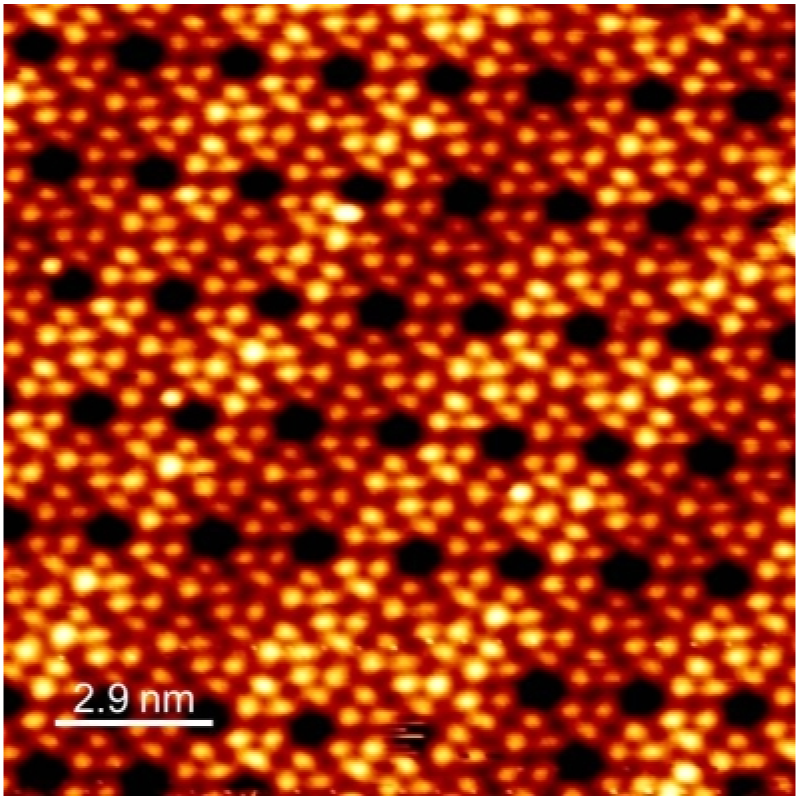
COLL 797

Formation of bioinorganic complexes by the corrosive adsorption of (*S*)-proline on Ni/Au(111)

Riho T Seljamae-Green[1]*, rg239@st-andrews.ac.uk, Grant J Simpson*[1]*, Federico Grillo*[1]*, John Greenwood*[1]*, Stephen M Francis*[1]*, Renald Schaub*[1]*, Paolo Lacovig*[2]*, Christopher J Baddeley*[1]*.Â (1) EaStCHEM School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, United KingdomÂ (2) Elettra - Sincrotrone Trieste S.C.p.A, Trieste, Italy*

The etching of nickel by chiral carboxylic or amino acids is an important consideration in the preparation of chirally modified Ni catalysts for enantioselective hydrogenation reactions[1]. We have investigated the adsorption of (*S*)-proline onto 2D Ni nanoclusters

grown at the elbows of the herringbone reconstruction of the Au{111} surface[2]. X-ray photoelectron spectroscopy (XPS) reveals that the adsorption of proline causes oxidation of the Ni particles. Scanning tunnelling microscopy (STM) shows that the Ni particles decrease in size and ordered molecular arrays are observed to form. The nature of the ordered structures is dependent on thermal treatment, initial Ni coverage and (*S*)-proline exposure. The fundamental building block of the majority phase observed is a trimeric unit which we conclude consists of a nickel (III) prolinate unit via analysis of a combination of XPS and high resolution electron energy loss spectroscopy (HREELS). Several of the phases exhibited well defined nano-sized pores which have potential for use as docking sites for prochiral reagents which may have important implications in the design of novel enantioselective heterogeneous catalysts.



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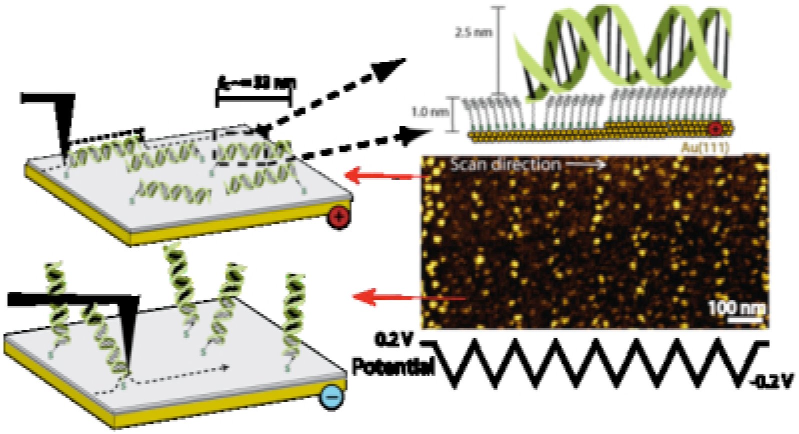
COLL 798

Imaging DNA on dynamic self-assembled monolayers: Single molecule insight into DNA biosensors

***Tao Ye**, tao.ye@ucmerced.edu.Chemistry and Chemical Biology, University of California, Merced, Merced, CA 95343, United States*

The binding affinity, selectivity and kinetics of surface-based DNA sensors are profoundly impacted by the nanoscale arrangement of immobilized DNA molecules (probes) on the surface. Although atomic force microscopy (AFM) has the potential to visualize individual biomolecules on biosensor surfaces *in situ*and with nanometer resolution, successes in this area remain limited because the high mobility of probe and target molecules on sensor surfaces precludes high resolution imaging.

By exploiting the transient electrostatic pinning enabled by an applied electrochemical potential, we have enabled AFM to visualize the conformational changes of single DNA molecules tethered to self-assembled monolayers on gold. Using potentiodynamic imaging and analysis, we were also able to probe the kinetics of switching that is too fast for frame-by-frame imaging. Our study has revealed a high sensitivity to the nanoscale chemical environment: the electrostatic interaction of the DNA with the surface is dominated by defects in the passivating self-assembled monolayer (SAM) and that the SAM, often regarded as a static structure, is not only high mobile but is actively remodeled by the DNA at different applied potentials. Moreover, by directly visualizing single hybridization events, we have provided nanoscale and single molecule level evidence that the hybridization efficiency is impacted by the presence of neighboring probe molecules. Such molecular level insights into hybridization on surfaces may inform new strategies to engineer more robust and reliable DNA sensors.



COLL 799

Interactions and structure formation at the solid - liquid interface

Florian Buchner[1], Benedikt Uhl[1,2], Katrin Tonigold[1], Axel Groß[1,3], ***R. Jürgen Behm***[1,2]*, juergen.behm@uni-ulm.de.Â (1) Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage, Ulm, GermanyÂ (2) Institute of Surface Chemistry and Catalysis, Ulm University, Ulm, GermanyÂ (3) Institute of Theoretical Chemistry, Ulm University, Ulm, Germany*

Ionic liquids (ILs) are promising electrolytes in Li-ion batteries, and the behavior of the ILs at the electrode | electrolyte interface is crucial for the performance. A detailed understanding of the interaction of relevant ILs with solid surfaces / electrodes, on a molecular scale, is, however, still missing, and studies on this topic are at their very beginning. As a first step, we investigated the adsorption behavior and structure formation in monolayer IL films deposited on Au, Ag and Cu single crystal surfaces in a combined experimental and theoretical approach, employing scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) as well as calculations based on density functional theory (DFT). Measurements were performed under UHV conditions and at temperatures between 100 K and 298 K, using 1-Butyl-1-methyl-pyrrolidinium-bis(trifluoro-methyl-sulfonyl)imide ($[BMP]^+[TFSA]^-$) and related ILs as model substance.

High resolution STM measurements resolve ordered structures at low temperatures, which, however, transform into a disordered 2D liquid phase at temperatures well below room temperature. These structural characteristics point to the existence of distinct, but nevertheless relatively weak intermolecular interactions. Substrate effects are indicated by subtle differences in the resulting structures and their stability. Comparison with theory allows to identify and distinguish between adsorbed cations and anions and provides information on the nature of the substrate – adsorbate and adsorbate – adsorbate interactions and on the extent of charge transfer upon adsorption. Overall, these results provide a detailed picture on the interaction of these ILs with noble metal surfaces, as a first stop towards a more general understanding.

COLL 800

Interrogating the thermodynamics of self-assembly by flow microcalorimetry: Functional group effects

Adam J Matzger, *matzger@umich.edu.Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, United States*

A thorough understanding of the thermodynamics of self-assembly is a prerequisite for understanding and ultimately controlling self-assembly behavior. The thermodynamics of two-dimensional self-assembly at the liquid/solid interface, as in physisorbed monolayers, has heretofore been rather limited in system scope. Although molecular mechanics can be used to investigate assembly thermodynamics, a global experimental approach to study self-assembly that considers all contributions to self-assembly simultaneously (analyte-analyte, analyte-substrate, analyte-solvent, and solvent-substrate) is still desirable. Using flow microcalorimetry, we have investigated the enthalpy of adsorption from solution for a series of aliphatic adsorbates in which the terminal functional groups are varied. Using information about the structure of each monolayer in the series from the STM literature, the lattice energy for the two-dimensional crystal of each analyte was also calculated. Comparing the experimental and calculated values for this series of adsorbates indicates that it is not only the strength of available intermolecular interactions (captured by the lattice energy data) but also behavior in solution and the range and directionality of strong intermolecular interactions which influence the degree to which lattice energy approximates the enthalpy of adsorption. A detailed understanding of such exceptions is critical to a complete understanding of the thermodynamics of self-assembly at the liquid/solid interface.

COLL 801

Structural analysis of peptide assemblies by using scanning tunneling microscopy

***Chen Wang**, wangch@nanoctr.cn.National Center for Nanoscience and Technology, Beijing, China*

We present the structural analysis of single peptide molecules, folding structures of the amyloid peptides, interaction modes between peptide and dye or drug molecules, and modulation of peptide assemblies by small molecules. By using scanning tunneling microscopy, molecularly resolved core regions of the amyloid peptide assembly structures are identified. The effects of mutation and phosphorylation on the folding structures and core regions were also revealed in the assembly characteristics. It is illustrated that chaperon-like molecular modulators can be introduced for effectively modulating the assembly behavior of vital analogues of amyloid peptides relating to Alzheimer's disease (AD), diabetes, etc. In addition, the introduction of chaperon-like modulators could affect the morphology of beta-amyloid peptide aggregates and cytotoxicity. These results on peptide adsorption and assembly will benefit the understanding the mechanisms for protein-protein interactions, protein-drug interactions and the pathogenesis of amyloidoses, and provide a potential approach toward the modulation of disease-related fibrillation processes

COLL 802

Advances in the characterization of mixed self-assembled monolayers on curved surfaces

***Francesco Stellacci**, francesco.stellacci@epfl.ch.Institute of Materials, Ecole Polytechnique FÃ©dÃ©rale de Lausanne, Lausanne, Switzerland*

In this talk I will highlight recent progresses in the characterization of gold nanoparticles coated with a binary mixture of dis-like molecules. These advancements will include true high resolution images as well as diffraction and spectroscopic analysis.

Particles that show stripe-like domains as well as particles with Janus arrangements will be presented. These particles have shown unique properties ranging from non-monotonic dependence on composition of the solubility and the interfacial energy, as well as unique molecular recognition properties. A subclass of these particles has shown the ability to cross cell membranes in an energy independent way. In this talk a mechanism for this process will be proposed together with a set of novel properties.

COLL 803

Polystyrene and Janus particle monolayers at the air/water interface

*Jessica Lenis[1,2], Kathleen Cao[2], Raymond S. Tu[1], Ka Yee C. Lee[2], **Ilona Kretzschmar**[1], kretzschmar@ccny.cuny.edu.Â (1) Chemical Engineering, The City College of New York, New York, NY 10031, United StatesÂ (2) Department of Chemistry, Gordon Center for Integrative Science (GCIS), University of Chicago, Chicago, IL 60637, United States*

Gold nanoparticle tri-layers and lung surfactant model monolayers have been shown to undergo two stages upon compression at an air/liquid interface. In the first stage, their elastic energy is delocalized in wrinkles. In the second stage, the elastic energy is localized into folds. This two stage behavior is in good agreement with predictions from linear and non-linear elastic theory when applied to an inextensible thin film located at a fluid/fluid interface.

In an attempt to extend this concept to micrometer sized particles, we have studied the behavior of negatively charged polystyrene (PS) particle monolayers floating on a NaCl/glucose density-matched aqueous mixture. Upon compression of the PS monolayer with a Langmuir trough, aggregates are formed first followed by formation of a close-packed monolayer. Just below the point of collapse, the system begins to buckle, represented by the formation of wrinkles. Beyond the collapse point, folds are observed showing behavior similar to the gold nanoparticle trilayers and the lung surfactant model monolayers.

Addition of anisotropic interactions to the system in form of a Janus-cap modification on the PS particles, i.e., a hemisphere of the particle is covered with a 5/20 nm Ti/Au film, leads to a distinctly different behavior during compression. Rather than formation of wrinkles and folds, black patches are observed as the monolayer is compressed. Analysis of the Langmuir trough data reveals a subduction mechanism.

COLL 804

Self-assembly of monolayers of aromatic carboxylic acids on metals at the liquid-solid interface: Comparison of Cu and Ag

***Hannah Aitchison**[1], ha74@st-andrews.ac.uk, Izabela Cebula[2], Hao Lu[3], Michael Zharnikov[3], Manfred Buck[1].Â (1) Department of Chemistry, University of St Andrews, St*

Andrews, Fife KY16 9ST, United KingdomÂ (2) Department of Experimental Physics, University of Wroclaw, Wroclaw, PolandÂ (3) Department of Applied Physical Chemistry, UniversitÃ¤t Heidelberg, Heidelberg, Germany

Aromatic carboxylic acids are very widely used components of supramolecular self-assemblies, in particular of 3D metal-organic frameworks (MOFs) where they constitute versatile organic linkers. Similarly, they have been investigated on surfaces as building blocks for 2D supramolecular networks where the plane of the aromatic system is orientated parallel to the surface.

In contrast, studies on the assembly of such molecules on surfaces in a non-flat adsorption geometry are scarce even though this is of interest for accessing the third dimension as in the layer-by-layer growth of thin film MOFs (SURMOFs) where carboxylic acid moieties provide convenient coordination points for metals.

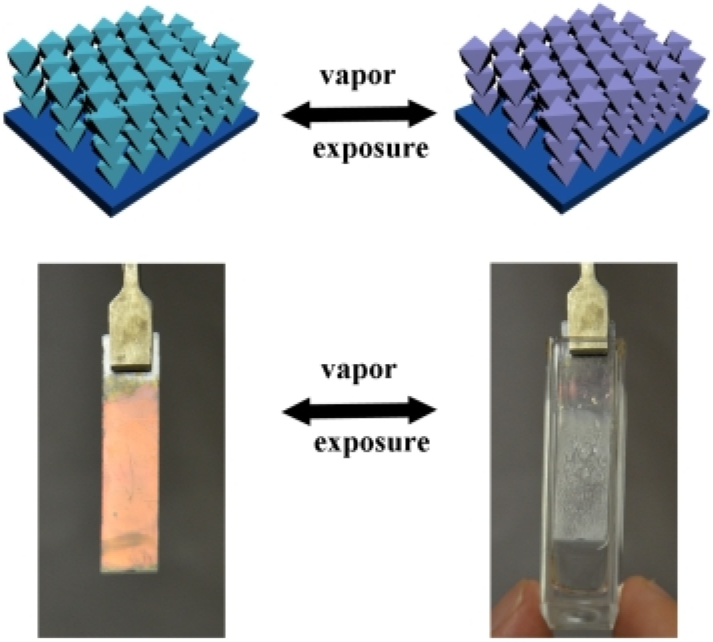
We present our microscopic and spectroscopic studies of upright aromatic carboxylic acid layers on Cu and Ag surfaces. Au(111)/mica substrates modified by under-potential deposited (UPD) layers of Cu and Ag were used as the basis to study the influence of substrate on the formation of self-assembled monolayers (SAMs) of aromatic carboxylic acid molecules. The SAMs were analysed by STM under ambient conditions and by synchrotron based X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. On the Cu surface, STM revealed highly commensurate crystalline structures, with molecules forming very well defined rows aligned along the high symmetry axes of the underlying metal. In contrast, on Ag the molecules were seen to form incommensurate row structures with significant waves and kinks. XPS and NEXAFS reveal pronouncedly different binding and coordination geometries on Cu and Ag modified surfaces. The substrate dependent film structures arise from a change in the balance of molecule-substrate and intermolecular interactions due to the differing coordination strength between the carboxylic acid groups and the Cu and Ag surfaces.

COLL 805

Synthesis and self-assembly of monodispersed metal-organic framework nanoparticles for dynamic sensing

***Chenlong Cui**, cuic0002@e.ntu.edu.sg, Fengwei Huo, Weina Zhang.School of Materials Science and Engineering, Nanyang Technological University, Singapore, Singapore 639798, Singapore*

3D metal-organic framework (MOF) nanoparticles film was obtained via Langmuir-Blodgett technique and used as a photonic sensor for chemical vapor detection. The MOF nanoparticles film exhibits both acute responses towards various chemical vapors and high controllability in terms of peak intensity and position. The method represents a general, facile and flexible strategy for the fabrication of MOFs-based photonic sensors.

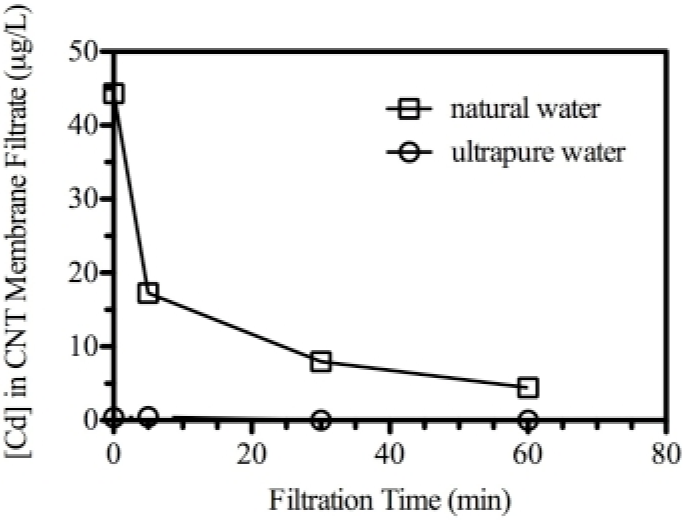


COLL 806

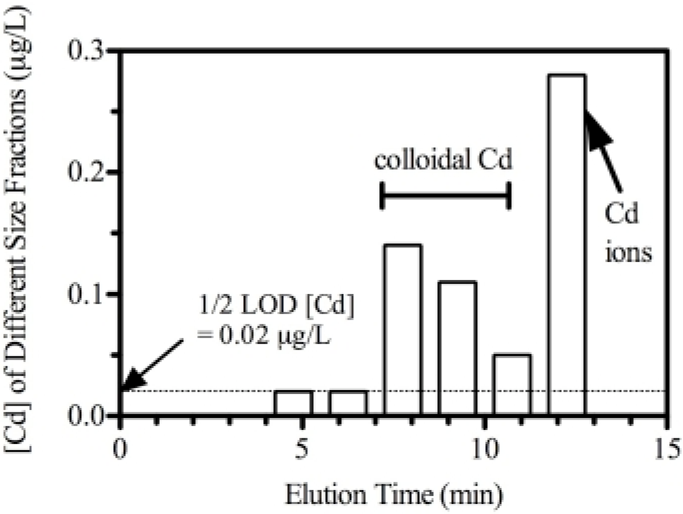
Effects of natural organic matter on cadmium removal by carbon nanotube layered membranes

Haiou Huang[1,2], *huanghaiou@bnu.edu.cn, Gaurav Ajmani*[2], *Howard Fairbrother*[3], *Gallagher Miranda*[3]*.Â (1) Beijing Normal University, School of Environment, HaiDian District, Beijing 100875, ChinaÂ (2) Environmental Health Sciences, Johns Hopkins Bloomberg School of Public Health, Baltimore, Maryland 21205, United StatesÂ (3) Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218, United States*

Carbon nanotube (CNT) layered membrane with customizable treatment capacities has been successfully prepared for enhanced removal of waterborne contaminants. This study investigated the removal of cadmium from a simple solution and a natural surface water with high natural organic matter (NOM) content. Complete removal of Cd was obtained during the filtration of $Cd(NO_3)_2$dissolved into ultrapure water. In the presence of NOM, Cd removal decreased to 55% at the onset of the filtration and increased to 95% as the filtration proceeded.



Size fractionation of NOM and Cd species by gel filtration chromatography revealed that Cd spiked into the natural water reacted with humic substances to form colloidal particles that were not subject to adsorption by the oxidized CNT. Instead, sieving became an important mechanism for the removal of these colloidal Cd species. This finding manifests the importance of contaminant speciation and NOM composition to the design of novel CNT membrane filters for environmental applications.

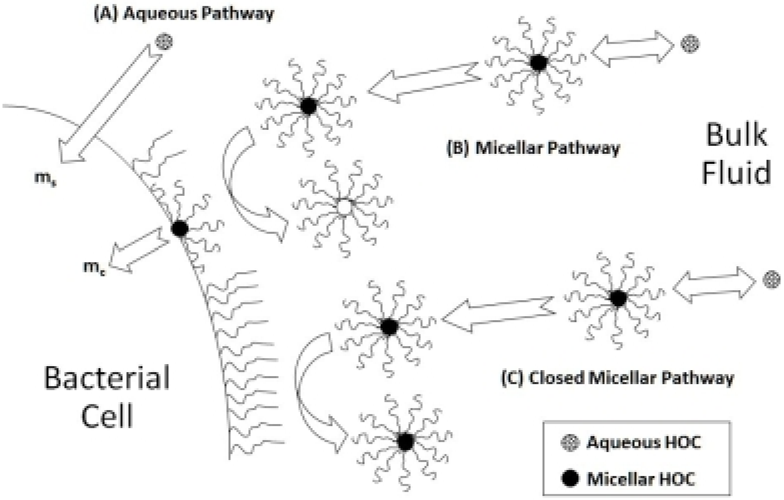


COLL 807

Partitioning of hydrophobic organic compounds into surfactant hemi-micelles on the bacterial cell surface and its relationship to surfactant-enhanced HOC bioavailability and biodegradation

***Derick G. Brown**, dgb3@lehigh.edu.Department of Civil & Environmental Engineering, Lehigh University, Bethlehem, PA 18015, United States*

Bioremediation of hydrophobic organic contaminants (HOC) in the environment is often limited by their low aqueous solubility and strong sorption to soil. One promising means to enhance HOC bioavailability is through the use of surfactants. At low aqueous concentrations, surfactants are present in solution as individual molecules, called monomers, which have distinct hydrophobic and hydrophilic moieties. As the surfactant aqueous concentration is increased to a critical value, called the critical micelle concentration (CMC), the surfactant monomers begin to aggregate to form spherical or ellipsoidal structures called micelles that have a hydrophobic core and a hydrophilic exterior. HOC's can partition into the core of the surfactant micelles and it has been demonstrated that a fraction (*f*) of micellar-phase HOC is directly bioavailable to bacterial cells. Here, a model is presented that incorporates hemi-micellar formation on the cell surface into the pathway describing micellar HOC bioavailability and the model is validated against HOC bioavailability data for five different $C_{12}E_y$. This enhanced bioavailability is put into context with microbial kinetics and system partitioning processes, and it is demonstrated that the addition of surfactant can enhance, have no effect, or inhibit HOC biodegradation depending upon surfactant concentration and microbial growth rate. Understanding these non-linear relationships between surfactant-enhanced HOC bioavailability, biodegradation kinetics, and system partitioning will assist in the design and implementation of surfactant-enhanced bioremediation programs.



COLL 808

Supramolecular nanoprobes for enzyme sensing

*Lye Lin Lock, Claudia Reyes, **Honggang Cui**, hcui6@jhu.edu.Department of Chemical and Biomolecular Engineering, Johns hopkins University, Baltimore, Maryland 21218, United States*

Molecular probes are typically water soluble molecules that can convert specific chemical reactions or binding events into detectable signals. One typical drawback of such water soluable molecules is their undesired hydrolysis or degradation by other molecules. In this presentation, we demonstrate our recent efforts to design and control supramolecular assembly of molecular probes into nanoprobes of well-defined size and shape. The resulting supramoelcular probes offer not only protection to the assembled molecular probes but also provide a high local concentration allowing for highly sensitive detection of targeted enzymes. Our results have shown that these supramolecular nanoprobes can be used as effective sensors for visualization and quantification of cathepsin B.

COLL 809

Novel "smart" nano-sized composite micelle system (CMS) for tumor targeting delivery

Lin Xiao[1]*, xiao_forest@yahoo.com, Guang Yang*[1]*, Mario Gauthier*[2]*.Â (1) College of Life Science and Technology, Huazhong University of Science and Technology, Wuhan, Hubei 430074, ChinaÂ (2) Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada*

Poly(ethylene glycol) (PEG) is used as a coating material in the emerging field of polymer-based drug delivery to prolong the circulation time of nanoparticles in the bloodstream. Yet, after localizing in the pathological site, the coating is expected to shed so that nanoparticles can deliver their contents in an efficient manner. In present study, a novel "smart" nano-sized composite micelle system (CMS) was designed and developed for tumor targeting delivery. CMS is chemically composed of an amphiphilic poly(L-lactic acid)- poly(ethylene glycol) conjugate with a cleavable acetal group as a linker between the hydrophobic PLLA chain and the hydrophilic PEG chain (PLLA-acetal-PEG), and an amphiphilic poly(L-lactic acid)-b-poly(L-lysine) diblock copolymer end-functionalized with a targeting ligand, eg. RGD peptide (PLLA-b-PLL-RGD). CMS was prepared from the mixed self-assembly of PLLA-acetal-PEG and PLLA-b-PLL-RGD in dioxane/water. The micelle morphology of CMS was verified by transmission electron microscopy (TEM) and dynamic light scattering (DLS). Since the acetal group is acid-cleavable, the shell-forming PEG chains will fall off automatically from CMS after arriving in the acidic tumor environment, exposing the RGD targeting ligands and positively charged PLL chains, which promote the tumor cell binding of particles and subsequent drug release. Preliminary study has shown that this novel CMS has good drug-loading capacity and efficient tumor targeting and binding abilities *in vitro*. Further study including more physical and biological assessment of CMS is being conducted in our lab.

COLL 810

Hydrodeoxygenation of bio-oils model compounds over Pt catalyst supported on hierarchical ZSM-5 zeolites

***Yuxin Wang**, swang@latech.edu, Yinbo Zu, Shengnian Wang.Department of Chemical Engineering, Louisiana Tech University, Ruston, Louisiana 71272, United States*

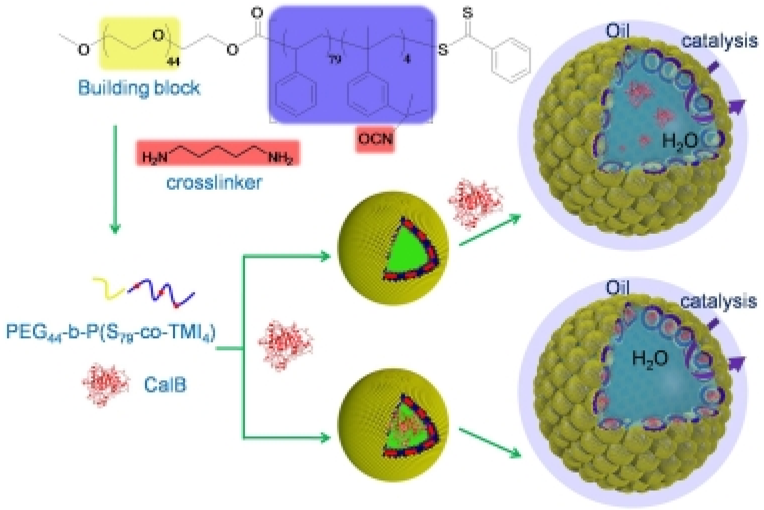
Biofuel shows promising potentials to answer our current globule challenges on energy and environment. The key to its success lies on the conversion of biomass to high quality biofuel and/or chemical feedstocks. But unlike fossil fuel, biofuel is composed of many carbohydrates with high oxygen content and low hydrogen/carbon ratios, which leads to the low heat capacity, poor thermal and chemical stability of biofuel. Further hydrogenation and deoxygenation must be done before biofuel can serve as attractive replacements of the conventional fuel. We hypothesize that catalyst supported mesoporous zeolites (i.e., hierarchical zeolites) could provide superior activity and selectivity than other common support materials (e.g., alumina and silica): zeolites offer strong acidity for hydrogenation and good hydrothermal stability while the hierarchical structure improves the diffusion of large compounds (presenting with a high percentage in bio-oil), the reduction of pore blocking, and/or the lessening of deactivation of catalyst from coking. To demonstrate our concept, a novel dual-template synthesis approach was used to produce new mesoporous ZSM-5 zeolites and Pt catalyst was impregnated for catalytic hydrodeoxygenation of bio-oil. We found better catalytic activity of mesoporous ZSM-5 zeolites based catalysts than their conventional counterparts (i.e., microporous zeolites) and those on alumina or silica in the deoxygenation or hydrogenation of phenol-type bio-oil compounds. Exploring on new synthesis strategies for more desired hierarchical zeolites (e.g., with large mesopores, strong acidity, or their combinations) and/or better catalytic performance of these new hierarchical zeolites are currently under investigation. Our efforts are expected to help make biomass/biofuel a truly renewable and environmental friendly energy source.

COLL 811

Polymersome Pickering emulsion for enzyme catalysis in a biphasic system

***Zhipeng Wang**, zhipeng.wang510@gmai.com, Matthijs C.M. van Oers, Jan C.M. van Hest, Floris P.J.T. Rutjes.Institute for Molecules and Materials, Radboud University Nijmegen, Nijmegen, The Netherlands*

A polymersome-stabilized Pickering emulsion was successfully prepared and applied in a biphasic enzymatic reaction.[1] This type of Pickering emulsion was stabilized by fully packed crosslinked polymersomes at the water/oil interface. CalB, as a model enzyme, was loaded either in the water phase or in the lumen of the polymersomes of the Pickering emulsion, which highly enhanced its catalytic performance. The conversion of the esterification reaction of 1-hexanol and hexanoic to hexyl hexanoate reached 80–90% at equilibrium within Pickering emulsions. The specific activity of CalB was improved by 4.4 times (enzyme loaded in the water phase) and 12.3 times (enzyme loaded in the lumen of polymersome), comparing to native CalB in the biphasic system. Furthermore, the recyclability of CalB in the polymersome Pickering emulsion system could be effectively realized. Since the special structure of the polymersome Pickering emulsion naturally creates a system with different compartments, different enzymes or other catalysts can be loaded in separate spaces; this is ideal for performing cascade reactions. [1] Z. Wang, M. C. M. van Oers, F. P. J. T. Rutjes, J. C. M. van Hest, *Angew. Chem. Int. Ed.* **2012** , *51*, 10746 –10750.



COLL 812

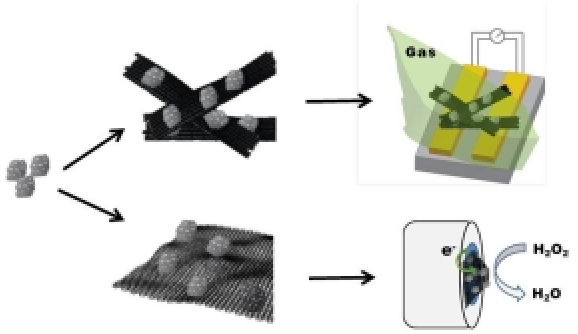
Hybrid metal nanobox/carbon composites for environmental and biomedical sensing applications

Adriana Popa[1], *anp29@case.edu, Jing Li*[2], *Anna C Samia*[1]*.Â (1) Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, United StatesÂ (2) NASA Ames Research Center, Moffett Field, CA 94035, United States*

Nanoarchitectured materials have attracted significant interest over the years due to their unique properties that can be tuned by controlling their size, shape, and morphology. Moreover, metallic hollow nanostructures are an intriguing class of nanomaterials that has shown superior properties that can be attributed mainly to the nanostructures' increased surface area, low density, high void ratio, and highly tunable localized surface plasmon resonance. Combining the unique properties of metallic hollow nanostructures with those of carbon based materials can result in nanocomposites that are ideal for environmental and biomedical sensing applications.

We report on a novel gas sensing material based on hybrid metal nanobox/carbon nanomaterial composites. Sensors fabricated from platinum nanobox (PtNB)/semiconducting SWCNT composites showed increased sensitivity and recovery

time as compared to sensors that only contained SWCNTs, when exposed to chlorine gas at room temperature. The enhanced gas sensor response is attributed to the increase in efficiency of the charge transfer process between the non-polar electron withdrawing gas molecule and the SWCNTs with the introduction of the metal NBs. In addition, PtNBs/graphene composites have been used as glassy carbon electrode modifiers for the non-enzymatic detection of hydrogen peroxide. As previously observed from the gas sensing application of the nanocomposites, the surface morphology of the PtNBs plays a key role on the sensitivity of the material, thereby demonstrating the importance of nanostructuring of catalysts for electrochemical sensing applications.



Schematic of hybrid metal nanostructures/carbon nanomaterial composites and sensing applications.

COLL 813

Hybrid iron oxide@carbon nanochains as highly efficient antibacterial agent

***Shu F. Situ**, sfs38@case.edu, Anna Cristina S. Samia.Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, United States*

Hybrid nanomaterials have recently attracted great scientific interest owing to the enhanced properties that results with the integration of different types of functional nanomaterials, which in turn is beneficial for environmental, energy, and biomedical applications. In this study, we report on a cost-effective and environmental-friendly hydrothermal carbonization synthesis approach to prepare functional nanomaterials that combine iron oxide nanoparticles (IONP) and carbon nanostructures, into hybrid self-assembled nanochains with high antibacterial activities. Utilizing this green chemistry method, we coat the IONPs with a layer of amorphous carbon with various thicknesses using D-glucose as carbon source. The resulting iron oxide nanoparticle@carbon (IONP@C) nanochain assemblies are evaluated for their structural and magnetic properties. The porous carbon shell is hydrophilic, thus it can be readily dispersed in water and possesses remarkable ability to capture and eliminate *Escherichia coli (E. coli)*. The iron oxide nanoparticle serves as a magnetic core to enable the nanochains to retain its structure and facilitate magnetic removal of the novel antibacterial agent.

COLL 814

Engineering Graphene-metal nanocomposite for enhancing oxygen reduction and methanol oxidation reactions

***Shaojun Guo**, shaojun.guo.nano@gmail.com.Physical Chemistry & Applied Spectroscopy, Los Alamos National Lab, Los Alamos, NM 87544, United States*

Developing new synthetic methods for the controlled synthesis of Pt-based or non-Pt nanocatalysts with low or no Pt loading to facilitate sluggish cathodic oxygen reduction reaction (ORR) and organics oxidation reactions is a key issue in the development of fuel cell technology. Various nanoparticles (NPs), ranging from the size to shape, composition and structure, have shown the good potential to catalyze the sluggish cathodic and anodic reactions. In this presentation, I will talk about my recent advances on synthesis of graphene-FePt, graphene-Co/CoO and graphene-PtPd nanoparticles for effectively enhancing ORR and methanol oxidation reaction.

COLL 815

Toward boundary detection during breast cancer surgery

***Jenny Barriga**[1], jbarriga@k-state.edu, Dinusha N. Udukala[1], Hongwang Wang[1], Thilani N. Samarakoon[1], Deryl L. Troyer[2], Stefan H. Bossmann[1].Â (1) Department of Chemistry, Kansas State University, Manhattan, Kansas 66506, United StatesÂ (2) Department of Anatomy & Physiology, Kansas State University, Manhattan, Kansas 66506, United States*

Developing cancer diagnostics for recognizing breast cancer at the localized stage, in combination with the exact identification of the tumor boundaries during surgery, would be very advantageous, because virtually all breast cancer mortality occurs after the cancer has metastasized. In 2013, the National Cancer Institute anticipates approx. 230,500 new breast cancer cases and 40,000 deaths. The 5-year relative survival of breast cancer decreases to 23 percent at the distant stage, from 83 percent at the regional stage and 98 percent at the localized stage. Numerous proteases are overexpressed in breast cancer and surrounding tissue. Luminescence assays have the potential to be up to three orders of magnitude more sensitive, when compared to immunoassays. Furthermore, luminescence assays are able to detect only chemically active proteases, whereas immunoassays detect a mixture of active proteases and zymogens. In most breast cancers, the protease-activity is highest in the boundary region between healthy and cancerous tissue. Therefore, luminescence-based nanoassays have the potential to mark the boundary clearly, leading to the complete removal of cancerous tissue. I have studied the protease activity of 12 breast cancer samples from mastectomies, comprised of the tumor core, the boundary region and presumably healthy tissue (adjacent to the tumors). The results will be presented, together with a statistical analysis.

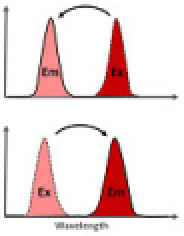
COLL 816

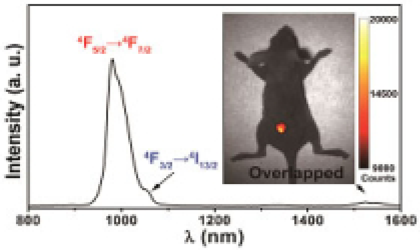
Near-infrared lanthanide nanoprobes for deep-tissue in vivo imaging

Ling-Dong Sun[1,2,3]*, sun@pku.edu.cn, Ye-Fu Wang*[1,2,3]*, Pei-Zhi Zhang*[1,2,3]*, Chun-Hua Yan*[1,2,3]*.Â (1) Beijing National Laboratory for Molecular Sciences, Beijing, ChinaÂ (2) State Key Laboratory of Rare Earth Materials Chemistry and Applications, Beijing, ChinaÂ (3) College of Chemistry and Molecular Engineering, Peking University, Beijing, China*

Compared with ultrasonography and magnetic resonance imaging (MRI), an obvious obstacle for fluorescent imaging is the limited tissue penetration depth. Development of deep-tissue fluorescent probes is thus of great interest, especially for *in vivo*applications such as early-stage cancer diagnosis. Near-infrared (NIR) photons are less absorbed and scattered by tissues, fluorescence probes with excitation and emission in NIR could act as ideal probes for in vivo imaging with high sensitivity.

Lanthanide ions with multiple and abundant *f* configurations, are the first choice of activators for luminescent materials. Here we introduce two types of NIR nanoprobes with two different intrinsic emissions from lanthanide ions. One is anti-stokes emission nanoparticles with Yb^{3+} and Tm^{3+} doping. With the stimulation at ca. 980 nm (Yb^{3+}, $^{2}F_{7/2}$®$^{2}F_{5/2}$), tow-photon upconverted emission at 800 nm (Tm^{3+}, $^{3}H_{4}$®$^{3}H_{6}$) is efficiently achieved. Another one is Nd^{3+} sensitized stokes emission of Yb^{3+}. With the excitation of Nd^{3+} at 808 nm ($^{4}I_{9/2}$®$^{4}F_{5/2}$), not only emission of Nd^{3+} at 1064 nm ($^{4}F_{3/2}$®$^{4}I_{13/2}$) could be observed, the emission of Yb^{3+} at 975 nm ($^{2}F_{5/2}$®$^{2}F_{7/2}$) with could also be observed. This emission behavior comes from efficient energy transfer from Nb^{3+} to Yb^{3+}. And the emission from Nd^{3+} and Yb^{3+} could be tuned with the doping ratio or core/shell structure design. To meet the requirements of in vivo imaging, these nanoparticles were dispersed in PBS buffer with removing the alkyl chain. The NIR imaging were obtained with subcutaneous injection and vein injection. The circulation and accumulation of the NPs could be examined in vivo. These NIR nanoprobes shows great advantage with higher quantum efficiency, lower tissue scattering than excitation or emission in visible range, and these may also make them a potential deep-tissue imaging probes.





COLL 817

Colloidal nanoparticles with ligand-tunable bioactivity and solvability

***Soumyo Sen**, ssen5@uic.edu, Guillaume Noell, Petr Kral.Chemistry, University of Illinois at Chicago, Chicago, Illinois 60607, United States*

In collaboration with experimentalists, we study how ligands influence the bioactivity and solvability of colloidal nanoparticles (NP). We model by molecular dynamics simulations the surface properties of small gold NPs with different types of ligands and correlate these results with the experimental observations. We show that the biological and physical activities of these NPs can be controlled by the solvent accessible surface area of the ligands, solvent residence times, dipole moment orientations, and other atomistic features of the NP surfaces. Our integrated studies provide a clear evidence that atomistic simulations are becoming a practical tool in designing and optimizing of active nanoscale systems.

COLL 818

Morphology control of giant vesicles by hydrophobic-hydrophilic balance of amphiphilic random block copolymers

***Eri Yoshida**, eyoshida@ens.tut.ac.jp.Department of Environmental and Life Sciences, Toyohashi University of Technology, Toyohashi, Aichi 441-8580, Japan*

Micrometer-sized giant vesicles are plausible artificial models for biomembranes composed of cells and organelles due to the similarity of their size and construction. In recent years, the importance of the giant vesicles has been increasing for industrial applications as microcapsules in drug and gene delivery systems, microreactors, and selective membranes. This paper describes novel methods to prepare micrometer-sized giant vesicles by amphiphilic block copolymers consisting of hydrophilic poly(methacrylic acid) (PMAA) and hydrophobic poly(methyl methacrylate (MMA)-*random*-methacrylic acid (MAA)) and to control the morphology of the giant vesicles through the hydrophobic-hydrophilic balance of the random copolymer block.

The giant vesicles were obtained by the nitroxide-mediated photo-controlled/living radical polymerization (photo-NMP)-induced self-assembly. The photo-NMP of MAA was performed at room temperature using 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (MTEMPO) as the mediator in the presence of (4-*tert*-butylphenyl)diphenylsulfonium triflate as the accelerator to prepare a PMAA prepolymer. The random block copolymerization of MMA and MAA were carried out in an aqueous methanol solution using the PMAA prepolymer to produce a PMAA-*block*-P(MMA-*random*-MAA) random block copolymer (PMAA-*b*-P(MMA-*r*-MAA)). PMAA_{155}-*b*-$\text{P(MMA}_{0.883}$-*r*-$\text{MAA}_{0.117})_{349}$ formed spherical vesicles with a 2.86 µm diameter. A differential scanning calorimetry analysis demonstrated that the vesicles had a bilayer structure consisting of a hydrophilic PMAA surface and hydrophobic P(MMA-*r*-MAA) interface. The wet vesicles before air-drying were flexible and easily transformed by stress, whereas the dry vesicles were fragile and cracked. Field emission scanning

electron microscopy observations revealed that the morphology of the giant vesicles was changed dependent on the MMA/MAA ratio in the random copolymer block. PMAA$_{155}$-*b*-P(MMA$_{0.782}$-*r*-MAA$_{0.218}$)$_{362}$ partly formed fibers in addition to spherical vesicles, while PMAA$_{155}$-*b*-P(MMA$_{0.701}$-*r*-MAA$_{0.299}$)$_{358}$ produced membranes retaining the bilayer structure. At the constant block length, the spherical vesicles were transformed into fibers and finally into bilayer membranes by increasing the MAA ratio of the random copolymer block.

COLL 819

Wettability and oil recovery by imbibition of modified magnetite nanoparticles from fractured and heterogeneous carbonates

***ayman m. atta**, aatta@ksu.edu.sa.department of chemistry, king saud university, riyadh, riyadh 11451, Saudi Arabia*

About one-half of petroleum oil reserves are held in carbonate formations. The remaining oil in carbonate reservoirs is regarded as the major domestic target for improved oil recovery. Carbonate reservoirs are often fractured and have great complexity even at the core scale. This work addresses quantification of crude oil/brine/rock interactions and the impact of reservoir heterogeneity on oil recovery by spontaneous imbibition and viscous displacement from pore to field scale. In this respect, this work aims to prepare new hydrophobically modified magnetite nanoparticles to alter the wettability of carbonate rocks. The chemical structures and morphology of the prepared nanoparticles were studied by FTIR and TEM, respectively. The surface activity of the modified nanoparticles was measured to study the ability of particles to displace the crude oil from carbonate rock. The wettability of the prepared magnetite nanoparticles was measured from contact angle measurements. Wettability control was achieved by adsorption from crude oils obtained from producing carbonate reservoirs. The induced wettability states were compared with those measured for reservoir cores.The products show interested characteristics and caused water-wet carbonate cores to become markedly less water-wet or even oil-wet. Relatively minor effects on wetting were observed with base oils that did not destabilize asphaltenes.

COLL 820

Effect of fluorocarbon-hydrocarbon hybrid tail on phase behavior and aggregate nanostructure of surfactant in supercritical carbon dioxide

***Masanobu Sagisaka**[1], sagisaka@cc.hirosaki-u.ac.jp, Shinji Ono[1], Tsuyoshi Narumi[1], Atsushi Yoshizawa[1], Ci Yan[2], Craig James[2], Shirin Alexander[2], Julian Eastoe[2].Â (1) Graduate School of Sciecen and Technology, Hirosaki University, Hirosaki, Aomori 0368561, JapanÂ (2) School of Chemistry, University of Bristol, Bristol, United Kingdom*

To clarify how a fluorocarbon (FC)-hydrocarbon (HC) tail of a hybrid surfactant acts for aggregation and solubilization in supercritical CO_2, this study examined the phase behavior and aggregate nanostructures of both hybrid and non-hybrid surfactants in a water/supercritical CO_2 mixture. By high-pressure small-angle neutron scattering (HP-SANS) technique, symmetric double-FC-tail surfactants (non-hybrid, FC length = 4, 6 and 8) with an Aerosol-OT-like headgroup and backbone were found to form spherical reversed micelles in CO_2 at 45 ºC, 350 bar and water-to-surfactant molar ratios (*W*) of 0-80. These reversed miceller systems were identified as a Winsor-II or IV W/CO_2 microemulsion. On the other hand, phase behavior and solubilizing capacity of hybrid surfactants (FC length m = 4 and 6, HC length n = 2, 4, 5, 6 and 8) were strongly affected by HC length as well as FC one, and the short FC (m = 4) and/or HC (n=2) remained surfactant precipitates in water/CO_2 mixture at W=20, 350 bar and 45 ºC. The hybrid surfactants with m = 6 and $n \geq 4$ were able to yield transparent single-phases at the same P and T conditions, and the solubilizing capacity became the maximum value of W =~60 at hydrocarbon chain length close to that of the hybridized FC (m = 6). The HP-SANS experiments for the hybrid surfactants interestingly found not only spherical reversed micelles but also non-spherical (rod-like) one in the transparent single-phases. The length and aspect ratio of the rod-like reversed micelles depended on W and surfactant concentration, and these values at W=10 and 50 mM reached 360 Å and 10, respectively.

COLL 821

Probing physico–chemical properties of sodium dodecyl sulfate (SDS) in presence of antimicrobial drug (Levofloxacin) for perspective drug applications

Kundan Sharma[1]*, kundanvashisht@gmail.com, Suvarcha Chauhan*[1]*, Varun Bhardwaj*[2]*, Poonam Sharma*[2]*.Â (1) DEPARTMENT OF CHEMISTRY, HIMACHAL PRADESH UNIVERSITY, SHIMLA, HIMACHAL PRADESH 171005, IndiaÂ (2) DEPARMENT OF BIOTECHNOLOGY, BIOINFORMATICS AND PHARMACY, JAYPEE UNIVERSITY OF INFORMATION TECHNOLOGY, WAKNAGHAT/SOLAN, HIMACHAL PRADESH 173234, India*

In the present manuscript, the advantages of surfactant micelles as vehicle are taken into consideration and the impact of potential antimicrobial drug (levofloxacin) on micellar system of anionic surfactant (SDS) has been studied. It would therefore be interesting to evaluate the region of micelle formation in order to design such system which could prove valuable in pharmaceutical formulations. For this, from conductance study, critical micelle concentration (CMC), standard thermodynamic parameters of micellization namely , and have been evaluated at four different temperatures (298.15 to 313.15) K. Molar volume and compressibility measurements have also been carried out to evaluate the apparent molar volume and apparent molar adiabatic compression of drug–surfactant complex and discussed in terms of the solute–solute and solute–solvent interactions. In addition spectroscopic analysis (FTIR and ^{1}H–NMR) has also been carried out which confirmed the presence of intermolecular interaction present between levofloxacin–SDS moiety and provide information regarding locus of levofloxacin in micellar structure [Figure 1]. Conclusively, this study provides a hint to assess and develop surfactant immobilized levofloxacin for better biological action.

COLL 822

Shape-persistent micelles bearing calix[4]arene building block

Kazuo Sakurai, *sakurai@kitakyu-u.ac.jp.Department of Chemistry and Biochemistry, University of Kitakyushu, 1-1 Hibikino, Kitakyushu, Fukuoka 808-0135, Japan*

A series of calix[4]arene-based lipids with alkyl chains of varying length were newly synthesized and found that some of them form spherical micelles with a defined aggregation number. These aggregation numbers are 6, 8, and 12, interestingly coinciding the number of the Platonic solid. Synchrotron small-angle X-ray scattering (SAXS) patterns exhibited a sharp intensity dump, indicating high symmetry and shape monodispersity. The size monodispersity of the micelles was confirmed with analytical ultracentrifugation. The present results indicate that a suitable combination of tail length, head volume, and rigidity of the building block is necessary to attain the shape persistency. With a shape determination program of Dummy and molecular dynamics calculatrion, the micellar architecture was determined.

COLL 823

Lubrication properties of phospholipid liposome coated silk microspheres

RUBO ZHENG[1], *rzheng@tulane.edu, Jingjing Zhan*[1], *Xiaoqin Wang*[2], *David Kaplan*[2], *Noshir Pesika*[1], *Vijay T John*[1]*.Â (1) Chemical and Biomolecular Engineering, Tulane University, New Orleans, LA 70118, United StatesÂ (2) Biomedical Engineering, Tufts University, Medford, MA 02155, United States*

We present results of our work to develop an aqueous 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) liposome coated silk microsphere suspension as an effective lubricant, capable of providing a low coefficient of friction (COF) on the order of 0.02, minimizing surface wear and avoiding degradation even over relatively prolonged cycling conditions. We propose that the lubricating properties of the silk microspheres are a result of an efficient rolling mechanism. The phospholipid coating was added with the intent that inserting a “lubricant” between rolling elements may avoid jams caused by sticking between the rolling elements and motion under the hydration layer would also decrease sliding wear in the slip step of the rolling process. Details of the nanostructure of DOPC liposome-coated silk microspheres, its lubrication properties, and nano-scaled surface wear are characterized using a confocal laser scanning microscope, scanning electron microscope, the universal materials tester and an atomic force microscope. These results may have implications for biomedical applications especially in joint lubrication. With current therapeutic options for improving joint comfort being limited, silk microspheres, which are biocompatible and slowly degradable, especially with appropriate tribological properties, offer an intriguing opportunity.

COLL 824

Structure and rheology of micelle and micelle-nanoparticle solutions from molecular dynamics simulations

*Subas Dhakal, **Radhakrishna Sureshkumar**, rsureshk@syr.edu.Syracuse University, Syracuse, NY 13244, United States*

Coarse grained molecular dynamics (MD) simulations are used to study equilibrium structure as well as shear-induced structure changes and rheology of cationic cylindrical micelles of Cetyl-trimethyl ammonium chloride (CTAC) solutions. These simulations extend of our earlier work [1-2] which was limited to studying single micelle dynamics and binary micelle interactions. In the current work, systems that consist of O(100) cylindrical micelles are simulated in presence of explicit solvent and salt (NaSal) interactions. Utilizing an algorithm that tracks the direction of the maximum density of the head groups, we evaluate the micelle contours and orientation correlations from which micelle lengths, persistence length and shape anisotropy are calculated as functions of salt concentration. Probability distribution function (pdf) of micelle length is found to be an exponential function for an equimolar ratio of salt to surfactant ratio, consistent with theoretical predictions [3]. However, a log normal pdf is observed for lower salt to surfactant concentration ratio. The average micelle length for a given surfactant concentration increases sub-linearly with a power law exponent of 0.4. By varying the salt and surfactant concentration a phase diagram that consists of dilute, semi-dilute and entangled systems is obtained. Non-equilibrium MD simulations are performed to understand the molecular mechanisms underlying the phenomenon of shear-induced structure (SIS) formation in observed in cylindrical micelle solutions. This and the effect of nanoparticle addition on structure and rheology of micelle networks will be discussed.

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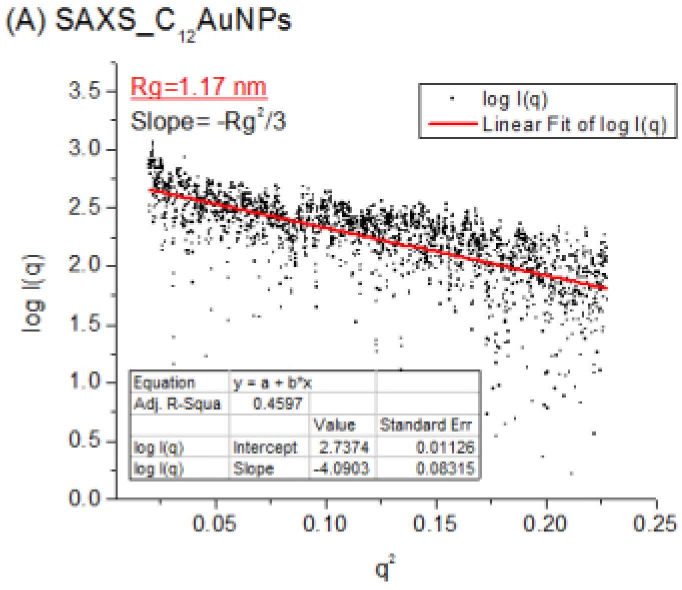
COLL 825

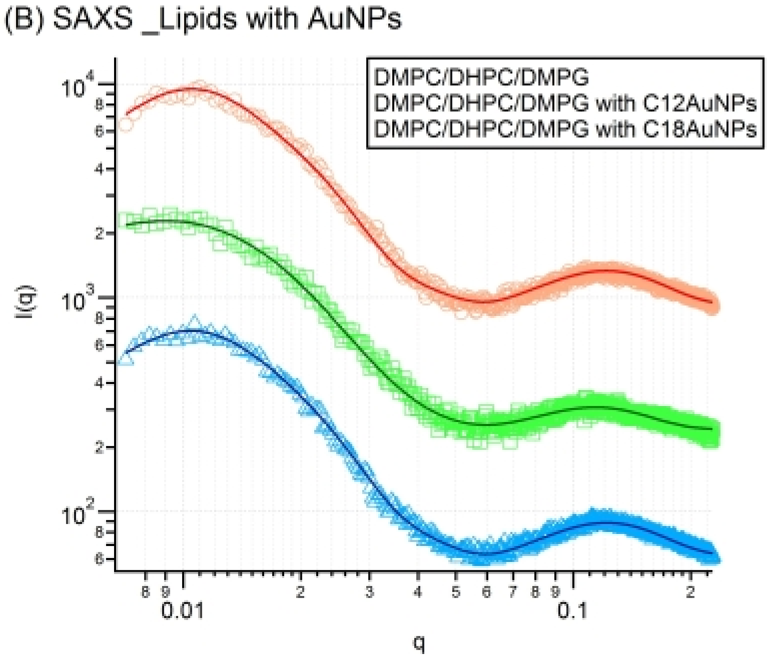
Self-assembly of unilamellar vesicles (ULV) with lipids and hydrophobated gold nanoparticles

***Hyun-Sook Jang**[1], hyun-sook.jang@uconn.edu, Flavio Maran[2], Mu-Ping Nieh[1,3].Â (1) Institute of Materials Science, Polymer program, University of Connecticut, Storrs Mansfield, CT 06269, United StatesÂ (2) Department of Chemistry, University of*

Padova, Via Marzolo, Padova 35131, ItalyÂ (3) Department of Chemical & Biomolecular Engineering, University of Connecticut, Storrs, CT 06269, United States

The design of hydrid liposome containing nanoparticles (NPs) has been attracted as therapeutics and therapeutics carriers. However, it was challenging to load NPs in the lipid bilayers due to the lack of hydrophobicity and difficulties of structural analysis of this system. In this paper, the hydrophobated NPs, C_{12}AuNP, (1.17nm by SAXS) was synthesized and self-assembled in the bilayer of lipid-based nanodiscs. The nanodiscs are composed by different lipids (i.e., charge, chain length) of 1,2-dimyristoyl-sn-glycero-3-phosphocholine(DMPC)/ 1,2-dihexanoyl-sn-glycero-3-phosphocholine(DHPC)/ 1,2-dimyristoyl-sn-glycero-3-phospho-(1'-rac-glycerol) (sodium salt) (DMPG). Also, by inducing the melting transition temperature of DMPC (23^{o}C), the transformation of morphology from bicelles to ULV has confirmed by SAXS and light scattering. Both self-assembled structures successfully encapsulated the hydrophobated AuNPs in the lipid bilayers. The size and morphologies are determined by TEM, SAXS yielding a best-fit disc radius of 87nm and vesicular radius of 380nm at low and high temperatures, respectively. The findings also suggest a versatile way to understand the interaction between bilayers and NPs with different morphologies.


(A) SAXS_C_{12}AuNPs



COLL 826

Hierarchical dendritic micronano structure a-Fe coated by SiO_2 nanoshell and enhanced microwave absorption performance

***zhenxing yu**, yuzhenxing@hit.edu.cn, zhongping yao, na zhang, zhaohua jiang.harbin institute of technology, China*

The hierarchical dendritic micro-nano structure a-Fe@SiO_2 nanocomposite materials have been synthesized by electric field-induced method and Stober process. From the results, it can be known that the SiO_2 nanoshell coated on the dendritic a-Fe is uniform. At the same time, the coating thickness increases with the quantity of TEOS added. The complex relative permittivity and permeability spectra exhibit that these a-Fe@SiO_2 nanocomposite materials show some regular changes of response peaks with the change of SiO_2 nanoshell thickness, which are caused by the free electronic polarization, nature resonance and exchange resonance. The maximum reflection loss value reaches about -57.8 dB when 1ml TEOS is added. And the widest frequency band between 4 and 17 GHz with RL < -20 dB is obtained when 1.5ml TEOS is used. The mechanism is analyzed based on the skin effect. The insulating SiO_2 nanoshell is conducive to enhance the free electronic polarization which further enhances the dielectric loss. Meanwhile the effective matching thickness of SiO_2 nanoshell contributes to that more microwave enters the materials and has been dissipated. So the microwave absorption properties have been successfully tuned by controlling the thickness of the coated SiO_2 nanoshell.

COLL 827

Reduction of Au(I) species to Au(0)-containing species during gold nanoparticle growth and the effects of solvent

***Brian M. Barngrover**, bribarn@k-state.edu, Tim J. Manges, Christine M. Aikens.Department of Chemistry, Kansas State University, Manhattan, Kansas 66506, United States*

This theoretical investigation examines the formation of non radical Au(0) species from the reduction of Au(I) species. The Au(I) complexes of interest are $AuCl_2^-$, $AuClPH_3$, and $AuCl(H)SCH_3^{(-)}$, which are precursors for gold nanoparticle and cluster formation. Reaction of two of the Au(I) species with a hydride results in the ejection of two of the ligands and the formation of Au_2 with two ligands still attached. The reaction energy for two $AuCl_2^-$ in methanol is -1.34 eV and in benzene is -0.07 eV. $AuClPH_3$ reactions can either eject chloride, HCl, or PH_3. The reaction energy to form $Au_2(PH_3)_2$ in methanol is -1.06 eV and the energy to form $AuClPH_3^-$ is -0.73 eV. $AuClHSCH_3$ reactions are similar to the phosphine reactions, where a chloride, HCl, or a thiol can be ejected. It is more favored to form $Au_2(HSCH_3)_2$ than $Au_2ClHSCH_3$ with reaction energies of -1.36 eV and -1.21 eV. $AuClSCH_3$ can also be used it has the option to eject chloride, HCl, thiol, or thiolate. The most favored reaction is the formation of $Au_2ClSCH_3^{2-}$ with a thiol and a chloride with a reaction energy of -1.21 eV. The next favored reaction is the formation of $Au_2(SCH_3)_2^{2-}$ with a reaction energy of -0.52 eV. The least favored reaction is $Au_2ClSCH_3^{2-}$ and a thiolate and HCl formation with a reaction energy of 0.009 eV. The $Au_2Cl_2^{2-}$ complex then can further react with the $AuCl_2^-$ starting material, which forms $Au_3Cl_3^{2-}$ and a chloride anion with a reaction energy in methanol of -0.57 eV and in benzene of -0.56 eV. The new $Au_3Cl_3^{2-}$ species can further react with either of the initial structures or with another $Au_3Cl_3^{2-}$. This is the first investigation to show how Au(0)-containing species can be formed without assuming the formation of Au(0) atoms (radical species).

COLL 828

Size-dependent Faraday rotation of gold nanoparticles

***George V Podaru**[1], gvp@ksu.edu, Chris Ramirez[1], Nathan Young[1], Raj K Dani[1], Gary Wysin[2], Viktor Chikan[1].Â (1) Department of Chemistry, Kansas State University, Manhattan, KS 66506, United StatesÂ (2) Department of Physics, Kansas State University, Manhattan, KS 66506, United States*

There is great interest to design new materials with enhanced Faraday rotation (FR). In this study, the FR of gold nanoparticles is investigated experimentally. Here, a simple method of measuring FR of gold nanoparticles and observe the size dependence FR of gold nanoparticles is presented. The Faraday rotation of gold nanoparticles is studied by static and pulse magnet in a few Tesla range. The verdet constant of the gold nanoparticles ranges

from 5 to value 20 Rad/Tesla/m exhibiting strong variation near the plasmon resonance of the gold. The experimental data show good agreement with classical electromagnetic theory.

COLL 829

Synthesis and characterization of gold nanomolecules capped by aromatic ligands

Praneeth Reddy Nimmala, *prnimmal@go.olemiss.edu, Amala Dass.Chemistry and Biochemistry, University of Mississippi, University, MS 38677, United States*

Gold nanomolecules are entities in the nanometer size regime that contain a specific number of gold atoms and passivating organic thiolate ligands with distinct chemical and physical properties. Some of the well known stable clusters synthesized in this research area are $Au_{25}(SR)_{18}$, $Au_{144}(SR)_{60}$, $Au_{38}(SR)_{24}$, $Au_{68}(SR)_{34}$, and $Au_{102}(SR)_{44}$. These are highly stable compounds which can be synthesized, dried, redispersed in solutions and stored in ambient conditions for years without any change in their physical or chemical properties.

Typically these clusters are characterized by analytical techniques like UV-Vis, NMR, Mass-spec, Electrochemistry and XPS. But acquiring the crystal structure of these species was a major challenge. Capping them with aromatic ligands would favor the crystallization owing to the rigidity of the ligands. In this talk, we will present the successful synthesis, isolation, characterization and crystallization of gold nanomolecules capped by aromatic ligands.

COLL 830

Resonant secondary light emission from plasmonic Au nanostructures at high electron temperatures created by pulsed laser excitation

Jingyu Huang[1]*, huang142@illinois.edu, Wei Wang*[2]*, Catherine J Murphy*[1]*, David G Cahill*[2]*.Â (1) Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United StatesÂ (2) Department of Materials Science and Engineering, and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States*

Resonant secondary light emission contributes significantly to the background commonly observed in surface-enhanced Raman scattering and to the non-linear light emission generated by pulsed laser excitation of metallic nanostructures that is often attributed to two-photon absorption followed by fluorescence. We study continuous-wave (cw) and pulsed laser excitation of aqueous suspensions of Au nanorods as a model system for secondary light emission from plasmonic nanostructures. We present an alternate quantitative description of the secondary light emission as a resonant electronic Raman scattering process from the continuum electron-hole pairs. Spectra

collected using cw laser excitation at 488 nm show an enhancement of the broad spectrum of emission at the electromagnetic plasmon resonance of the nanorods. The intensity of anti-Stokes emission collected using cw laser excitation at 785 nm is described by a 300 K thermal distribution of excitations. Excitation by sub-picosecond laser pulses at 785 nm broadens and increases the intensity of the anti-Stokes emission in a manner that is consistent with electronic Raman scattering by a high temperature distribution of electronic excitations predicted by a two-temperature model. Experiments using a pair of sub-picosecond optical pulses separated by a variable delay show that the time-scale of resonant secondary emission is comparable to the time-scale for equilibration of electrons and phonons. The results will facilitate the design of imaging experiments and understanding of background in surface-enhanced Raman scattering.

COLL 831

Studying the assembly and structure of the peyglated gold nanoparticles using adenine and mercaptobenzimidazole as molecular probes

***W-K-Kumudu D Siriwardana**, wds192@msstate.edu, Dongmao D Zhang.Department of Chemistry, Mississippi State University, Mississippi State, MISSISSIPPI 39762, United States*

Presented is an experimental study of nonspecific and specific ligand binding onto pegylated gold nanoparticles (AuNPs) where adenine and mercaptobenzimidazole (MBI) are used as the nonspecific or specific model ligand, respectively. Pegylation is not effective in passivating AuNPs against subsequent ligand adsorption onto AuNPs for either adenine or MBI, but it can completely stabilize AuNPs against adenine and MBI adsorption induced AuNP aggregation. Study on the effect of aging of the PEG-SH/AuNP mixture on the subsequent MBI and adenine adsorption reveals that PEG-SH takes at least 2 hrs to reach a static-state binding on the AuNPs. The highest possible packing density of thiolated PEG (MW=5000 Dalton) on the AuNP is ~200 pmol/cm^2, which is estimated on the basis of the maximum fraction of AuNP surface passivated by PEG-SH. Besides providing new insights to the assembly and structure of PEG-SH on the AuNPs, the methodology provides in this work should be of general significance in studying the polymer interactions with metallic nanoparticles.

COLL 832

One-pot synthesis and plasmonic characteristics of colloidal gold nanorings

***Yue Hu**[1], yhu3@stevens.edu, Tsengming Chou[1], Hongjun Wang[2], Henry Du[1].Â (1) Department of Chemical Engineering and Material Science, Stevens Institute of Technology, Hoboken, New Jersey 07030, United StatesÂ (2) Department of Chemistry, Chemical Biology, and Biomedical Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030, United States*

We report a novel one-pot method for the synthesis of monodisperse colloidal gold nanorings (Au NRs). Au NRs were obtained *via* galvanic replacement of sacrificial Co nanoparticles (Co NPs) with gold in the presence of low molecular weight poly(vinylpyrrolidone) (PVP, Mw = 2,500) as a stabilizing agent. The outer and inner diameters of Au NRs were controlled by the size of Co NPs and the concentration of gold salt, leading to tunable surface plasmon resonance (SPR) from visible to near infra-red range. Numerical simulation using finite different time domain (FDTD) approach was used to calculate the electric field distribution around individual as well as clustered Au NRs. The field was found to be most intense in the center for discrete Au NRs and yet the strongest at the joints clusters form, commonly referred to as hot spot. Au NRs immobilized on quartz slice substrates at various coverage densities were utilized for surface-enhanced Raman scattering (SERS) measurements using *trans*-1,2-bis(4-pyridyl)ethylene (BPE) and Rhodamine 6G (R6G) as model analytes. The Raman intensity of BPE was shown to increase linearly with the coverage density of Au NRs when discretely distributed but exponentially when clustered. In contrast, the Raman intensity of R6G exhibited a linear correlation with the coverage density with or without cluster formation. The results will be interpreted based on the different adsorption behavior of the two analyte molecules on Au NRs especially when clusters are formed.

COLL 833

High sensitive SERS (surface enhanced Raman spectroscopy) nanoplatforms based on controlled gold nanospheroids

***Ran Liu**, nanoranliu@gmail.com, Catherine Murphy.Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States*

In this study, we have developed SERS (Surface Enhanced Raman Spectroscopy) nanoplatforms (e.g. gold nanoparticle dimers with hot spots as shown in Figure 1a) based on noble metal nanoparticle assemblies for detecting small and large molecules of biological interest in a label-free, no-sample processing, multiplexed manner. Novel surface chemistries and outermost surface functionalization are being developed to bind or partition target analytes at clinically relevant concentrations. Colloidal chemistry (seed-mediated growth with the surfactant assisted) was used to synthesize gold nanospheroids. Mixed solvents (EtOH:H_2O=1:1) are used to induce the assembly and aggregation of gold nanospheroids) then a quenching method is adopted to control the aggregation before the final silica coating (TEM image can be seen in Figure 1 inset). Satisfactory EF is achieved at 5×10^8 (as shown on the Figure 1b: the black line represents SERS while the red line is the normal Raman spectra). Currently efforts are being made to scale up the reactions for potential manufacturing.

COLL 834

Water-based synthesis of Au nanoparticles by using cynarin

***ZEYNEP KATIRCIOGLU**, zkatircioglu@gmail.com, Mustafa Selman YAVUZ, Ahmet Ceyhan GÖREN.Department of Metallurgy and Materials Engineering, Selcuk University, Konya, Selcuklu 42075, Turkey*

Gold nanoparticles (AuNPs) are being employed to nano-sensing and nano-device manufacturing owing to their unique optical and electronic properties. Here we describe a protocol 'green' AuNPs by using novel material 'cynarin'. On the contarary of a typical reaction AuNPs, we did not use two different agent, such as reductant and stabilizer. In addition, water was used as a solvent. Au cynarin nanoparticles generates one-pot, green, facile and water based solutions by using $HAuCl_4$ and cynarin.

COLL 835

Cellulose fiber immobilized gold nanoparticles: SERS substrate and catalytic activity

***Bharat Baruah**, bbaruah@kennesaw.edu.Chemistry and Biochemistry, Kennesaw State University, Kennesaw, Georgia 30144, United States*

The current study demonstrates the deposition of gold nanoparticles on nonwoven fibers in baby wipes (a mixture of synthetic fiber and cellulose fiber). Au^{3+} ions are first impregnated into the micronanopores of the nonwoven fibers and then reduced into gold nanoparticles using ascorbic acid as reducing agent. The structure and properties of the composite wipes with deposited nanoparticles were verified by electron microscopy, XPS, FTIR, surface enhanced Raman spectroscopy (SERS) and catalytic reduction tests. The nanoparticles immobilized composite baby wipes exhibited a good catalytic activity for the reduction of 4-nitrophenol to 4-aminophenol in presence of sodium borohydride and demonstrated significant SERS activity for Raman active analyte molecules.

COLL 836

Adsorption, desorption, exchange, and reaction of adenine and 2-mercaptobenzimidazole (MBI) on aggregated gold nanoparticles (AuNPs)

***MANUEL GADOGBE**[1], mg862@msstate.edu, Willard E Collier[2], Dongmao Zhang[3].Â (1) Mississippi State University, STARKVILLE, Mississippi 39759, United StatesÂ (2) Tuskegee University, Tuskegee, Alabama 36088, United StatesÂ (3) Mississippi State University, STARKVILLE, Mississippi 39759, United States*

Understanding the interfacial interaction of ligands with gold nanoparticles (AuNPs) is critical in nanoparticle (NP) research. Reported herein is a UV-vis and surface enhanced Raman spectroscopy (SERS) study of the adsorption, desorption, exchange, and reaction of model ligands, including adenine and 2-mercaptobenzimidazole (MBI), on gold nanoparticles (AuNPs). The key findings of this research are; 1) both adenine and MBI adsorption induce spontaneous AuNP aggregation and complete AuNP

settlement, 2) neither MBI nor adenine can be spontaneously desorbed from AuNP aggregates, 3) ligand molecules in the aggregated AuNPs, including junction molecules, are mostly available for ligand exchange, and 4) organothiol binding affinity to AuNPs is higher than that of adenine in water. This study should be of general importance to understanding AuNP aggregation and ligand exchange. It also raises important questions about the stability of an analyte's SERS spectrum in biofluids where organothiols are abundant.

COLL 837

Preparation of novel AgPd/Pt trimetallic multiply twinned particles and their atomic resolution images by Cs-corrected STEM

***Subarna Raj Khanal**, subarnakhanal@gmail.com, Nabraj Bhattarai, Jesus Velazquez, Daniel Bahena, Miguel Jose-Yacaman.Physics and Astronomy, University of Texas at San Antonio, San Antonio, Texas 78249, United States*

The synthesis of noble metals (e.g. Pd, Pt, Au, Ag etc.) nanoparticles with controlled atomic distributions have attracted significant interest due to their size-tunable properties depending up on the variation of composition and structure. Recently, various researchers have been focused on fabrication of tri- and multi-metallic nanoparticle catalysts due to their tunable properties implemented in diverse potential applications. The addition of a third metal in to the nanoparticle catalyst is expected to produce a combination of effects such as modification of the electronic structure, change in the *d*-band center, reduction of the lattice distance and enhances the overall electronic charge shift. Therefore, tri- and multi-metallic nanoparticles possess the higher catalytic activity and selectivity in comparison to mono- and bi-metallic counterparts. Controlling the morphology of nanostructures can provide a great opportunity to stimulate their possible applications such as catalytic, electronic, sensing, and optical properties and to enhance their reactivity, selectivity and stability. The fabrication of AgPd/Pt trimetallic nanocrystals with multiply twinned structures, possessing the icosahedra morphology with a high density of compressed twins and high fraction of Pt atoms on the (111) surfaces are expected to be the most active catalysts for their many applications in fuel cells [1-5].

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[5] Acknowledgments: The authors would like to acknowledge NSF grants DMR-1103730, “Alloys at the Nanoscale: The Case of Nanoparticles Second Phase” and NSF PREM Grant # DMR 0934218

COLL 838

Synthesis of PEGylated low generation dendrimer-entrapped gold nanoparticles for CT imaging applications

*Hui Liu[1], Han Wang[2], Yanhong Xu[2], Jinglong Zhao[2], Mingwu Shen[1], Guixiang Zhang[2], **Xiangyang Shi**[1], xshi@dhu.edu.cn.Â (1) Department of Bioengineering, College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai, Shanghai 201620, ChinaÂ (2) Department of Radiology, Shanghai First People's Hospital, School of Medicine,, Shanghai Jiaotong University, Shanghai, Shanghai 200080, China*

We report the synthesis of polyethylene glycol (PEG)-modified low generation dendrimer-entrapped gold nanoparticles for *in vivo* computed tomography (CT) imaging applications. In this study, amine-terminated generation 2 poly(amidoamine) (PAMAM) dendrimers were pre-modified with PEG monomethyl ether with carboxyl end group (*m*PEG-COOH), and then employed as templates to form gold nanoparticles (AuNPs). The formed PEGylated Au DENPs were characterized via different techniques. We show that the formed PEGylated Au DENPs with Au core size of 2.8 nm are stable under different pH (5-8) and temperature (4-50 ^{o}C) conditions, as well as in different aqueous media. X-ray absorption coefficient measurements show that the attenuation intensity of PEGylated Au DENPs is much higher than that of Omnipaque (a clinically used CT contrast agent) at the same concentration of the radiodense elements (Au or iodine). MTT cell viability assay data reveal that the PEGylated Au DENPs are non-cytotoxic in the given particle concentration range. Importantly, the PEGylated Au DENPs enable *in vivo* blood pool CT imaging and tumor CT imaging via the known enhanced permeation and retention (EPR) effect. With the simple synthesis approach and the use of cost-effective low generation dendrimers, the developed PEGylated Au DENPs hold great promise to be used as contrast agents for CT imaging of different biological systems.

COLL 839

Functionalized gold nanoclusters as site-specific labels for imaging of enteroviruses

***Kirsi Salorinne**[1], kirsi.salorinne@jyu.fi, Hannu Hakkinen[1,2].Â (1) Department of Chemistry, Nanoscience Center, University of JyvÃ¤skylÃ¤, Jyvaskyla, 40014, FinlandÂ (2) Department of Physics, Nanoscience Center, University of JyvÃ¤skylÃ¤, Jyvaskyla, 40014, Finland*

Monolayer protected gold nanoclusters of a few nanometers in size have proven to be promising site-specific labels for various biomolecules due to their unique properties that come from the small size and molecule-like characteristics that can be studied *e.g.* by transmission electron microscopy (TEM).[1,2] In addition, by properly designing the protecting monolayer to include specific linker molecules to allow site-specific

conjugation to biomolecules, this technique enables the investigation of different mechanisms or pathways of complex biomolecules, or tracking of the biomolecule-gold cluster conjugates inside cells using the appropriate imaging technique. Here we describe a recent success in labeling of enteroviruses for TEM studies by maleimide-functionalized $Au_{102}(pMBA)_{44}$ clusters (pMBA = *para* mercaptobenzoic acid).[3]

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COLL 840

Renal clearable luminescent gold nanoparticles with molecular pharmacokinetics

***Chen Zhou**[1,3], zhou@ucmo.edu, Guiyang Hao[2], Patrick Thomas[2], Jinbin Liu[1], Mengxiao Yu[1], Shasha Sun[1], Orhan K Oz[2], Xiankai Sun[2], Jie Zheng[1].Â (1) Department of Chemistry, The University of Texas at Dallas, Richardson, Texas 75080, United StatesÂ (2) Department of Radiology and Advanced Imaging Center, The University of Texas Southwestern Medical Center, Dallas, Texas 75390, United StatesÂ (3) School of Environmental, Physical and Applied Sciences, University of Central Missouri, Warrensburg, Missouri 64093, United States*

Inorganic nanoparticles (NPs) with tunable and diverse material properties hold great potential as multimodal imaging probes for better disease management. However, the severe nonspecific accumulations and unfavored pharmacokinetics of inorganic NPs after systemic administration significantly hamper their future translation into clinical practices. Thus, multifunctional nanoprobes with efficient clearance profile and optimal in vivo pharmacokinetics are highly desirable. In this talk, we will present a class of ~2 nm glutathione-coated luminescent AuNPs (GS-AuNPs) with strong intrinsic triplet-state emission, which renders AuNPs with the desired stealthiness to the reticuloendothelial system (RES) and efficient renal clearance due to the small particle size and the low affinity of glutathione to the serum proteins. ICP-MS results confirmed only 3.7±1.9 % and 0.3±0.1 % of the particles were accumulated in the liver and spleen, and over 65 % of the injected dose can be cleared out through urine within 72 h after IV injection. Further studies on the pharmacokinetics of GS-AuNPs showed that these nanoprobes exhibit two-compartment pharmacokinetics with a rapid diffusion half-life of 5.0 min and a desirable elimination half-life of 12.7 h, which is comparable to those of the clinically available small molecule contrast agents but different from those of most known nanoprobes. The readily detection of these AuNPs with different imaging techniques including CT, SPECT and fluorescence imaging suggested that these NPs might serve as multi-modality imaging probes in the future.

COLL 841

Thiolate-protected $Au_{38}(SR)_{24}$ nanocluster: Size focusing synthesis, structure determination, intrinsic chirality, and beyond

***Huifeng Qian**, hq2@rice.edu.Department of Chemical and Biomolecular Engineering, Rice University, Houston, TX 77005, United States*

Thiolate-protected gold nanoclusters with core diameters smaller than 2 nm have captured considerable attention in recent years due to their diverse applications ranging from biological labeling to photovoltaics and catalysis. This new class of nanomaterials exhibits discrete electronic structure and molecular-like properties, such as HOMO-LUMO electronic transition, intrinsic magnetism, chiroptical properties, and enhanced catalytic properties. This work focuses on the research into thiolate-protected $Au_{38}(SR)_{24}$—one of the most representative nanoclusters, including its identification, size focusing synthesis, structure determination, and intrinsic chirality. The properties of two size-adjacent gold nanoclusters ($Au_{40}(SR)_{24}$ and $Au_{36}(SR)_{24}$) are also discussed. The experimental and theoretical methodologies developed in studies of the $Au_{38}(SR)_{24}$ model nanocluster open up new opportunities in the synthesis and properties investigation of other atomically precise $Au_n(SR)_m$ nanoclusters.

COLL 842

Electrochemical and optical characterization of highly monodisperse gold nanoclusters protected with hexanethiolate

***Kyuju Kwak**, kkj818@yonsei.ac.kr, KyungLim Pyo, EunSol Ko, Dongil Lee.Department of Chemistry, Yonsei University, Seoul, Republic of Korea*

Recently, thiolate ligand-protected gold nanoclusters (AuNCs) with excellent stability have been the subject of intensive research due to their unique size-dependent properties. However, the size-dependent electrochemical and optical properties of atomically monodisperse AuNCs have not been clearly delineated due to the size polydispersity and ligand effects. This poster is focused on the comparative electrochemical and optical studies of atomically monodisperse gold nanoclusters protected with the same hexanethiolate ligand (C_6S), namely, $Au_{25}(C_6S)_{18}$, $Au_{38}(C_6S)_{24}$, $Au_{67}(C_6S)_{35}$, $Au_{102}(C_6S)_{44}$, $Au_{144}(C_6S)_{60}$, and $Au_{333}(C_6S)_{79}$. The cluster synthesis was carried out by reducing $HAuCl_4 \cdot 3H_2O$ with $NaBH_4$ in the presence of hexanethiolate ligand, and further size separation was performed with solvent fractionation using dichloromethance/acetonitrile mixture. Transmission electron microscopy image and mass spectra manifested excellent monodispersity of the isolated AuNCs. These AuNCs exhibited size-dependent optical and electrochemical characteristics. The optical absorption and voltammetry studies of$Au_{25}(C_6S)_{18}$,

$Au_{38}(C_6S)_{24}$, and $Au_{67}(C_6S)_{35}$ showed increase in the energy gap opening at the Fermi level with increasing size, revealing the molecule-like optical and electrochemical properties of these clusters. . On the other hand, $Au_{102}(C_6S)_{44}$, $Au_{144}(C_6S)_{60}$, and $Au_{333}(C_6S)_{79}$ clusters invariably exhibited the optical gaps of less than 0.5 eV and quantized double-layer charging behavior, manifesting the metallic properties.

COLL 843

Entropy-driven pattern formation of hybrid vesicular assemblies of binary molecular and nanoparticle amphiphiles

Yijing Liu[1]*, yliu1214@umd.edu, Yanchun Li*[2]*, Jie He*[1]*, Kaleb Duelge*[1]*, Zhongyuan Lu*[2]*, Zhihong Nie*[1]*.Â (1) Department of Chemistry & Biochemistry, university of maryland college park, College Park, MARYLAND 20742, United StatesÂ (2) State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun, Jilin 130023, China*

Molecular amphiphiles (lipids, amphiphilic block copolymers (BCPs)) can self-assemble into a rich variety of well-defined nanostructures such as spherical micelles, cylindrical micelles, and vesicular micelles. Similar to molecular amphiphiles, inorganic nanoparticle (NP) amphiphiles, created by BCPs onto the surfaces of NPs, are representative metal-like NPs. Recently NP amphiphiles (NPAs) have become an interesting research area, because they have the unique shapes, dimensions, and intrinsic optical, electronic, and magnetic properties that are unattainable by molecular amphiphiles. The controlled assembly of NPAs enables us to tune the collective properties of NP ensembles, thus facilitating their applications in biosensing, biomedical imaging and delivery, optoelectronics, and energy production and storage. <ins cite="mailto:Yijing%20Liu" datetime="2013-10-25T07:46">

The key to fully realize the potential of these materials is to design materials with increased complexity and functionalities. A promising approach to prepare such hybrid materials is simultaneous self-assembly of multiple types of amphiphiles. However, to date, it still remains a grand challenge in achieving controllable concurrent self-assembly of molecular and colloidal amphiphiles into discrete structures. .

Here we report a study on the self-assembly of binary BCPs and NPAs into polymer/inorganic nanoparticle hybrid vesicles with various morphologies by entropy-driven lateral phase separation within multi-component membranes. The morphologies include patchy vesicles with multiple small NPA domains surrounded by free BCP phase, Janus vesicles with distinguished NPA and polymer halves, and heterogeneous vesicles with uniform distribution of NPAs. The different morphologies arise from the delicate interplay between the mismatch of the chain length of the two amphiphiles, the entanglement of polymer chains, and the diffusion rate of NPAMs. Remarkably, this strategy allows the preparation of hybrid Janus vesicles with intriguing non-spherical shapes. The ability to directly integrate multiple amphiphiles with significantly different

compositions, geometries, and dimensions in discrete assemblies opens new avenues to the fabrication of structurally complex hybrid materials with entirely new properties.

COLL 844

Finite-size effects on gold and platinum clusters

Lin Li[1,2]*, lli2010@stanford.edu, Ask H Larsen*[3]*, Nichols A. Romero*[4]*, Frank Abild-Pedersen*[2]*, Jeffrey P Greeley*[5]*, Jens K Nørskov*[2,6]*.Â (1) Department of Chemistry, Stanford Univeristy, Stanford, CA 94305, United StatesÂ (2) SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, United StatesÂ (3) Nano-bio Spectroscopy Group, Universidad del PaÃs Vasco, San SebastiÃ¡n, SpainÂ (4) Leadership Computing Facility, Argonne National Laboratory, Argonne, IL 60439, United StatesÂ (5) Department of Chemical Engineering, Purdue University, West Lafayette, IN 47907, United StatesÂ (6) Department of Chemical Engineering, Stanford Univeristy, Stanford, CA 94305, United States*

On metal clusters below 2 nm, the electronic states are discrete, and the catalytic properties depend on the spacing around the Fermi level, resulting in a quantum size effect. In addition, for metal clusters with filled d-electrons, the s-shell effects also have an impact on the size of the gap around the Fermi level, especially near a shell closing. We are interested in finding a way to separate these electronic effects from other phenomena that exist at this length scale. We have used density functional theory to study the finite-size effects on relaxed gold and platinum clusters, ranging from 13 to 923 atoms, as well as, on their island analogs that have no shell structures or gaps around the Fermi level. Calculations of this size have been made possible by leadership computing resources, containing up to 40,960 nodes, at Argonne National Laboratory. Looking at the density of states, a metal-like band structure starts to form at around 147 atoms. Oscillation in oxygen binding was observed on gold particles, consistent with oscillations in the Fermi-level due to s-shell effects. We find that gold particles experience significant quantum size effects below the critical size of 561 atoms. In contrast, quantum size effect ends more quickly on platinum, at only 147 atoms.

COLL 845

Assembly of nanoions via electrostatic interactions: Ion-like behavior of charged noble metal nanoclusters

Qiaofeng Yao*, qiaofeng.yao@nus.edu.sg, Zhentao Luo, Xun Yuan, Yue Yu, Chao Zhang, Jianping Xie, Jim Yang Lee.Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore, Singapore*

The assembly of ultrasmall metal nanoclusters (NCs) is of interest to both basic and applied research as it facilitates the determination of the cluster structure and the customization of cluster physicochemical properties. We present herewith a facile and general method to assemble charged noble metal NCs in water based on the electrostatic interaction between oppositely-charged species. We treat the ultra-small uniformly structured NCs with negative surface charge through the ionization of surface ligands (carboxylate anions) as ion-mimic nanomaterials (nanoions) which may be bridged by divalent cations (M^{2+}, *e.g.,* Zn^{2+} and Cd^{2+}) into extensive assemblies. The assembly is step-like and occurs only when the solubility product (K_{sp}) (the product of the equilibrium concentrations of surface carboxylate ions and divalent cations) is exceeded. The assembly formed as such can display a number of customizable morphologies (*e.g.,* spherical and tape-like) by controlling the diffusion of the divalent cations. The close packing of the NCs in the assembly also leads to the photoluminescence enhancement of NCs.

COLL 846

Regulating membrane adsorption of luminescent gold nanoparticles through pH

***Mengxiao Yu**, mxy091000@utdallas.edu, Chen Zhou, Jinbin Liu, Julia D. Hankins, Jie Zheng.Chemistry, The University of Texas at Dallas, Richardson, Texas 75080-1407, United States*

Inorganic nano particles with diverse functionalites hold great promise to address current challenges in biomedical research. However, control of interactions between NPs and cell membrane in a native biological environment is still hardly achieved due to nonspecific serum protein adsorption. Herein, we report that through surface engineering, luminescent gold nano particles can exhibit pH-dependent membrane adsorption even in the presence of serum proteins, which opens up a path to control in vivo behaviors of inorganic NPs at the in vivo level.

COLL 847

Electrochemical properties of gold nanomolecules

***Vijay Reddy Jupally**, vijayreddy0116@yahoo.com, Amala Dass Antonysamy.Chemistry and Biochemistry, University Of Mississippi, University, MS 38677, United States*

Gold nanomolecules comprise of precise number of gold atoms and ligands. Several magic sized gold nanomolecules are formed during conventional Brust-Schiffrin synthesis, which can be purified and isolated using techniques like size exclusion chromatography. Gold nanomolecules, like $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$, $Au_{67}(SR)_{35}$ and $Au_{144}(SR)_{60}$ show size depended optical and electronic properties. Smaller gold nanomolecules, behave similar to small molecules with large HOMO-LUMO gap and distinct optical absorption features. As the size of the gold nanomolecules increases, the properties shift toward bulk metal type behavior with smaller HOMO-LUMO gaps. In the present work, the electrochemical properties of several magic sized gold

nanomolecules are studied using cyclic voltammetry and differential pulse voltammetry techniques. Highly monodisperse gold nanomolecules are tested for electrocatalysis of oxygen reduction reaction, with potential applications towards development of fuel cells.

COLL 848

Green—gold $Au_{30}(S\text{-}t\text{-}C_4H_9)_{18}$ molecules: Mass spectrometry, optical, and structural studies

***Dave W. Crasto**, dwcrasto@go.olemiss.edu.Chemistry and Biochemistry, University of Mississippi, Oxford, MS 38655, United States*

Owing to their fascinating size-dependent properties, gold nanoparticles (<2nm) are of great interest in the forefront of various fields of scientific studies. In order to fully understand these properties, determination of the 3-dimensional arrangement of these molecular gold entities' atoms in space is of the utmost necessity. Recently, it has been shown that introducing bulky ligands to stabilize the overall framework in the methodological scheme serves to alter the discrete sizes of nanoparticles formed[1-2]. Results indicate a heightened Au:SR ratio in the product, an indication of the alteration of the core geometry as a factor of the increased crowding on the monolayer. However, a lack of structural knowledge pertaining to this new family of nanoparticles impedes further comprehension and understanding of the properties. Here, we present the total isolation of a 30 gold atom, 18 thiolate ligand nanoparticle, confirmed using MALDI-TOF Mass Spectrometry. Electrospray Ionization Mass Spectrometry was employed, taking advantage of the high-resolution isotopic distribution modeling, in order to assign the chemical formula $Au_{30}(S\text{-}t\text{-}C_4H_9)_{18}$, with the experimentally determined structure using SC-XRD.

1. *ACS Nano*, 2012, 6(**6**), *4903-4911.*

2. *J. Am. Chem. Soc.*, 2012, 134(**35**), *14295-14297*