COLL 1

Nanoparticles at the water-decane interface: equilibrium multi-scale simulations

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Pickering emulsions are finding practical applications in areas including cosmetics, drug-delivery, and even in-situ upgrade of bio-oil to fungible bio-fuels [Science 327 (2010) 68]. It is known that solid particles adsorb at water-oil interfaces to reduce the contact area between the two immiscible phases. Stable emulsions are obtained when the particles strongly adsorb at the interfaces. We will report here equilibrium MD simulation results employed to differentiate the behavior of silica-based nanoparticles used to stabilize either water-in-decane or decane-water emulsions. We will compare nanoparticles with similar surface properties, but different distribution of the surface groups. Particular attention will be given to Janus as opposed to homogeneous nanoparticles. The all-atom simulation results were used to parameterize dissipative particle dynamics simulations. Using DPD, we obtained interesting morphologies depending on nanoparticle concentration, and water-decane molar ratio in the various simulated systems. The simulation results will be discussed in relation to available experimental data.

COLL 2

Suppressing the coffee stain effect: How to control colloidal self-assembly in evaporating drops using electrowetting

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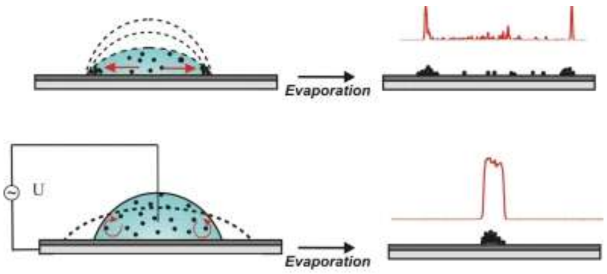
We study the influence of electrowetting on the formation of undesired solute residues, so-called coffee stains, during the evaporation of a drop containing non-volatile solvents. Electrowetting is found to suppress coffee stains of both colloidal particles of various sizes aand DNA solutions for alternating (AC) frequencies ranging from a few Hertz to a few tens of kHz. Two main effects are shown to contribute to the suppression: (i) the time-dependent electrostatic force prevents pinning of the three phase contact line. (ii) internal flow fields generated by AC electrowetting counteract the evaporation driven flux and thereby prevent the accumulation of solutes along the contact line.



COLL 3

Self-assembly of gold nanoparticles at the water/vapor interface

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The self-assembly of coated gold nanoparticles at the water/vapor interfaces are studied using explicit-atom molecular dynamic simulations. While it is often assumed that uniformly coating spherical nanoparticles with short organic lead to symmetric nanoparticles, we find that the high curvature of small nanoparticle and the relatively short dimensions of the coatings can produce highly asymmetric coating arrangements. At an interface this asymmetry of the ligands tends to orient the nanoparticles with the surface so as to minimize free energy. First results for individual gold nanoparticles of diameter 2-8 nm coated with alkanethiol ligands of various lengths and different end group will be presented. Results for the self-assembly of the multiple nanoparticles at the water/vapor interfaces will then be presented for the diameter 2 and 4 nm nanoparticles which show how these asymmetric and oriented coatings effect the interactions between nanoparticles and the structure of the resulting aggregate.

COLL 4

Composition-induced changes of particle laden oil-water interfaces, studied with microfluidics

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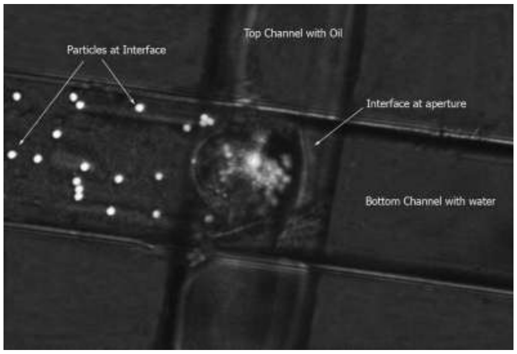
We developed a microfluidic chip in which two microchannels, containing aqueous and oil phases, meet each other at a horizontal interface. Confocal microscopy is used to study the adsorption, assembly and dynamics of colloidal spheres at water/decane interfaces. The aqueous phase composition, which controls dissociation and electrostatics, is explored for its effects on adsorption and assembly. The oil phase is

used to deliver fatty acids to the interface. This induces formation of a solidlike layer, which modifies the particle dynamics.



COLL 5

Colloidal particle interactions at the oil-water interface

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Colloidal particle interactions at the oil-water interfaceColloidal dispersions at fluid interfaces share many of the characteristics of bulk suspensions, including the ability to control the colloidal interactions to tailor their stability, structure and rheology. As a result, interparticle interactions between particles at the interface of immiscible fluids have been intensely studied. At interfaces in which one of the fluids has a low dielectric permittivity, repulsive interactions arise from the asymmetric charge dissociation across the interface, which creates a dipole-dipole repulsion that is significantly stronger and longer-ranged than screened Coulomb interactions in an aqueous medium. Under pristine conditions, these interactions lead to remarkable two-dimensional crystals that are stable for weeks. Upon the addition of salt or surfactants, particles aggregate to form clusters and ramified microstructures. Here, we show by direct particle pair measurements that the attraction between spherical particles is consistent with capillary forces caused by local deformation of the interface. A combination of dipole-dipole repulsion and capillary attraction is sufficient to describe all of the pairwise interactions measured between colloids at an oil-water interface [1].

[1] Park, B. J.; Furst, E. M. Soft Matter 2011, 7, 7676–7682.

COLL 6

Generation of Janus bubbles and their behavior at an air-water interface

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Janus particles are colloidal particles with one of the hemispheres hydrophilic and the other hydrophobic. Due to their anisotropy, they have been shown to have unique assembly behaviors in solutions. They also can be useful in numerous applications including emulsion stabilization and fabrication of optical displays. In this study, we introduce a method to generate Janus bubbles. Janus bubbles present a unique opportunity to study the behavior of Janus particles at an air-water interface due to their buoyancy. Janus bubbles are prepared by gold deposition onto a dried monolayer of SiO_2 nanoparticle-shelled bubbles on a planar substrate. These nanoparticle-shelled bubbles – the precursors to the Janus bubbles – are generated with a microfluidic approach that allows for the generation of monodisperse and stable bubbles. The gold hemisphere of the Janus bubbles is subsequently modified with an alkane-thiol. Interfacial assembly of amphiphilic Janus bubbles at an air-water interface shows that they interact with one another via long-range attractions. The origin of this long-ranged attraction is believed to be quadrupolar capillary interactions due to the undulation of the three-phase contact line around the Janus boundary. We directly measure the interparticle forces between the Janus bubbles using a particle tracking method. We also investigate the orientation of Janus bubbles using a gel-trapping technique, which shows that most of the bubbles are in their equilibrium position.

COLL 7

Dynamic adsorption of micro- and nanoparticles to fluid-fluid interfaces in a microchannel

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Using microfluidic tools, we will study the dynamic adsorption of particles to highly-curved interfaces inherent in microfluidic systems. Using a microtensiometer capable of measuring interfacial properties of small (radius ~10^{-5} *m*) droplets, we will measure the dynamic interfacial tension and interfacial elasticity during bulk diffusion of nanoparticles to an interface. In tandem with these experiments, we will use microfluidic devices to observe particle adsorption to a clean, mobile droplet interface under geometric confinement. We will show that the combined effects of fluid shear on the interface and dynamic interfacial properties of the droplet lead to unique droplet shapes that relate to the particle coverage at the interface. Using this technique, we are capable of tailoring the surface concentration of particles on the interface.

COLL 8

Near-field capillary interaction between colloidal rods: Cylinders and ellipsoids

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Owing to their anisotropic shape, rod-like particles – including ellipsoids and cylinders - adsorbed at fluid interfaces experience strong, anisotropic capillary interactions. While in the far field ellipsoids and cylinders behave similarly, upon contact cylinders assemble end-to-end forming linear chains and ellipsoids assemble side-to-side to form flexible structures. We explain why small differences in shape between cylinders and ellipsoids can lead to dramatic differences in near-field capillary interactions, and relate these interactions to the mechanics of the microstructure. We present experimental results to confirm that chains of cylinders exhibit a large resistance to bond-bending deformations. These results have important implications for the rheology of particle-laden monolayers.

COLL 9

ATR-IR Spectroscopy for studying particle-particle interaction at solid-liquid interface during sedimentation and under applied electric fields

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We have developed a new method to study the dynamics of particle mobility in coating suspensions using the principles of ATR spectroscopy. Experiments have been performed with paper coating formulations consisting of kaolin and calcium carbonate pigment particles and styrene - butadiene latex binders. Principles such as binder migration will be presented and are observed dynamically under different drying conditions and conducted under sedimentation and application of external electric fields. In this presentation, we will describe the experimental methods used to measure particle mobility under sedimentation and applied fields and present data and theoretical models for describing the migration of particulates during drying.

COLL 10

Measuring protein structural and stability changes upon protein-nanoparticle interactions

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Properties of nanoparticles (NP) in biological system strongly depend from the structure and stability of the proteins that interact with them. Unfortunately, this information is very difficult to obtain.

Here we show that by using Synchrotron Radiation Circular Dichroism (SRCD) it is possible to detect changes in the secondary structure and stability of different classes of proteins upon interaction with nanoparticles. In some cases, it is also possible to identify the protein-nanoparticle interaction site by using Nuclear Magnetic Resonance spectroscopy [1]. In particular, we show that by using the SRCD beam line we can detect structural changes of proteins in the nanomolar concentration range when they form protein-nanoparticle complexes. The adsorption of protein on NP modifies their melting point in a composition and size dependent manner, indicating that the protein corona formation is strongly depending on the nanoparticle physic chemical properties

[1] Calzolai et al., Nano Lett. 2010, 10:3101-5.

COLL 11

Characterizing linear light harvesting complex II assemblies in native photosynthetic membrane of purple bacteria

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How light energy is harvested in a natural photosynthetic membrane through energy transfer is closely related to the stoichiometry and arrangement of light harvesting antenna proteins in the membrane. The specific photosynthetic architecture facilitates a rapid and efficient energy transfer among the light harvesting proteins (LH2 and LH1) and to the reaction center. Here we report the identification of linear aggregates of light harvesting proteins, LH2, in the photosynthetic membranes under ambient conditions by using atomic force microscopy (AFM) imaging and spectroscopic analysis. Our results suggest that the light harvesting proteins, LH2, can exist as linear aggregates of 2 to 8 proteins in the photosynthetic membranes, and the protein distributions are highly heterogeneous. LH2 antenna proteins are responsible for absorbing most of the light energy for photosynthesis, and efficient intra- and inter-molecular energy transfers of LH2 complexes are important for the overall efficiency of the light harvesting mechanism. We combined AFM imaging and spectroscopic analysis with *J* aggregate theoretical calculations to characterize the linear aggregation of LH2. AFM images reveal the linear aggregation of LH2, where the LH2 complexes are tilted to the plane of the photosynthetic membrane. The spectroscopic results support the attribution of LH2 complexes in the membrane to linear aggregates. The calculated values for the absorption, emission and lifetime using a model developed from *J* aggregate theory are consistent with the experimentally determined spectroscopic values, further proving a *J* type aggregation of the LH2 complexes in the photosynthetic membrane.

COLL 12

Protein adsorption onto poly-carboxybetaine methacrylamide (PCBMA)-grafted Si nanoparticles (NPs): A thermodynamic investigation

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Understanding the factors regulating biofouling is crucial for the design and implementation of biomaterials. PCBMA belongs to a family of zwitterionic polymers, where the formation of a strong hydration layer is thought to inhibit protein adsorption. However, a mechanistic understanding of how both polymer layer (hydration, charge, etc.) and protein properties (size, charge, 'stiffness', etc.) affects protein-surface interactions is largely ill-defined. In this study, we are presenting a comprehensive thermodynamic profile for the adsorption of Human Serum Albumin (HSA) and α-lactalbumin onto PCBMA-NPs with chains varying in end-group chemistry (phosphonate and TEMPO) and spacer-group length in the zwitterion. In general, preliminary results indicate that protein adsorption onto PCBMA-NPs is entropically-driven; with electrostatic forces playing the main role in α-lactalbumin adsorption and hydrophobic interactions being important in HSA adsorption. Furthermore, calorimetric studies suggest that maintaining water molecules within the polymer-protein interface may largely inhibit protein adsorption.

COLL 13

Molecular recognition of esterase plays a major role on the removal of fatty soils during detergency

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We describe for the first time, the use of an esterase with null activity on the removal of fat from the surface of a cotton substrate. Similar levels of fat removal were found for both null and wild-type proteins, despite that only the wild type protein yielded fatty acids. Our results show that **molecular recognition of esterase plays the major role on the removal of fatty soils** , giving important guidelines for the design of detergent enzymes for the future. The advantage of using null esterase enzymes it is the avoidance of the rancid smell for short chained fatty acids after esterase treatment.

COLL 14

Structural, morphological, and kinetic studies of beta-amyloid peptide aggregation on self-assembled monolayers

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The interaction of ß-amyloid (Aß) peptides with cell membrane and other artificial surfaces are important for the fundamental understanding of Aß aggregation and toxicity mechanisms in Alzheimer's disease. In this work, using circular dichroism, atomic force microscopy, surface plasmon resonance, and molecular dynamics simulations, we studied the adsorption, aggregation, and conformational changes of $Aß_{1-42}$ from monomers to intermediate oligomers to mature fibrils on the SAMs terminated with CH_3, OH, COOH, and NH_2 groups. The seeding effect of Aß on the kinetics of Aß aggregation on different SAMs is also examined. Experimental data show that all of these SAMs greatly accelerate the formation of ß-sheets and amyloid fibrils through surface-enhanced interactions, while simulation results reveal that both hydrophobic and electrostatic interactions contribute differently to different Aß-SAM systems at different aggregation stages. A postulated mechanism is proposed to describe the structure and kinetics of Aß aggregation from aqueous solution to the SAMs.

COLL 15

Densely packed poly(ethylene glycol) improves orientation of antibody on substrate surface

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Protein-immobilized substrates have been widely used in a number of applications for biosensing and bioseparation systems. We have been focusing on construction of antibody/poly(ethylene glycol) tethered chain hybrid surface in detail. In order to examine the adsorption behavior of antibody fragments (Fab') directly immobilized on a gold surface through S-Au linkage, analyses by surface plasmon resonance (SPR), fluorometry, and atomic force microscopy (AFM) with an excellent blocking technique by the consecutive treatments of longer-poly(ethylene glycol) (PEG) (MW = 5k) and shorter-PEG (MW = 2k), abbreviated as mixed-PEG layer formation, were performed.

From these analyses, orientation of the surface antibody was maintained with densely packed PEG chains tethered on substrate surface. We have also investigated immobilization conditions of whole antibody on active ester surface and found that basic pH disfavored conjugation of anti-hFT to the surface, but remarkably increased its antigen recognition in comparison to that at neutral pH.

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COLL 16

Effect of spatial distribution of epitopes within glycopolymer brushes on the binding of Con A: From monovalent to multivalent interaction

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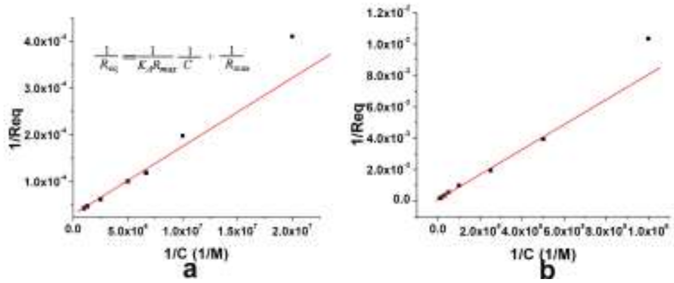
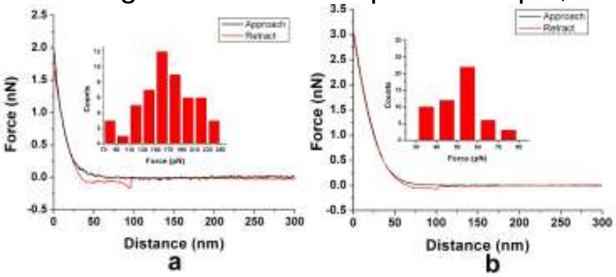
Glycopolymer brushes with different spatial distribution of epitopes were successfully prepared on the SPR chips. The interaction between lectin and carbohydrate residues in brushes were evaluated by SPR and AFM force spectroscopy. The apparent affinity constant, sensitivity to change of solution, unbinding force between Con A and carbohydrate residues in brushes show dependence on the composition, not on grafting density. The brushes with different mannose contents exhibited the affinity constant from 1.8×10^4 to 2.2×10^6 M^{-1},



unbinding force from 51.3 pN to 171 pN,



which is characteristic for monovalent and multivalent interaction between Con A and mannose. The difference in affinity constant and unbinding force is attributed to not only the effective concentration of the ligand in the close proximity of the binding sites of Con A but also the steric interference arising from the inert galactose units.

COLL 17

Effects of proteins hydrophobicity and charge anisotropy on their adsorption behavior onto polyelectrolyte layers

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Ellipsometry was used to investigate the influence of ionic strength (*I*) and pH on the adsorption of bovine serum albumin (BSA) or b-lactoglobulin (BLG) onto preabsorbed layers of two polycations: poly(diallyldimethylammonium chloride) (PDADMAC), or poly(4-vinylpyridine bromide) quaternized with linear aliphatic chains of two (QPVP-C2) or five (QPVP-C5) carbons. Comparisons among results for the three polycations reveal hydrophobic interactions, while comparisons between BSA and BLG -- proteins of very similar isoelectric points (pI) - indicate the importance of protein charge anisotropy. At pH close to pI, the ionic strength dependence of the adsorbed amount of protein (Γ) displayed maxima in the range $10<I<25$ mM corresponding to Debye lengths close to the protein radii. Visualization of protein charge by Delphi suggested that these ionic strength conditions corresponded to suppression of long-range repulsion between

polycations and protein positive domains, without diminution of short-range attraction between polycation segments and locally negative protein domains, in a manner similar to the behavior of PE-protein complexes in solution. This description was consistent with the disappearance of the maxima at pH either above or below pI. In the former case, Γ values decrease exponentially with $I^{1/2}$, due to screening of attractions, while in the latter case adsorption of both proteins decreased at low *I* due to strong repulsion. Close to or below pI both proteins adsorbed more strongly onto QPVP-C5 than onto QPVP-C2 or PDADMAC, due to hydrophobic interactions with the longer alkyl group. Above pI, the adsorption was more pronounced with PDADMAC, because these chains may assume more loosely bound layers due to lower linear charge density.

COLL 18

Control and switching of the interaction of model proteins with polymer brushes

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Polymer brushes are a versatile tool to control and switch interfacial properties. By composing polymer brushes of two or more specific polymers/ polyelectrolytes a big variety of possibilities arises to control the interaction of those surfaces with proteins. Using polymers responsive to environmental conditions as pH or temperature, the interfacial properties of mixed brushes may be switched. For using this possibility to switch protein adsorption too, it is essential to study mechanism and kinetics of protein adsorption in detail to identify the leverage for an adsorption/desorption control. We studied the adsorption of model proteins on swelling polymer brush systems by using *in-situ*-ellipsometry, *in-situ*-ATR-FTIR spectroscopy as well as AFM. With a coupled spectroscopic ellipsometry (SE) - quartz crystal microbalance (QCM-D) experimental setup, we obtained quantitative information about the amount of buffer components coupled to a polyelectrolyte brush during swelling and protein adsorption.

COLL 19

ToF-SIMS characterization of immobilized Protein G orientation

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Surface analysis instrumentation provides significant information about the protein immobilization process and the structure of immobilized proteins. Our recent studies have used Protein G B1 variants to examine protein orientation when the size of the protein is similar to the ToF-SIMS sampling depth (~2-3nm). Two variants with a single cysteine introduced at either end were immobilized via the cysteine thiol onto maleimide oligo(ethylene glycol) (MEG) self-assembled monolayers (SAMs). XPS was used to measure the amount of immobilized protein and ToF-SIMS was used to measure the protein orientation and to confirm covalent attachment of protein. ToF-SIMS data showed enrichment of mass peaks from amino acids located at the end of the protein opposite the cysteine surface position, consistent with end-on protein orientations. ToF-SIMS also showed a charged mutant of Protein G B1 was immobilized in opposite orientations on positively (amine) and negatively (carboxylic acid) terminated SAMs.

COLL 20

Controlling trans-membrane ion conductance through gramicidin-based nanopores

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A significant challenge in designing self-assembled molecular systems is the development of reliable and predictable methods to control the function of these assemblies. Here, we evaluate the effect of charged groups conjugated to gramicidin A (gA, an ion channel-forming peptide) on the lifetime of these self-assembled ionic pores. We demonstrate that charged groups attached to the C-terminus of gA can dramatically affect the lifetime (τ) and conductance (γ) of the channel in bilayers of phosphatidylcholine lipids. Since τ and γ dictate ion flux through gA pores, they represent the most important functional parameters of these self-assembled structures. Interestingly, we observed opposing trends for the difference in τ and γ of positively versus negatively charged derivatives of gA as a function of the ionic strength in the electrolyte. This contrasting behavior made it possible to control the functional properties (τ and γ) of gA pores with light of different wavelengths by introducing a photoactive spiropyran group, which can be switched dynamically between a positive and a neutral state. The methods reported here for using charge to influence the function of gramicidin channels in membranes represents a step towards achieving the level of control between structure and function of self-assembled structures that is typically observed only in nature.

COLL 21

Molecular interactions between model cell membranes and antimicrobial peptides, cell penetrating peptides, and nanoparticles

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Sum frequency generation (SFG) vibrational spectroscopy has been applied to investigate molecular interactions between model cell membranes and various materials including antimicrobial peptides, cell penetrating peptides, and nanoparticles. Solid substrate supported single lipid bilayers were used as model cell membranes. SFG can probe the molecular structure of each leaflet of the bilayer and the peptide or nanoparticles individually in situ in real time. A variety of peptides, including magainin 2, MSI-78, pep-1, cecropin, and tachyplesin I were examined. For the nanoparticle studies, the results obtained from the model cell membrane studies using SFG can be well correlated to those obtained from the live cell studies using fluorescence imaging.

COLL 22

Energetics and dynamics of direct cell-penetrating peptide translocation using atomic force microscopy

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Many drugs and molecular biology reagents require drug delivery agents, like cell penetrating peptides (CPPs), that can shuttle the drugs into cells. In these delivery systems it is important to control the CPPs' translocation mechanism to avoid endosomal degradation and harmful side effects. There is currently much controversy whether these agents can directly penetrate lipid membranes or not. Here we demonstrate that atomic force microscopy (AFM) with "δ"-functionalized probes can characterize a CPP's tendency to directly penetrate cells. To mimic cell membrane translocation, CPP-functionalized probes are pushed through stacks of lipid membranes. The position of the CPP during translocation, as well as the energy barrier to bilayer penetration, indicate: whether CPPs reduce the energy barrier to penetration; whether CPPs disrupt lipid bilayers; and the energy landscape during translocation. We describe the results for three different CPPs to show that AFM can differentiate between drug delivery agents that are likely to spontaneously penetrate lipid bilayers (penetratin) and those that do not (TAT and a lysine oligomer).

COLL 23

Small-angle X-ray scattering studies of chemically-tailored polymers for regulating membrane function

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The use of amphiphilic block copolymers as agents to modify cell membrane structure and function has been an area of increasing research interest. Of particular interest has been the use of commercially available amphiphilic triblock copolymers of PEO_n-PPO_m-PEO_n, so-called Pluronics or Poloxamers. Numerous investigations have explored their use in a wide range of biomedical applications, including modifiers in drug delivery, in-situ generated implants, synthetic chaperones, barriers against bacterial adsorption, neuroprotective and restorative agents, and soft tissue injury treatments (including stroke and electrical / thermal burns). In our prior work, we have identified specific polymer architectures among this family of triblock copolymers that seal defects or that form anti-microbial barriers on cell surfaces.[1] Specifically, Small-angle X-ray scattering studies permitted determination of the 1D electron density maps of the polymer associated with a model biological membrane. More recently, we have chemically modified these polymers with quorum sensing regulating groups (e.g., phosphate) and examined how introduction of these groups alters the polymers interaction with the lipid bilayer. This work provides a strong foundation for a significantly larger effort coupling basic research on the physical principles of polymer architecture and their relationship to the association and function of cell membranes.[2]

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COLL 24

Polymer-tethered lipid bilayer: A versatile model membrane platform of tunable dynamic and elastic properties

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The solid-supported, physisorbed polymer-tethered lipid bilayer consisting of phospholipids and lipopolymers represents a highly versatile model membrane architecture. This membrane system is not only well-suited for biophysical studies on transmembrane proteins in well-defined lipid environments, but also exhibits fascinating tunable dynamic and elastic properties. Experiments on glass-supported, physisorbed polymer-tethered monolayers illustrate that the biaxial stress in the membrane system can be regulated by the molar concentration of lipopolymers and/or cholesterol. Interestingly, membrane buckling structures can be observed as a quantitative measure of biaxial stress. A metric can be derived between elastic properties and buckling structures by combining mean-field calculations of polymer-tethered lipid membranes with buckling theory of an Euler column. We also demonstrate that lipopolymers and cholesterol have a substantial influence on membrane organization and obstructed diffusion of lipids/membrane proteins in a polymer-tethered lipid bilayer. The versatility of the membrane system is furthermore demonstrated by biophysical studies on the ligand-mediated sequestering of integrins in raft-mimicking lipid mixtures using sensitive optical detection methods. Our data show that binding of native ligands notably enhances the affinity of $\alpha_v\beta_3$ and $\alpha_5\beta_1$ integrins for cholesterol-enriched lipid environments without altering the integrin oligomerization state, thus highlighting the importance of lipid heterogeneities in membrane protein functionality.

COLL 25

Polymer cushoned lipid membranes from the molecular to macro-scale

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Over the past several decades, supported lipid bilayers have been used as model systems of cellular membranes, to investigate various membrane interactions, and as platforms for development of bio-sensors. Precise structural characterization by neutron and x-ray scattering [figure 1] offers a wealth of insight into membrane organization, self-assembly, and domain formation as well as how membranes respond to changes in their environment, e.g. temperature, protein binding, etc. In this talk, I will discuss some recent advances in our understanding of polymer cushioned membranes (Nano Letters 2011), lateral domain formation, a novel lipid phase due to specific-multivalent protein binding, their potential use in biotechnology applications, and highlight the importance of scattering techniques for structural characterization.

COLL 26

Structure-function relationship: Importance of molecular interactions in cellular membranes investigated with Langmuir monolayers

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Model cell membranes can be used to pinpoint the molecular characteristics of certain molecules that enable them to interact with cell membranes in relation to medical purposes. Langmuir Monolayers of phospholipids formed at an air-water interface allow for the measurement of molecular interactions by monitoring surface pressure as a function of molecular area. Through the analysis of isotherm plots, non-ideal mixing, and compression moduli, these model membrane systems provide insight into the structural characteristics that enable cholesterol precursors to interact with inner leaflet lipids in relation to Alzheimer's Disease; the components in honey that result in its ability to act as an antibacterial agent; and the types of drug-delivery vehicles that are used.

COLL 27

Increasing Surface Enhanced Raman Spectroscopy effect of RNA and DNA components by changing the pH of silver colloidal suspensions

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This research focused on establishing the parameters for enhancing the Raman signals of DNA and RNA constituents using silver nanoparticles as surface enhanced Raman scattering substrates. Silver nanospheres had a surface plasmon band at ~ 384 nm and an average size of 12 ± 3 nm. The nanoparticles' surface charge was manipulated by changing the pH of the Ag colloidal suspensions in the range of 1 to 13. At pH ~1, 11, and 13 the SERS signal decays noticeably compared with neutral pH values. At pH 3, 5 and 7 the spectral profiles of adenine were clearly observed with a high enhancement in the ring-breathing band. The phosphate and sugar stretching modes are observed at 1010 and 1099 cm^{-1} respectively in the normal Raman spectra. However, the SERS spectra of dAMP and AMP did not have any increase of these signals. This indicates that the biomolecules are bound to the nanoparticle surface through the adenine moiety. The adenine ring-breathing band dominates the SERS spectra of all the biomolecules. DLS results showed the effect of pH changes in the particle size and aggregation after mixing. The high Z values at pH 1 and 13 demonstrated the decrease of the SERS signals as result of aggregation and flocculation of the silver colloid. Before aggregation the nanoparticles at pH 7 had a Z value of 58.66 nm. Moreover, when mixing with adenine, the Z results revealed the degree of aggregation of adenine-silver NPs at pH 7 with a Z value of 768 nm. This hydrodynamic radius is higher compared with the rest of biomolecules and reflects the high SERS effect and low detection limit of adenine. Low concentrations as 0.7 μM were detected under the experimental conditions.

COLL 28

Plasmonic properties of gold nanocrescents as isolated structures and in ordered arrays

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Gold nanocrescent (AuNC) structures demonstrate localized surface plasmon resonances (LSPR) that occur at highly tunable wavelengths over a broad spectral

range, support localized, enhanced electromagnetic fields and can be selectively excited via polarization of light. We used nanosphere template lithography based on polystyrene bead templates to fabricate AuNCs. Random dispersion of the polystyrene templates resulted in isolated nanocrescents with optical properties that were studied using ensemble-based measurements. Dense, ordered arrays of AuNCs were also fabricated by hexagonally close-packing monolayers of polystyrene beads and using an etching process to reduce template diameter while maintaining organization. Nanocrescent arrays exhibit higher extinction values, infrared peak broadening, visible peak narrowing and overall blue-shifting of the plasmon bands compared to isolated nanocrescents. Implications of the plasmonic properties of isolated and ordered arrays of nanocrescents for application as substrates for surface enhanced spectroscopies, LSPR sensing and non-linear spectroscopy and imaging will be discussed.

COLL 29

Modified gold nanorods as extrinsic surface enhanced Raman labels for bioassays

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Chemically modified spherical gold nanoparticles have been used as extrinsic labels for surface enhanced Raman scattering (SERS) detection of surface based assays. Rod-shaped gold nanoparticles should provide higher sensitivity and potentially stronger binding via multivalent interactions. The challenge in employing gold nanorods for this application is the replacement of the shape directing surfactant layer on the surface. We have developed a modification procedure to replace the cetyltrimethylammonium bromide (CTAB) layer on gold nanorods with a self-assembled monolayer (SAM) teminated with ethylene glycol (EG) and COOH groups. The nanorods are made SERS active by place exchange with 4-nitrobenzenethiol (NBT). We will present results that track the modification procedure. Antibodies are conjugated to the nanorods through the terminal –COOH group. The antibody conjugated nanorods were used for SERS readout in sandwich immunoassays and provide extremely low detection limits. A direct comparison with spherical nanoparticles will be presented.

COLL 30

Lab on a bubble (LoB): Separations and analysis on buoyant SERS bubbles

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Our presentation will describe the development and preparation of a new class of materials for surface enhanced Raman scattering (SERS) comprised of gold

nanoparticles coated onto buoyant silica microbubbles. These materials allow create a new type of molecular assay designated as a Lab on a Bubble (LoB). LoB materials serve as a convenient platform for the detection of analytes in solution and offer advantages over traditional colloidal gold and planar SERS substrates. An example assay is presented using LoB materials and cyanide detection. Cyanide binds to SERS-active, gold-coated LoBs and is detected directly from the corresponding SERS signal. A second example, a sandwich LoB assay for cholera toxin (CT) will be presented. The CT assay is composed of antibody modified silica bubbles and modified silica coated nanoparticle reporters. Our current detection level for CT is ~ 2000 ng where the assay format is a mass determination -- independent of the sample volume.

COLL 31

Surface functionalization of nanoparticles in the aerosol state: An alternative preparation strategy for SERS substrates

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Noble nanoparticles (Ag and Au) were generated using a home-built source in which aerosol particles were formed by flowing nitrogen gas over near-molten metal. The surfaces of mobility-selected particles were thermally processed in the aerosol state by allowing them to interact with gas-phase molecules of interest. Particle concentrations and size distributions were characterized by differential mobility analysis (DMA). Changes in mobility diameter resulting fro thermal processing were monitored by tandem differential mobility analysis (TDMA). Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) were used to charaterize particle morphology, structure and surface chemistry. The resulting mobility-selected and surface modified particles were used as probes for surface-enhanced Raman spectroscopic (SERS) studies. These results suggest an alternative route to the production of surface-modified particles, and they establish a correlation between particle size and surface in SERS applications.

COLL 32

Controlling nanoparticle architecture for directly monitoring drug metabolism

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Nanomaterials are being used to improve disease diagnostics and treatment. Undoubtedly, for more nanoparticle based assays, tests, and treatment plans to reach the clinic; detection sensitivity, target selectivity, and assay versatility must be realized in a robust, low cost, and field-portable package. Herein, unique solution-phase surface enhanced Raman scattering (SERS) substrates will be used to detect drug and drug metabolites in the presence and absence of relevant enzymes. The importance of

nanoparticle engineering, surface chemistry, and stability will be emphasized. Advantages of using these materials for detection and challenges in achieving reproducible detection will be discussed.

COLL 33

Chemical assembly of modified Au nanoparticle clusters on diblock copolymer templates for SERS enhancement

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Using chemical self-assembly techniques, we attached monodisperse, colloidal gold nanoparticles on self-organized polymer templates, patterning arrays of nanoparticle clusters with sub-10 nanometer interparticle spacing to engineer enhanced optical fields. Poly(methyl methacrylate) domains in phase-separated polystyrene-*b*-poly(methyl methacrylate) diblock copolymer thin films were chemically modified with surface amine chemical groups for controlled arrangements. Chemically synthesized gold nanoparticles, from 10 and 20 nanometer diameter sample sets, were attached to the amine-functionalized surfaces using EDC crosslinking chemistry with thioctic acid ligand-bound to the nanoparticle surface, preferentially immobilizing the Au nanoparticles on PMMA domains of the copolymer template. By controlling particle size relative to PMMA domain size, nanoparticle clustering was controlled. SERS measurement of the planar nanoparticle assemblies showed uniform signal enhancement across each samples with 10^7 maximum signal intensity enhancement factor and reusability of SERS substrates with simple analyte removal between application.

COLL 34

Fabrication of SERS devices by combining controlled synthesis with lithographic methods

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Plasmonic structures have been of great intrerests due to their various applications such as surface-enhanced Raman spectroscopy (SERS) and plasmon-enhanced photovoltaics. Driven by these specific applications, control over individual plasmonic structures and manipulation of them into ordered assemblies have been two major focuses in the field. In this presentation, I will demonstrate the combination of control synthesis with lithographic methods in efforts for two aspects: 1) tunable surface plasmonic bands by controlling shapes and structures; 2) ordered assemblies formed through soft lithography, etc.. Specifically, their applications in SERS detection have

been explored based on the fabrication of plasmonic structures. It is expected that the present work will enable us to manipulate plasmonic structures and their assemblies and open the door to new applications in plasmonics.

COLL 35

Fundamental studies of rhamnolipids and their synthetic mimetics: Enhanced understanding of structure-function

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Rhamnolipids are biosurfactants produced by various strains of *Pseudomonas aeruginosa*. The chemical structure-surface activity relationships for rhamnolipids and synthetic rhamnolipid mimetics were investigated using surface tension measurements and their aggregation was characterized by dynamic light scattering measurements. In order to probe these relationships, rhamnolipid mimetics were designed by a strategy of 'truncation modification' of the naturally-occurring rhamnolipids and synthesized. Studies will be presented in which the behavior of the biosynthesized monorhamnolipids from *P. aeruginosa* ATCC 9027, predominantly the L-rhamnosyl-β-hydroxydecanoyl-β-hydroxydecanoate, is compared to the single chain analogue, the L-rhamnosyl-β-hydroxydecanoic acid, and a series of synthetically produced rhamnopyranoside mimetics. Large differences in critical micelle concentration are observed across this series of molecules that is rationalized by molecular structure and resulting molecular shape.

COLL 36

Cubosomes and hexasomes from bis(triazolium) gemini surfactants

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Gemini surfactants have recently been shown to exhibit unusual aqueous lyotropic self-assembly behavior, especially, the ability to form bicontinuous cubic morphologies with non-constant mean curvatures such as double gyroid, double diamond, and primitive structures. We have recently developed a modular synthesis of gemini bis(triazolium) surfactants that enables facile access to a wide variety of surfactant structures, and we have fully characterized their aqueous self-assembly behavior. These studies show that these bis(triazolium) surfactants exhibit a pronounced tendency to form cubosomes and hexasomes in aqueous media over large amphiphile concentration windows (10-30 wt% wide). Furthermore, we have demonstrated that the choice of counterion plays a critical role in governing both the morphologies as well as the stabilities of these assemblies.

COLL 37

Surface active ionic liquids: Head-group effect on micellar properties and dynamics of 1-alkyl-3-(n-hexadecyl)imidazolium chlorides

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The impetus for the increasing interest in studying surface-active ionic liquids, SAILs, is the potential for their use, *e. g.*, in nanotechnology and biomedicine. These applications require understanding the relationship between surfactant structure and aggregation in solution. This need has prompted us to synthesize and study a novel series of SAILs, 1-R-3-(1-hexadecyl)imidazolium chlorides; R = ethyl, propyl, butyl and pentyl) and compare the results with 1-(1-hexadecyl)-3-methylimidazolium [1].

The thermodynamic parameters of micellization were determined in 15-75 °C range. The cmc decreases when the cationic headgroup volume is increased by an alkyl substituent, probably due to hydrophobic interactions. Self-diffusion coefficients, $D_{\mathbf{obs}}$, were determined at 25 °C by pulsed field gradient $^{\mathbf{1}}$ H-NMR (PFG-NMR). Their values indicate the formation of pre-micellar aggregates, which is strongly influenced by the alkyl substituents.

[1] P. D. Galgano, O. A. El Seoud, J. Colloid Interface Sci. 345 (2010) 1.

COLL 38

Influence of tetraalkylammonium bromides on the complexation behavior of poly(N-vinylformamide) and sodium dodecyl sulfate

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The effect of tetraalkylammonium bromides (R_4NBr) on the complexation behavior between PNVF and SDS has been investigated by using pyrene fluorescence, ^1H, 2D NOESY, and PFG diffusion NMR experiments. The effect of addition of Me_4NBr and Et_4NBr to PNVF-SDS complexation is only to decrease the SDS *cac*, which is similar to the inorganic salt such as NaCl. The affinity between SDS with both Bu_4N^+ and Pr_4N^+ is very strong through the hydrophobic interaction. Therefore, in the ternary PNVF/SDS/R_4NBr solution, only the Bu_4N^+-conjugated SDS micelles can be found as the [SDS]/[$Bu_4N^+Br^-$] ratio < 1 (for $Pr_4N^+Br^-$, < 0.6). Interestingly, once the [SDS]/[$Bu_4N^+Br^-$] ratio > 1 (for $Pr_4N^+Br^-$, > 0.6), the PNVF chains could penetrate into the Bu_4N^+-conjugated aggregates, resulting in the ternary PNVF-(SDS-Bu_4N^+) complexes. The complexation of PNVF and SDS in the presence of R_4NBr is proposed in

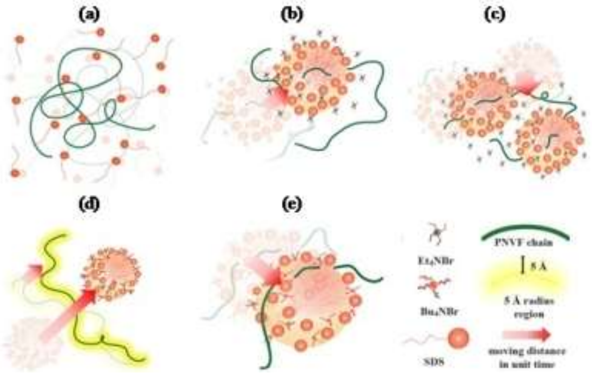

figure1 . Complexation behavior for 2 mM SDS + 5 g/L PNVF (a), 13.2 mM Et_4NBr + 2 mM SDS + 5 g/L PNVF (b), 13.2mM Et_4NBr + 10mM SDS + 5g/L PNVF (c), 13.2 mM Bu_4NBr + 10 mM SDS + 5 g/L PNVF ([SDS]/[$Bu_4N^+Br^-$] ratio < 1) (d) and 13.2 mM Bu_4NBr + 20 mM SDS + 5 g/L PNVF ([SDS]/[$Bu_4N^+Br^-$] ratio > 1) (e).

COLL 39

Relationships between structure-interfacial-functional properties: The rheology at interfaces from small to polymeric carbohydrate-based surfactants

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Amphiphilc molecules are one of the most important compounds in our planet owing to their fundamental role as catalysts of interfacial free energy in nature, biological systems, and manufacturated products [1]. Their chemical structure and configuration, which governs their properties and activities, may be classified in small, intermediate, and large sizes. To better understand the effect of such a parameter, the behaviors of various carbohydrate-based surfactants, from small to polymeric molecular structures at the air-water interface, and in bulk liquid for their ability to form and stabilize related colloidal systems like micelles and foams have been investigated. In particular, rheological properties including elasticity and viscosity components at the air-water interface have been determined by oscillatiory mode under different oscillation frequency and surfactant concentration conditions using a pending drop tensiometer system. Their micellar and foaming properties have been characterized and evaluated in terms of CMC-micelle size and formation-stability, respectively.

Reference:
1. Razafindralambo, H.; Blecker, C.; Paquot, M., Screening of Basic Properties of Amphiphilic Molecular Structures for Colloidal System Formation and Stability. In Amphiphiles: Molecular Assembly and Applications, American Chemical Society: 2011; Vol. 1070, pp 53-66.

COLL 40

Synthesis and surfactant properties of oligofructan esters

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Surfactants based on oligofructans were prepared by esterification with lauryl phosphonate, which was synthesized by reaction of lauroyl chloride with trimethylphosphite. Series of lauryl esters were made with fructose (F), sucrose (S) and oligofructans from Orafti®P95 (FO) in N-methylpyrrolidone using NH as catalyst. The degree of substitution (DS) was controlled by stoichiometric amounts of lauryl phosphonate. The products obtained were $FO_{0.98}$ (lauryl-oligofructose with DS 0.98), $FO_{0.34,}$ $FO_{0.16,}$ $F_{1.54,}$ $F_{2.04}$ and $S_{1.14}$ as determined by ^{1}H- and ^{13}C-NMR. The theoretical HLB of the products ranged in between 6.8 and 16.9 of the Griffin scale. CMC was determined by a colorimetric method. It was found that CMC of FO esters was directly proportional to the GS, contrary to the behavior of F and S. Foaming and emulsion stability properties of monosaccharide esters were superior to FO esters. It can be concluded that the properties of surfactants based upon oligofructans can be tuned by varying the HLB.

COLL 41

Shape-persistent micelles bearing calix[4]arene building block

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A series of cationic calix[4]arene-based lipids with alkyl chains of varying length were newly synthesized and found to form spherical micelles at low pH (protonated state of the amine headgroup) for propyl and hexyl tails. The size monodispersity of the CaL[4]C3 spherical micelles was confirmed with analytical ultracentrifugation, whereas CaL[4]C6 showed polydispersity. From SAXS, static light scattering, and analytical ultracentrifugation, the aggregation numbers for the CaL[4]C3 and CaL[4]C6 spherical micelles were evaluated at 6 and 12, respectively.

COLL 42

Reversible photorheological fluids induced by transition between vesicles and wormlike micelles in aqueous system

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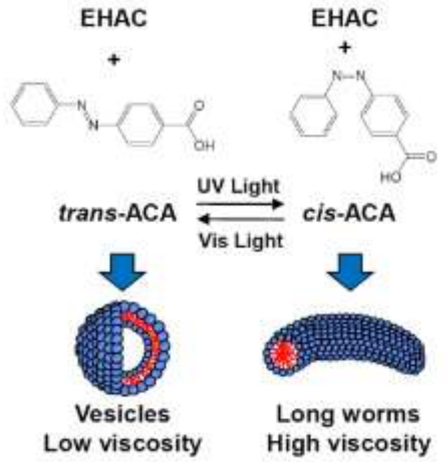
Fluids whose rheological properties, such as viscosity, can be tuned by light are of interest to scientists and engineers. Such fluids can be termed photorheological (PR) fluids. Because light can be directed at a precise point with a resolution on the order of microns, PR fluids may be useful in microscale or nanoscale devices as the basis for valves or flow sensors. However, in most cases, the synthesis of complex photosensitive molecules is required in order to create PR fluids. Due to such chemical synthesis, the widespread use of these fluids is hindered. Here, We show simple reversible PR fluids based upon combining an azobenzene derivative, 4-azobenzene carboxylic acid (ACA), into micelles of the cationic surfactant erucyl bis(2-hydroxyethyl)methyl ammonium chloride (EHAC). At certain concentrations of EHAC/ACA samples, we have found an increase in viscosity by 5 orders of magnitude upon UV irradiation, which correlates with a trans to cis photoisomerization. In addition, when the sample is exposed to subsequent visible light, we have observed a decrease in viscosity, which corresponds to a cis to trans reverse photoisomerization. The resultant change in the geometry of ACA alters the molecular arrangement of the EHAC/ACA complex, inducing reversible transition between vesicles and wormlike micelles. This change in viscosity can be repeated, leading to a substantial reversible change in viscosity that can be cycled many times over.



COLL 43

Simulating the self-assembly of mixed surfactant micelles with graphics processing unit accelerated coarse-grained molecular dynamics

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Despite interest from both industry and academia, simulating mixed surfactant micelles remains a challenge for modern computational chemistry. The problem for molecular dynamics (MD) simulations is two-fold: i) The concentration of surfactants is low, millimolar or less, which requires a large number of waters per surfactant, and ii) micellization timescales are on the order of microseconds, far longer than a typical MD simulation. Presented in this work is a method to overcome these constraints, which combines a coarse-grained model of aqueous surfactants with graphics processing unit accelerated MD software. Using this method, we have investigated micellization of mixtures of both non-ionic (polyethylene glycol) and ionic (sodium alkyl sulfate) surfactants as a function of hydrocarbon chain length and relative surfactant concentration. A number of thermodynamic, morphological, and dynamic properties are predicted from the simulation data, including aggregation number, polydispersity, critical micelle concentration, radius of gyration, molecular eccentricity, and monomer exchange lifetimes.

COLL 44

Property-structure relationships in natural nanoparticles: How does size matter?

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An ongoing discussion concerning mineral nanocrystals is how their properties (e.g. redox and sorption activity, transformation kinetics) may differ from the corresponding bulk phases. Recent work shows why surface electrostatic properties would be influenced by “curvature”, and by near surface deviation from stoichiometry. Other work suggests an important contribution from several layers of highly ordered water at the interface, and poses questions about the nature of the electrical double layer near nanoscale particles. Many properties can be inferred from molecular structure, but such studies of nanominerals can be limited by inherent disorder, strain, grain to grain inhomogeneity, and aggregation. Surface passivation (or possibly activation) of natural nanocrystals creates further complications.

Focusing on the iron oxyhydroxides, the known and expected variations in properties will be discussed. Studies and calculations being developed to examine several property dependencies in analog systems, including both homogenously and heterogeneously nucleated nanophases, will be described.

COLL 45

Reactivity of iron oxyhydroxide nanoparticles with dissolved metal(loid)s as a function of size, pH, and concentration

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Nanoparticles of inorganic mineral phases are widespread in aqueous environmental systems; however, the effects of nanoparticle size on metal(loid) uptake are not well understood yet hold significant implications for contaminant sequestration and mobility. Selected iron oxyhydroxide nanoparticle suspensions of 5, 25, and 75 nm in diameter were prepared to generate macroscopic uptake curves for As(V), Cu(II), Hg(II), and Zn(II) as a function of both pH and initial metal(loid) concentration.

Results show that the smallest particles exhibit greater overall uptake yet have reduced surface loadings relative to larger particles. EXAFS spectroscopy of the resulting solids indicate that metal(loids) on the 5-nm particles display slightly longer (0.1-0.3 Å) second-neighbor metal(loid)-iron distances than larger particles. This suggests significant surface distortion consistent with the oblong morphology and surface curvature observed by TEM in the 5-nm particles. Thus observable differences in both the extent and mode of metal uptake onto nanoscale iron oxyhydroxides appear to be largely dependent on size and morphology.

COLL 46

Effect of nanoparticle size on the aqueous solubility of polymer-coated silver nanoparticles as predicted by the modified Kelvin's equation

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Solubility of Ag NPs can affect their toxicity and persistence in the environment. We measured the aqueous solubility of eight Ag NPs having particle diameters from 5 to 80 nm that were synthesized using various methods, and with different coatings including polyvinylpyrrolidone and gum Arabic. The size of the Ag NPs was characterized by transmission electron microscopy. The local structure, crystal lattice parameters and structure of the Ag NPs were determined by X-ray Absorption Spectroscopy and synchrotron-based total X-ray scattering and pair distribution function analysis. Aqueous solubility of the Ag NPs was found to be correlated with particle size based on the TEM

sizes as predicted by the modified Kelvin equation (Fig.1). Solubility was relativley unaffected by the synthesis method and coating compared to particle size. The surface tension of Ag NPs was found to be ~ 1 J/m^2, which is expected for bulk face centered cubic silver.

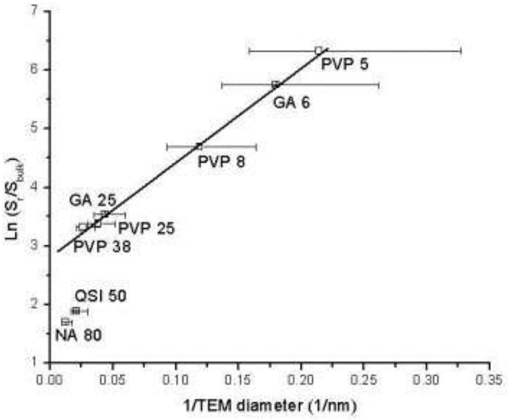

Figure 1. Correlation between Ln S_r/S_{bulk} and 1/TEM diameter of 8 Ag NPs measured in this study, $R^2 = 0.993$.

COLL 47

Controlled evaluation of silver nanoparticle dissolution using atomic force microscopy

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Investigations of silver nanoparticle (AgNP) dissolution are complicated by nanoparticle aggregation. In this study, atomic force microscopy (AFM) was used to monitor the dissolution of un-aggregated, immobilized AgNPs fabricated on glass substrates by nanosphere lithography (NSL). The utility of this method for evaluating nanoparticle dissolution in the absence of aggregation was demonstrated by analyzing the effect of NaCl on AgNP dissolution. Over the first day of exposure to ≥10 mM NaCl, the in-plane AgNP shape changed from triangular to circular, the sidewalls steepened, and the height increased by 6-12 nm. Subsequently, particle height and in-plane radius decreased at a constant rate over a 2-week period. Dissolution rates varied linearly from 0.4 to 2.2 nm/d over the 10-550 mM NaCl concentration range tested. These results suggest that the high levels of NaCl present in biological media and saline waters have the potential to enhance AgNP dissolution.

COLL 48

Theoretical studies of the reactive properties of environmental oxide nanomaterials

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Oxide nanomaterials have highly reactive surfaces and comprise a ubiquitous category of environmental interfaces. Computational modeling studies play a key role in uncovering the effects of nanomaterials in the environment by providing complementary information to experiments, predicting properties that can not be measured, and providing fundamental information about structure and reactivity. Quantum-based methods such as density functional theory (DFT) are desirable for their ability to provide molecular-level detail about the nanomaterials in the environment. However, full consideration of all of the geochemical parameters contributing to surface processes of nanomaterials relevant to environmental science is prohibitive to first principles modeling. A reductionist approach based on comparative DFT modeling studies of oxide nanomaterials is highlighted, with an emphasis on the interpretation of results in terms of substrate and adsorbate physical and chemical properties.

COLL 49

Impact of surfaces of nanoparticles on micro- and macroscopic properties: Ferrihydrite

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The reactivity of the metal (hydr)oxide fraction of soils strongly originates from the presence of nanoparticles. A pedon of just one m^2 of soil may contain millions of m^2 of oxide surfaces (Hiemstra et al. 2010). Nano oxide particles are particularly important in regulating oxyanion adsorption, will interact with organic matter, and contribute to the specific binding of heavy metal ions. Ferrihydrite (Fh) is the most important natural nano oxide particle. Discussion on the structure is in progress (Michel et al. 2010). Knowledge of a mineral structure is highly relevant for understanding the related surface reactivity. The structure of synthesized Fh as a function of particle size will be evaluated in relation to the surface composition and vice versa. We are able to unify the relationship between microscopic and macroscopic properties.

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Michel FM et al. 2010 *PNAS*, 107, 2787-2792 (2010)

COLL 50

Total X-ray scattering study of the effect of benzoic acids on the structure of ferrihydrite

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The formation of poorly crystalline Fe-oxyhydroxide phases in aquatic systems, soils, and sediments typically occurs in the presence of natural organic matter (NOM) such as humic and fulvic acids. Carboxyl and phenol functional groups are abundant in NOM and known to interfere with the polymerization of Fe(III) and impact ferrihydrite formation. This study of synthetic ferrihydrite using X-ray total scattering examines how the number and position of the phenol groups in hydroxybenzoic acids affect the size and structure of the ferrihydrite precipitate. We show that hydroxybenzoic acids decreased the coherent scattering domain size of the ferrihydrite and increased apparent strain in the order 4-hydroxybenzoic acid~2,4-dihydroxybenzoic acid<<3,4-dihydroxybenzoic acid. Developing a deeper understanding of the effects of organic solution constituents on the structure of ferrihydrite is important in order to predict the nanomineral's biogeochemical reactivity in the environment.

COLL 51

Thermodynamics of manganese oxides: Effects of particle size and hydration on oxidation-reduction equilibria among hausmannite, bixbyite, and pyrolusite

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Surface enthalpies of manganese oxide nanophase hydrous and anhydrous surfaces, hausmannite (Mn_3O_4), bixbyite (Mn_2O_3), and pyrolusite (MnO_2), were determined using high temperature oxide melt solution calorimetry in conjunction with water adsorption calorimetry. Redox energetics at the nanoscale for this Mn-O system with water present was calculated, which revealed significant phase equilibrium shift in favor of the nanoscale manganese oxide with low surface energy – Mn_3O_4 relative to Mn_2O_3 and Mn_2O_3 relative to MnO_2. Supporting preliminary findings (Navrotsky et al. 2010), the spinel phase (hausmannite) has a lower surface energy than bixbyite, while the latter has a smaller surface energy than pyrolusite. Additionally observed were rapidly reversible structural and phase changes associated with water adsorption / desorption for the nanophase manganese oxide assemblages.

COLL 52

High resolution elemental mapping and X-ray absorption spectroscopy of ferruginous bodies from lung tissue using synchrotron radiation

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Exposure to asbestos fibers is associated with mesotheliomas and lung cancer; nevertheless, the mechanism by which asbestos causes cancer is still not well understood. *Ferrouginous Bodies (FB)* consist of inorganic fibers with an iron-rich coating, which was generally accepted to be a protective mechanism produced by macrophages to segregate the cytotoxic fibers from the organic tissues. However, more recently, other authors suggested that the coating material may enhance the cytotoxic properties of the asbestos fibers by increasing the production of free radicals. In this work, samples of human lung tissue rich in *FB* were collected from three subjects who were affected by lung cancer. The high resolution x-ray fluorescence maps acquired at the synchrotron revealed that the external coating is mainly composed of Fe, Cu, Zn, and As (plus Ge and Ba in some subjects), while x-ray absorption spectroscopy indicated that iron is present in the form of ferritine.

COLL 53

N-heterocyclic carbenes as ligands for the stabilization of ruthenium nanoparticles: Ligand location and surface chemistry

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Ruthenium nanoparticles stabilized by N-Heterocyclic Carbenes ligands, N,N-di(tert-butyl)imidazol-2-ylidene (L1) or 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (L2), were easily synthesized by decomposition of [(Ru(COD)(COT)] in mild conditions. The nanoparticles have been characterized by TEM, NMR, IR and WAXS.

Reactivity studies carried out with these nanoparticles show that they display a different reactivity for CO oxidation in the solid state but a comparable one for styrene hydrogenation in solution. Using ^{13}C labeled carbene ligands and ^{13}CO as a probe molecule, solid state NMR studies evidenced the strong binding of the NHC ligands to

the surface of ruthenium and allow us to propose a location for them, explaining the different reactivities.

This work represents an attempt at the full molecular characterization of the surface of catalytically active nanoparticles and it has been recently accepted for publication.[1]

[1] P. Lara, O. Rivada-Wheelaghan, S. Conejero, R. Poteau, K. Philippot, B. Chaudret, *Angew. Chem. Int. Ed.* accepted (VIP, DOI: 10.1002/anie.201106348).

COLL 54

Regulating catalytic activity and selectivity of thiolate ligand-capped palladium nanoparticles

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Ligand-capped metal nanoparticles are considered as semi-heterogeneous catalysts that can be easily separated from products and other reaction medium. In addition, the high solubility of metal nanoparticles and the presence of ligands around the catalytic metal nanoparticle core can provide the higher catalytic efficiency and/or selectivity. Recently, our group discovered a synthetic method utilizing Bunte salts to generate catalytically active Pd nanoparticles capped with a low density of alkanethiolate ligands. This presentation focuses on the examination of various factors in the synthetic process of thiolate ligand-capped Pd nanoparticles (LcPdNP) that control the particle core size and the surface ligand density and their effects on the catalytic property of various LcPdNP catalysts. Factors which are manipulated include the molar equivalencies of sodium *S*-dodecylthiosulfate (capping ligand), tetra-*n*-octylammonium bromide (surfactant/phase transfer reagent), and sodium borohydride (reducing agent) and reaction temperature. In general, the results show that an increase in reaction temperature and a decrease in the concentration of tetra-*n*-octylammonium bromide result in a higher thiolate ligand density and smaller average particle size, while a decrease in the concentration of Bunte salts results in a lower surface ligand density and an increase in the average particle size. The amount of reducing agent, sodium borohydride, is also found to influence the size of Pd nanoparticles, producing particles with a smaller core with an increased borohydride concentration. The catalysis studies show that the controlling the particle size and the surface ligand density of LcPdNP leads to the optimization of catalytic activity and selectivity for various organic transformations including the isomerization of allyl alcohols, tandem semi-hydrogenation and isomerization of propargyl alcohols, microwave-assisted isomerization of terminal alkenes, and hydrogenation of 4-nitrophenol. Water-soluble LcPdNP are also synthesized and their catalytic properties are studied for heterogeneous and two-phase catalysis reactions.

COLL 55

Metal nanoparticles: from their organometallic synthesis to their application in catalysis in organic or aqueous media

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In our group, the synthesis of metal nanoparticles is performed through an organometallic approach. Metal organic complexes are decomposed in solution under mild conditions and in the presence of ligands as stabilizing agents. Our objective is to obtain well-dispersed nanoparticles with a narrow size distribution and a controlled surface composition, these parameters being important in catalysis. The choice of the ligand used as stabilizer is thus of prime importance as it can influence the properties of the nanoparticles, as their size, shape, or surface chemistry.

Examples of so-obtained nanoparticles will be presented. A particular attention will be devoted to the functionalisation of their surface that can lead to application in the field of catalysis, in organic[1] or aqueous media,[2] depending on the ligands used as stabilizers.

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2 M.Guerrero, A.Roucoux, A.Denicourt-Nowicki, H.Bricout, E.Monflier, V. Collière, K.Fajerwerg, K. Philippot, *Catal.Today,* 2011, *in press*.

COLL 56

Effects of various functional groups on the growth of platinum nanoparticles and catalytic activity toward ORR

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While many different capping agents have been used to mediate the synthesis of platinum nanoparticles from polymers to biomolecules, the effect the chemical structure of the ligands play on nanoparticle nucleation and growth as well as their catalytic activity is not yet fully understood. Understanding how chemical moieties affect platinum nanoparticle synthesis and activity is a critical step for rationally designing ligands to produce platinum nanoparticles with desired sizes, shapes, and surface functionality. Because monomeric functional groups do not yield well-defined metal nanoparticles, we recently explored the use of a macromolecular scaffold that shows no binding to platinum, specifically polyethylene glycol (PEG). By attaching unique groups to the end of linear and branched PEG, we could maintain the overall platinum binding of a larger molecule while still isolating the effects of the individual functional group on the morphology of the platinum particles and their catalytic activity towards oxygen reduction.

COLL 57

Surface chemistry of Pt based mono/bi/tri metallic nanocomposites on different carbon supports as probed by XPS

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Pt based nanocomposites (Pt+Au+Sn) on activated carbon (AC), carbon nanotubes (CNTs) and carbon nanofibers (CNFs) for methanol electro-oxidation were investigated. The studies demonstrated that the presence of Au and Sn significantly modified the catalytic properties while reducing the required precious Pt content and CNT based tri-metallic catalyst ($Pt_2Au_1Sn_1$/CNT) was found to show the best response to methanol oxidation. The surface species and compositions most likely responsible for the observed catalysis were investigated using X-ray Photoelectron Spectroscopy (XPS). High resolution spectra of Pt 4f, Au 4f and Sn 3d revealed the distribution of the metallic and oxidised states (oxide/hydroxide) of the different metals. All systems were found to be Pt enriched with Pt composition > 75% in PtAu bi-metallic nanocomposites and > 60% in PtAuSn tri-metallic nanocomposites compared to their respective nominal compositions. The synergistic role played by Au and Sn and the influence of the supporting carbon matrix on the dispersion of metals in the nanoparticles are also highlighted

COLL 58

Templated synthesis of noble metal nanorods in silica nanotubes

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A general template method to synthesize noble metal nanorods, including Au, Ag, Pt and Pd, is proposed and discussed in detail. This method involves procedures including the synthesis of silica nanotubes with defined dimensions, placing seed metal nanoparticles exclusively inside the silica nanotubes, the subsequent seeded growth of metal within the silica nanotubes, and finally selective removal of the silica shells. The silica nanotubes act as hard templates to confine the one-dimensional growth of the metal nanorods and define their aspect ratios. This method affords large quantities of noble metal nanorods with well-controlled aspect ratios and high yield, which may find wide use in the fields of nanophotonics, catalysis, sensing, imaging, and biomedicine.

COLL 59

How to pick the chips out of the chocolate chip cookie: Liberation and functionalization of germanium nanocrystals (Ge-NCs) synthesized in a germanium oxide matrix

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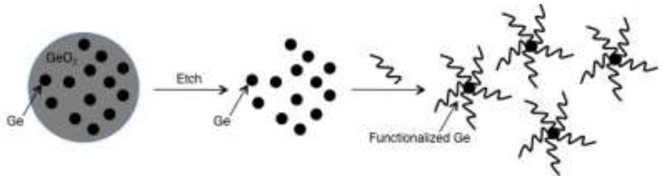
Our group has developed a sol-gel/thermolysis method to synthesize Ge-NC/GeO_2 composites. Germanium oxide removal and Ge-NC surface passivation, paramount if these materials are to be realized in solution-based applications, are hindered by a number of factors including carbon impurities in the Ge/GeO_2 composite, issues with selective removal of germanium oxides over germanium, and challenges with nanoscale surface chemistry such as the kinetic instability of H-termination. Recent advances in addressing these challenges will be discussed with detailed material characterization.



COLL 60

Modification of ruthenium nanoparticles by organometallic tin compounds: Location and surface chemistry

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Ruthenium nanoparticles, stabilized either by a polymer (PolyVinylPyrrolidone: PVP) or by a ligand (bisdiphenylphosphinobutane: dppb), were synthesized by decomposition of [(Ru(COD)(COT)] in mild conditions.[1] They were further reacted with an organometallic tin complexe to modify their surface.

These nanoparticles were fully characterized by TEM, NMR, IR and Mössbauer techniques. However, in comparison, with pure RuNPs, reactivity studies performed on these tin-modified RuNPs show differences as a function of the tin amount and the nature of the stabilizer. First, the quantity of hydrides present at the surface of these particles varies depending on the amount of tin. Second, any CO adsorption was observed for Sn-Ru/PVP, also in solid state NMR and IR, unlike for Sn-Ru/dppb. Third, the selective solution styrene hydrogenation, informs us about the tin location on the surface of the particles and explains the products obtained.

[1] F. Novio, K. Philippot, B. Chaudret, *Catal. Lett.* **2010** , *140*, 1–7.

COLL 61

Quasielastic light scattering of dendrimer-encapsulated metal nanoparticles

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Most studies of dendrimer-encapsulated nanoparticles focus on the properties of the nanoparticle rather than those of the entire dendrimer/nanoparticle composite (DNC). While knowledge of nanoparticle size is important, it is also essential to know the size of the composite, because they are large flexible molecules that may change conformation as a function of solution conditions. The hydrodynamic radii of DNCs were determined by quasielastic light scattering at high and neutral pH for various salt concentrations and identities. At high pH, the size of the DNC is about that of the empty dendrimer. At neutral pH, the size of the DNC approximately doubles while that of the empty dendrimer remains unchanged. This increase in size is counterintuitive. It occurs even though the positive charge on the DNC increases as the pH decreases. The unexpected increase in size of the DNC is likely due to electrostatic interactions involving the metal nanoparticle.

COLL 62

In situ spectroscopy to probe structure of bimetallic particles in reactive gases: CoPt, CoCu and CuNi

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Nanoparticles comprising of two metals allow fine tuning of key properties. Bimetallic nanoparticles are extremely important in many applications: electronics, sensing and especially catalysis. For nano-objects, surface adsorbates contribute dramatically to particle structure – bulk phase diagrams no longer apply. Very little is known about bimetallic nanoparticles' behaviour outside UHV, where TEM, XPS and other characterization techniques are typically applied.

Using Ambient Pressure XPS we have explored how their surface changes in the presence of different gases (up to 1 torr), mimicking possible operating conditions. Previously, we observed dramatic restructuring of precious metal bimetallics. Here we consider a series of transition metal bimetallics (all of particular interest for Fischer-

Tropsch chemistry). Composition was controlled using colloidal synthesis methods and confirmed using single particle STEM/EDS. AP-XPS demonstrates CoPt and CuNi surface segregate one metal reversibly in H_2 versus O_2, while CoCu changes irreversibly. Molecules interacting with the surface are key to nanoparticle structure.

COLL 63

Magnetic field-induced fabrication and assembly of bimetallic Janus particles

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Assembly of anisotropic colloidal structures is considered as a promising approach to produce 2D or 3D superstructures which are useful in important application areas of photonics, electronics, or sensing. In this work, we will discuss specific assembly of bimetallic Janus particles (BJPs) through control of the orientation of magnetic polystyrene microspheres in the presence of a uniform external magnetic field. The formation of magnetic BJPs into self-assembled hierarchical superstructures can be modified by varying the number density of particles, controlling the temperature and humidity, and adjusting the field strength. Subsequent transformation of metals into oxides or sulfides provides access to a wide selection of potential materials, resulting in complex soft materials that are expected to possess versatile physical and chemical properties.

COLL 64

One-step fabrication of supramolecular microcapsules from microfluidic droplets

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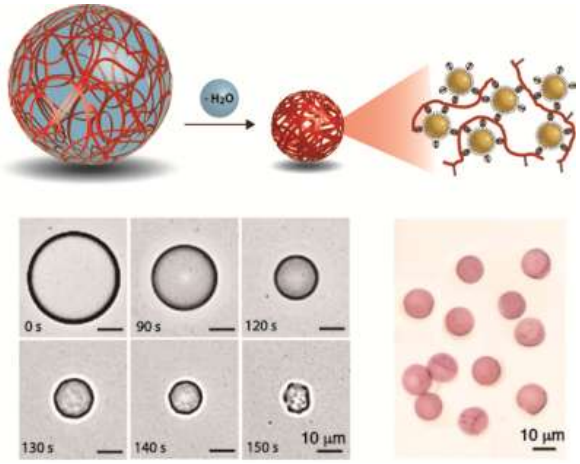
Microencapsulation is an important aspect of numerous scientific and industrial

applications. Although the state-of-the-art techniques for preparing microcapsules are powerful in many

circumstances, it is still challenging to make stable capsules in an efficient and scalable process without

compromising functionality and encapsulation efficiency. We demonstrate a remarkably simple one-step

approach that exploits a versatile host-guest system, and uses microfluidic droplets to generate porous microcapsules with easily customizable functionality. The capsules comprise a supramolecular polymer-gold nanoparticle (AuNP) composite, are dynamic yet highly stable, and can be loaded in one step during capsule formation. They are ameable to both passive and “on-demand” encapsulant release, and the incorporation of AuNPs provides added functionality of sensitive characterizing the internal chemical environment using surface enhanced Raman spectroscopy. Such an integrated fabrication approach promises access to a novel range of functional microencapsulation materials.



COLL 65

Emulsion-templated assembly of nanoparticles

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Control over the assembly of colloidal building units is of great significance to practical applications, but is also interesting from a more fundamental point of view of understanding the self-assembly of nanostructured materials. Joining together different spherical nanoparticles in a defined manner allows control over the shape, composition and surface roughness of the nanocomposites. The preparation of such hierarchically organized structures can be accomplished by agglomeration of particles that are dispersed in an emulsion. The particles adsorb on the surface of the emulsion droplets (Pickering effect) and coagulate in a well-defined way during the evaporation of the (dispersed) oil phase. If the constituents consist of different materials, the resulting heteroaggregates feature both compositional and interfacial anisotropy, offering unprecedented perspectives for rationally designed functional colloids, which are of fundamental importance to a broad range of applications including sensing, photonic, and electronic devices.

COLL 66

Curvature-induced capillary forces on spherical particles

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The interface between liquids provides a versatile platform for assembly of small particles for functional membranes, capsules, and other materials. Here I will focus on of the role of the interfacial curvature when spherical particles bind. Owing to the constant contact-angle condition at the particle's surface, binding to an anisotropically curved liquid interface causes deformation. I will describe a theoretical calculation of the deformation of an initially cylindrical interface, from which we obtain the binding energy of one sphere and the interaction between two spheres. We predict that spherical particles on constant-mean-curvature interfaces are driven toward lower Gaussian curvature, *i.e*., toward saddle-shaped regions. Experimental measurements of curvature-induced capillary forces between macroscopic spheres will be described. These results may help explain the stability of Pickering emulsions and point the way to new methods of directed particle assembly. We acknowledge support from the NSF-funded UMass MRSEC on Polymers and NSF grant CBET-0967620.

COLL 67

Forced desorption of nanoparticles from an oil-water interface

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While nanoparticle adsorption to fluid interfaces has received considerable attention, desorption remains relatively unexplored. Control over the partitioning of nanoparticles

between bulk and interface is key for applications including catalysis, oil recovery, and functional nanomaterials. We study gold nanoparticles capped with amphiphilic ligands, which spontaneously adsorb from aqueous suspension onto a pendant drop of oil. Using pendant drop tensiometry, we measure the surface pressure of the nanoparticle monolayer during adsorption and subsequent compression. Upon compression, the nanoparticles are mechanically forced out of the interface and into suspension. We developed an optical method to measure the nanoparticle area density *in situ*. The area density of particles at which desorption occurs suggests that ligand-induced repulsion plays a crucial role in enabling desorption. The mechanical properties of nanoparticle-laden interfaces will be discussed in light of this finding.

COLL 68

Electric-field assembly of colloidal dimers at liquid-liquid and liquid-solid interfaces

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Anisotropic colloids have anisotropic properties in chemical composition, surface functionality, or geometric size. As such, they can recognize each other and assemble via directional interactions, potentially making large numbers of close-packed and non-close-packed crystalline structures that isotropic spheres cannot form. In this talk, we will present our results in the directed assembly of the simplest form of anisotropic particles - colloidal dimers, at both fluid-fluid interface (water-oil, water-air) and liquid-solid interfaces under the influence of externally applied electric field. Rich phase behaviors in terms of both equilibrium phases and transient states will be reported. The orientation of colloidal dimers highly depends on the contrast in surface charges, geometric sizes, as well as dielectric properties between two lobes on the dimer. The observed 2D crystals indicates a promising route to making new types of photonic crystals.

COLL 69

Stimuli-responsive NPs interacting with hydrophilic/hydrophobic interfaces

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Biocompatible and stimuli-responsive Fe_3O_4@MEO_2MA_x-co-$OEGMA_y$ NPs have attracted our interest due to their possible use in biomedicine as magnetic resonance imaging contrast enhancers and cell manipulation agents. Therefore, it was important to know whether these NPs interact with cellular membranes or not? Thus, we investigated the interaction of those NPs with DPPC monolayers, used as a model of

the outer leaflet of a cell membrane. As a prerequisite of understanding this interaction, the system was widely investigated at the bare air/water interface. The NPs behave differently below and above their lower critical solution temperature (LCST) due to different hydration levels and conformational changes of the copolymer shell. Below the LCST, the NPs form stable Langmuir as well as Gibbs monolayers, and re-disperse into the subphase above the maximal interfacial concentration. Above the LCST, the NPs show high affinity for hydrophobic interactions, agglomerating at the interface and losing their re-dispersibility.

COLL 70

Controlling the morphology of silica particles in non-aqueous silicone dispersions

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Silica particles are normally prepared in an aqueous medium from the hydrolysis and condensation of alkoxysilanes, or condensation of silicic acid. We have surprisingly discovered that the controlled synthesis of silica of several different morphologies is possible within silicone oil and silicone pre-elastomers. The traditional precursor TEOS ($Si(OEt)_4$) was combined with a templating agent such as PEG in the presence of moisture. Key to the formation of silica was the use of a variety of amine catalysts rather than the tin catalysts more commonly used for elastomer synthesis. Solid, hollow or meso-macroporous particles could be obtained by controlling the relative rate of silica formation vs crosslinking. Morphological control of both the silica particles and the silicone elastomers were particularly dependent on the rate of ingress of water. The origins of the structure and the ability to control morphology of both silicone and silica using different silica precursors will be discussed.

COLL 71

Hierarchical porous materials templating from particle-stabilized emulsion

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Hierarchical porous materials occur widely in nature, such as the lungs of animals and the diatom skeletons. The synthesis of hierarchical materials containing macropores along with micro- and/or mesopores has recently become an exciting area of material chemistry. We report here an approach to fabricate hierarchically porous materials using particle-stabilized emulsions. By starting with emulsions stabilized by mixed soft microgels and solid particles, the initial emulsion droplets promote macropores and the formation of interconnecting windows, while the interfacially adsorbed soft microgels lead to the formation of nanoscale porosity throughout the macroporous walls.

Emulsification conditions can be adjusted to produce droplets with different mean sizes, whilst independently microgel emulsifiers with various sizes can be used to direct the structure of the nanopores. This synthesis thus allows direct and independent control of the small- and macropore dimensions and as a result the final pore structures can be easily tailored for different applications.

COLL 72

Metal-liquid interface: Adhesion and reactivity from first-principles simulations

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Probing the nature of the adhesion of an organic liquid on a metal surface is of high importance for understanding the stability and the chemical catalytic reactivity at these interfaces. However, to date, the morphology, the layering and the chemical properties of these systems are still insufficiently known. Using semi-empirical dispersion corrected density functional theory calculations and *ab initio* molecular dynamics simulations, we show that the adsorbed and physisorbed interface molecules of a thin film of ethanol confined at a platinum surface remain intact while a few interface molecules adsorb in a dissociative manner for the case of carbon tetrachloride on platinum. The dissociation of CCl_4 is assisted by the surrounding medium. In addition, the adsorption strength of the interface molecules is strongly increased in the condensed phase compared to gas phase. Finally, cooperative effects in ethanol reactivity at a Rh(111) surface will be discussed. We will show how hydrogen bonding between two molecules of ethanol at the Rh surface can assist OH bond dissociation.

Reference:

1) S. Laref, Y. Li, M.-L. Bocquet, F. Delbecq, P. Sautet and D. Loffreda, Phys. Chem. Chem. Phys., 13, 11827-11837 (2011); DOI: 10.1039/C0CP02285C

COLL 73

Designed synthetic polymer nanoparticles for capturing of proteins

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Nanoparticles (NPs) conjugated with biomacromolecular ligands, such as peptides and antibodies have been proven to be strong tools in diagnostics, molecular biology, drug delivery, disease therapy, and as antidotes for toxins and viruses. On the other hand, synthetic polymer NPs with an intrinsic affinity for biomacromolecules are also of significant interest as inexpensive and stable substitutes for antibodies. Previously, we

reported polymeric NPs (~30 nm) capable of binding the melittin[1-4], a 26 amino acid peptide toxin isolated from bee venom. Recently, we have expanded our targets to include proteins. By incorporation of appropriate combinations and ratios of functional monomers, it was possible to design NPs that can capture targeted proteins with high affinity. Currently, we are exploring the applications of these synthetic polymer NPs in the area of biomaterial engineering.

COLL 74

Mobile precursor determines amyloid-β peptide fibril formation at the liquid-solid interface

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The aggregation of peptides into amyloid fibrils plays a crucial role in various neurodegenerative diseases, such as Alzheimer's disease and Parkinson's disease. While extensive work has been devoted to the study of solution fibril formation in vitro, the situation differs fundamentally from that in a living cell where the effect of macromolecular crowding provides a very large surface area surrounding peptide and protein molecules. Here we study the dynamics of fibril formation of Alzheimer's amyloid-β peptide, Aβ42, on nanoscopic patterned block copolymer films and self-assembly monolayer modified surfaces with different hydrophobicities. We report the discovery of that weakly adsorbed peptides with two-dimensional diffusivity is a critifcal precursor to fibril growth. A balance between mobility and transient concentration of the peptide precursor state determines the kinetics of fibril formation.

COLL 75

Fibrinogen adsorption to plasma discharge deposited tetraglyme is ultralow but exhibits higher binding of monoclonal antibodies to the macrophage binding epitope than higher adsorbing surfaces

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Poly (ethylene oxide)-like glow discharge plasma polymerized tetraglyme surfaces prepared at low power (10W) display substantial *in vivo* monocyte/macrophage adhesion and a typical foreign body reaction, despite having very low fibrinogen adsorption (Γ_{Fg}). Γ_{Fg} measured under more rigorous conditions was substantially above the ultralow level needed to prevent cell attachment (63 or 55 ng/cm^2 from 3 mg/ml Fg in buffer or 100% blood plasma respectively), but the increased Γ_{Fg} did not correlate well to monocyte adhesion. The availability of the Fg epitope at $Y^{377-395}$ responsible for monocyte adhesion, measured using monoclonal antibody P2 binding, showed a strong

linear correlation with adhesion. However, P2 binding per unit of adsorbed Fg was much greater for Fg on 10W tetraglyme than on control surfaces with higher Γ_{Fg} (80W tetraglyme or FEP) suggesting Fg adsorbed to this nonfouling surface may be a less denatured state that increases its potency towards monocytes.

COLL 76

Protein activity and thrombosis at biomaterial interfaces

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The behaviors of proteins at interfaces are fundamental determinants of the success of medical devices. Traditionally, protein adsorption has been viewed as the critical predictor for blood compatibility of materials. More specifically, the adsorption of proteins such as fibrinogen for platelet adhesion and FXII for coagulation have been used to assess suitability of materials for blood contacting applications. Recently, there have been increased efforts in understanding the roles that protein function play in this process. These studies show that conformational changes and changes in protein activity can occur at both hydrophilic and hydrophobic interfaces, suggesting that both adsorptive and non-adsorptive protein-surface interactions have biological consequences. Recent studies in our lab have addressed the functional activity of proteins involved in both coagulation and thrombosis. These studies reveal a highly complex environment where activity depends on both surface chemistry and temporal aspects are involved in determining protein activity at interfaces.

COLL 77

Controlled surface conformations of fibrinogen polypeptides: Insights toward improving biocompatibility

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Biocompatibility represents the complex interplay between biomaterial, living tissue and biofluid. Biomaterial surface influences adsorbed protein conformation. Incoming cells “perceive” the pre-adsorbed dynamic surface protein signature, instead of the underlying biomaterial. In our work, AFM has been used to provide information on surface topology and fibrinogen adsorption. Fibrinogen peptide conformations were probed using monoclonal anti-fibrinogens specific to the alpha and gamma chains on five different surfaces using spectroscopic ellipsometry: hydrophilic SiO_2, hydrophobic OTS, charged amine, polyurethane (PU) and a hybrid nanocomposite (NC) surface combining polyurethane and siloxane nanocages. Surface polypeptide-cell interactions

were investigated with and without fibrinogen pre-adsorption. Our investigations revealed two distinct surface domains with different fibrinogen conformational structures. Cell attachment was clearly enhanced on NC surfaces and this performance was well correlated to the preferential exposure of gamma chains upon fibrinogen adsorption. This feature together with their viscoelastic properties makes NC biomaterials attractive for improving surface biocompatibility.

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COLL 78

Preparation and characterization of BSA nanospheres as drug delivery systems

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Protein nanospheres can be used in controlled delivery of pharmacological agents to the target site, thus reducing the dose, the frequency of drug administration and consequently the side effects. In this study, nanospheres of bovine serum albumin (BSA) were produced using a high-pressure homogenizer and different parameters were optimized in order to obtain particles that exhibit characteristics compatible with a potential application as drug delivery systems. Different formulations were prepared and their physicochemical properties were extensively characterized. Preliminary tests were performed to evaluate their potential *in vitro*. The obtained nanospheres presented adequate small sizes and polidispersity, and demonstrated stability over time. After several steps of optimization, the drug encapsulation, the introduction of imaging and targeting agents in the samples were performed and more complex nanospheres were obtained. The analysis of these samples indicated that these protein-based nanospheres exhibit suitable characteristics for application on specific drug delivery systems.

COLL 79

Watching membrane proteins at work: Understanding the function of the enzyme NADPH-cytochrome P450 reductase

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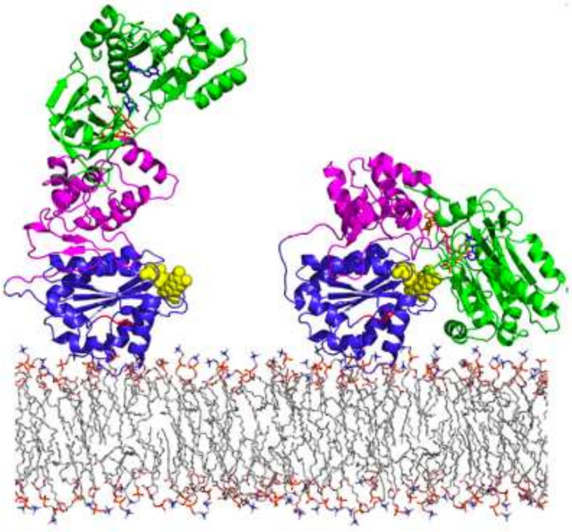
A deeper understanding of the factors governing the structure-function relation of membrane proteins is necessary, for example, in the development of better site-specific delivery drugs. Traditionally protein structure is assessed via high-resolution crystallography, which is a difficult task for membrane proteins as reflected by them corresponding to only 1.2% of all known protein crystal structures. We aim at developing biomembranes reconstituted on surfaces, where protein functionality is ensured. In particular, we attempt *to identify the effect of phosphorolation and redox state on the structure of the* enzyme NADPH-cytochrome P450 reductase *by developing strategies for their reconstitution onto surfaces.* This protein is believed to undergo a major conformation change as shown below, giving significantly different physical properties to the biomembrane that can be probed with a variety of surface sensitive techniques. Here we will briefly present the challenges we face and some of the strategies undertaken to address such issues.



COLL 80

Colloidal characterization of soy peptides

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Soy proteins are interesting biomolecule source for different applications. This stems from the fact that they are readily available, possess a variety of functional groups, and are able to interact with both hydrophobic and hydrophilic substrates. Soy proteins are amphoteric and biodegradable polymers that are suitable to form gels, films, and emulsions. Despite such variety of properties, soy protein industrial applications have been limited by their high molecular weight and low solubility. To overcome these limitations, different processes have been developed. In this work we discuss the results of acid hydrolysis of soy proteins under high concentration conditions. Techniques typical in protein analysis (SDS-PAGE and others) as well as colloid characterization (charge demand and electrophoretic mobility, etc.) were used to monitor the chemical and conformation changes that occur upon hydrolysis. In addition, the effect of chemical

reaction conditions and denaturation processes were evaluated in an attempt to clarify and describe their behavior and thus make their use relevant for industrial applications. Our results from surface modification, adhesion studies, and as well as the ability to produce gels will illustrate potential uses of the obtained soy protein fractions.

COLL 81

Bioinspired, smart, multiscale, interfacial materials

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Learning from nature, we revealed that a super-hydrophobic surface needs the cooperation of micro- and nanostructures. Considering the arrangement of the micro- and nanostructures, the surface structures of the water-strider's legs were studied in detail. Accordingly, a series of super-hydrophobic surfaces have been fabricated. Under certain circumstances, a surface wettability can switch between superhydrophilicity and superhydrophobicity, Most recently, we developed a superoleophobic and controllable adhesive water/solid interface which opens up a new strategy to control self-cleaning properties in water. To expand the “switching” concept of the smart 2D surface, we also did a lot of interesting work in 1D system. For example, we discovered the water collection ability of capture silk of the cribellate spider Uloborus walckenaerius and then prepared artificial spider silk which will have great applications in water collection. In addition, we developed the novel biomimetic ion channel systems with a variety of intelligent properties, which were controlled by our designed biomolecules or smart polymers responding to the single external stimulus, provided an artificial counterpart of switchable protein-made nanochannels. These intelligent nanochannels could be used in energy-conversion system, such as photoelectric conversion system inspired by rhodopsin from retina or bR, and concentration-gradient-driven nanofluidic power source that mimic the function of the electric eels.

COLL 82

Replication efficiency of soil-bound prion protein varies with soil type

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Prion diseases are fatal, transmissible neurodegenerative diseases including scrapie and chronic wasting disease. The infectious agent of prion diseases is the prion (PrP^{Sc}), an abnormally-folded isoform of a normal cellular protein (PrP^{c}). Prion attachment to soil is thought to play an important role in the transmission of scrapie and chronic wasting disease via environmental routes. Binding of PrP to soil and soil minerals is influenced by prion strain and species and soil characteristics; however, the ability of soil-bound

prions to replicate via conversion of PrP^{c} to PrP^{Sc} remains poorly understood. We evaluated replication efficiency of soil-bound prions using an *in vitro* technique. The replication efficiency of bound prions varied with soil type, where prions bound to clay and organic surfaces exhibited significantly lower replication efficiencies while prions bound to sand exhibited no apparent difference in replication efficiency compared to unbound controls. There were limited differences in replication efficiency observed between prions from different host species. Given that prion adsorption also varies with soil type, the overall balance between prion adsorption affinity and replication efficiency for the dominant soil types in an area may be a significant determinant in the environmental transmission of prion diseases.

COLL 83

Flippases, floppases, and scramblases: Transporters that regulate transbilayer phospholipid asymmetry in the eukaryotic plasma membrane

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The distribution of phospholipids across the plasma membrane of eukaryotic cells is generated and maintained through the action of several transmembrane transporters. ATP-dependent “flippases” and “floppases” move lipids in the inward or outward direction, respectively, while a “scramblase” has been associated with the bidirectional energy-independent movement of lipids across the membrane. Red blood cells possess a limited set of these lipid transporters and the focus of our studies is to identify and characterize these proteins, especially with regard to substrate specificity. The erythrocyte flippase belongs to a subclass of P-type ATPases and is structurally and stereochemically selective for phosphatidylserine. Red cell floppases belong to the ABC transporter superfamily and transport a variety of lipids. Scramblase activity is activated by Ca^{2+} and is non-specific for its lipid substrates. Our studies have also revealed that flippase and scramblase activities might be related; flippase activity-inhibiting antibodies also inhibit scramblase activity in intact cells.

COLL 84

Bacterial membrane curvature controls the formation of cardiolipin microdomains

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Recent data suggests that bacteria use geometric cues for the localization of proteins and lipids. We have recently tested the hypothesis that membrane anisotropy occurs by mechanisms governed by physical and geometrical constrains. We found that

microdomains of cardiolipin (CL) preferentially localize to regions of large, negative membrane curvature. In this presentation we characterize the response of CL microdomains to curvature and their function in protein localization. Using a top-down approach that combines in vivo and in vitro experiments, we present data for two functionally related bacterial division proteins, MinD (from *Escherichia coli*) and DivIVA (from *Bacillus subtilis*) that localize to regions of large membrane curvature in vivo. A critical difference in the radius of curvature $\Delta C > 0.5\ \mu m^{-1}$ is required to drive the polar localization of MinD and DivIVA. Our data provides support for curvature as a mechanism for regulating the spatial organization of biomolecules at bacterial membranes.

COLL 85

Visualizing membrane mechanics with a fluorescent sensor

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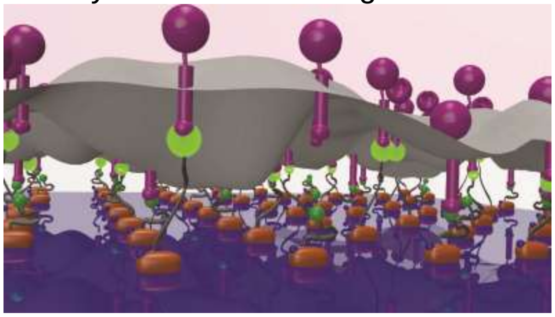
The interplay between physical inputs and chemical signaling regulates a significant number of biological processes that range from cell adhesion and migration to differentiation and immune response. These mechanical inputs are typically transmitted through membrane receptors that respond to the mechanical properties of their cognate ligands. A major challenge to elucidating the molecular mechanisms of mechanical signaling lies in the development of techniques to measure forces in the cell membrane. In this talk, we will report on the development of a fluorescent sensor to visualize the mechanical strain exerted by specific proteins in the membranes of living cells. The sensor allows one to quantify forces with high spatial and temporal resolution for a wide range of receptors and cell types using a conventional fluorescence microscopy. We demonstrate this approach by mapping membrane mechanical forces during endocytosis of the EGF ligand.



COLL 86

Equilibrium and kinetic aspects of BAR domain protein/membrane interactions

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Biological membranes consist of a lipid double layer containing proteins and other macromolecules. Such membranes surround biological cells and the organelles that cells contain. Biomembranes often show lateral structure and complex shapes. Importantly, membrane shape and local composition have been found to couple in important functional aspects involved in cell signaling and membrane trafficking. The mechanisms of such phenomena currently are not well understood.

Here we investigate the interrelation of membrane curvature generation, curvature sorting, and membrane binding of BAR domain proteins. We use giant as well as large unilamellar vesicles in combination with various fluorescence and mechanical manipulation methods to study both equilibrium and kinetic aspects of BAR domain protein function. We report modulation of BAR domain function by cooperativity and autoinhibition both of which likely have physiological relevance.

COLL 87

Binding of C-reactive protein to nanoparticle-supported lipid bilayers

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Supported lipid bilayers (SLB) are commonly used to study protein-membrane interactions. Here we utilize lipid-nanoparticles to create an SLB model that mimics the 25 nm size of low-density lipoprotein (LDL) particles. C-Reactive Protein (CRP) is known to cause aggregation of LDL and clustered LDL are selectively taken up by macrophage to produce foam cells. CRP is found in most atherosclerotic plaques, co-localized with LDL, however, the specific role of CRP is unknown and both pro- and anti-inflammatory activities have been suggested. We have discovered that CRP recognizes phosphatidylcholine (PC) coated nanoparticles (<30 nm diameter). CRP binds PC coated gold nanoparticles in a calcium-dependant manner and binding results in clustering. We have also observed that CRP binding to high curvature PC-membranes causes conversion to the modified isoform of CRP suggesting that membrane shape plays a role in this transformation.

COLL 88

Influence of phospholipid chemical structure on lateral diffusion rates in fluid bilayers

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Rapid lateral diffusion of lipids is a critical property for function of biological membranes. To better understand the principles that govern lateral diffusion, we measured diffusion rates for a large set of phospholipids that differed in their polar headgroups, ester vs. ether linkage of sn-1 and sn-2 hydrocarbon chains, hydrocarbon chain length, and degree of sn-2 chain unsaturation. Experiments were conducted over the temperature range from 10 to 60^{o}C using ^{1}H magic-angle spinning (MAS) NMR with application of pulsed magnetic field gradients. Most investigated lipids had perdeuterated, saturated sn-1 hydrocarbon chains that permitted measurement of chain order parameter profiles by solid-state ^{2}H NMR. For phosphatidylcholines we observed a decrease in diffusion rates with increasing chain length. Decreasing diffusion rates correlated with higher chain order parameters indicating a tighter lateral packing of lipids. Diffusion rates of lipids with identical hydrocarbon chains changed in the sequence phosphatidylcholine > phosphatidylserine > phosphatidylethanolamine. For lipids with increasing unsaturation of the sn-2 chain from one to six double bonds, we observed a large increase in diffusion rates that correlated with lower sn-1 chain order parameters, and a decrease in the thermal activation energy of lateral diffusion. Implications of our observations for models of lipid diffusion in bilayers will be discussed.

COLL 89

Influence of tension on phase separation and domain shape in phospholipid vesicles

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Phase separation of phospholipid vesicles occurs in the laboratory and can be visualized by fluorescence microscopy, providing insight into the physics of phase transitions in confined geometries. The biological importance of these processes is thought to arise from the possibility that micro-separation in the membranes of cells clusters receptors and alters local curvature in ways important to trafficking and signaling. The past decade has seen a dramatic increase in the study of these behaviors yet almost without exception, there is no control over the membrane tension or, the membranes are at low tension. Cell membranes on the other hand, are subject to tension from their connection (through proteins) to the underlying cytoskeleton and through external point contacts. We demonstrate here, that mixed membranes subject to modest tensions exhibit strikingly different phase separation than is seen at low tension. Not only can one detect a shifting of the phase transition temperature, but the type of domains observed is dramatically tension dependent. Beautiful flower shapes, ordered hexagons, and stripes can all be observed for different tensions and cooling histories. Our work presents a possible mechanism by which tension influences the type of phase separation and the resulting domain shape.

COLL 90

Measuring and controlling optical interactions at the molecular scale: Photoswitching and interference

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Light-molecule interactions are at the core of optical operations and analyses of molecular and supramolecular devices. We use molecular design, tailored syntheses, intermolecular interactions, and selective chemistry to direct molecules into desired positions to create nanostructures and to serve as test structures for measuring single or bundled molecules. Optical interactions within and between molecules can be designed, directed, measured, understood, and exploited at unprecedented scales. Such interactions can be used to switch reversibly isolated single molecules and assemblies on surfaces and can be probed by scanning tunneling microscopy and surface-enhanced Raman spectroscopy. We quantitatively compare experimental measurements to theoretical calculations. Lastly, we discuss our initial efforts in learning to assemble and to operate molecules together, both cooperatively and hierarchically, in analogy to biological muscles, in which we find and control vibrational interference.

COLL 91

Strong near-field coupling between quantum dots and popcorn-shaped gold nanoparticles for fluorescent enhancement

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Metal-enhanced fluorescence arises from the near-field interaction between fluorophores and metal structure. When a dye molecule is situated very close to the surface of a metallic nanoparticle, its fluorescence can be quenched or enhanced, depending on the magnitude of local field enhancement. In this work, we investigated the optical properties of quantum dots (QDs) conjugated to popcorn-shaped gold nanoparticles (PS-AuNPs) were investigated. These nanoconjugates exhibited enhanced fluorescence intensity as high as 150 times due to the strong local field at the edges of PS-AuNPs. In addition, the emission wavelength is found to shift from 530 nm to 625 nm. Finite difference time-domain (FDTD) computation was carried out to calculate the enhancement factor of local electric field experienced by QDs. As

expected, the obtained factor showed a linear relationship with the experimental fluorescence enhancement factor, validating the plasmon effect. The red-shift is attributable to strong coupling between surface plasmon and fluorescent emission; the excitons decay towards the surface plasmon along the nearby gold nanostructure accompanied by the heat loss during the propagation. These conjugates were then biotinylated for avidin binding, which resulted in the change of the local dielectric parameter and fluorescent intensity decrease.

COLL 92

Solute-solvent induced halogen and C-H···O hydrogen bonding by silver nanostructures

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A combination of surface-enhanced Raman spectroscopy (SERS), surface-enhanced infrared absorption (SEIRA), and density functional theory (DFT) calculations were used to show that silver nanoparticles (SNPs) could induced halogen and C-H···O hydrogen bonding in halogenated benzoate ion multilayers. SERS demonstrated that both 4-fluorobenzoic and 4-iodobenzoic acid ionized to 4-fluorobeonzoate ion (4FBI) and 4-iodobenzoate ion (4IBI) in the monolayer during adsorption on SNPs. SEIRA revealed significant 4FBI and 4IBI formation in the multilayer when using nonpolar deposition solvents such as CCl_4 and *n*-heptane. C-H···O hydrogen bonding was observed in a 4FBI/*n*-heptane multilayer, and halogen bonding was characterized between CCl_4 and 4IBI in the multilayer. DFT calculations were used to suggest the strength of these intermolecular attractions.

COLL 93

Hybrid approach to simulate plasmon enhanced spectroscopy

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It is by now well known that metal nanoparticles can strongly affect the response properties of molecules, which is explored in techniques like plasmon resonance sensing, surface-enhanced Ramanscattering (SERS) and metal-enhanced fluorescence. Here we will describe a discrete interaction model/quantum mechanics (DIM/QM) method that represents the nanoparticle atomistically, thus accountingfor the local environment of the nanoparticle surface on the optical properties of the adsorbed molecule. Using this DIM/QM method we will present results highlighting the size and absorption site dependence of SERS. The results will provide a bridge between fully first-principles results obtained for small metal cluster and experimental results obtained for large metal nanoparticles.

COLL 94

Analytical surface enhanced Raman scattering from nanoparticles and nanostructures

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Gold and silver nanostructures magnify optical fields near their surface when excited by light due to localized surface plasmon resonances. This enhancement greatly increases the weak Raman scattering from molecules near the nanoparticle surface, an effect referred to as surface enhanced Raman scattering (SERS). By focusing on a well-defined plasmonic interface rather than strong enhancement, we have used SERS to analyze the surfactant layer that surrounds gold nanorods. A structural transition was identified which may have a significant impact on efforts to functionalize and manipulate gold nanorods for applications. To further explore the potential of well-defined nanostructures for SERS, gold nanobelts were synthesized and studied. These elongated structures exhibit a strong plasmon resonance whose peak wavelength depends on their cross-sectional aspect ratio. Many interesting nanobelt morphologies were found, including a split structure that provides a strong SERS signal in a well-defined, single crystal geometry.

COLL 95

Ultrafast plasmonics: Surface enhanced-femtosecond stimulated Raman spectroscopy

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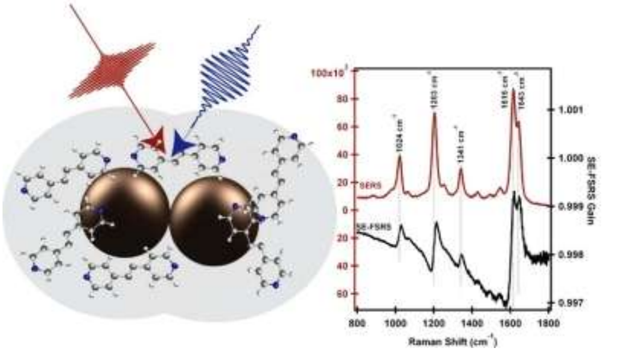
We present the first successful combination of the revolutionary techniques of SERS and femtosecond stimulated Raman spectroscopy (FSRS), demonstrating surface enhanced-FSRS (SE-FSRS). Using a picosecond Raman and femtosecond probe pulse, we obtain highly resolved stimulated Raman spectra with an enhancement factor of 10^4 – 10^6, now enabling structural probing of ultrafast reaction dynamics with the signal enhancement of SERS.



We also discuss our efforts towards monitoring ultrafast structural dynamics of molecules adsorbed to metal surfaces using three-pulse time-resolved SE-FSRS.

COLL 96

Colloidal organization fabricated by wrinkle assisted self-assembly: Highly uniform SERS substrates

Nicolas Pazos-Perez[1], Alexandra Schweikart[1], Ramon Alvarez-Puebla[2], ***Andreas Fery[1]****, andreas.fery@uni-bayreuth.de. (1) Department of Physical Chemistry II, University of Bayreuth, Bayreuth, Germany (2) Department of Physical Chemistry, University of Vigo, Vigo, Spain*

The electromagnetic behavior of plasmonic nanoparticles is highly dependent on their specific particle size and shape. There are different methods which allow us to fine tune the control over the particle shape and size thus, the materials properties. However, the lack of capability to form reproducible organized structures is still a very important challenge to solve in order to control the plasmonic intercoupling between particles.

In this work we report a novel method to produce organized structures of plasmonic nanoparticles in a macroscale range, forming linear parallel arrays[1]. The plasmonic behavior of these organizations was theoretically and experimentally investigated. Moreover, these structures, were effectively use for sensing using Surface-enhanced Raman scattering (SERS) spectroscopy as highly uniform substrates.

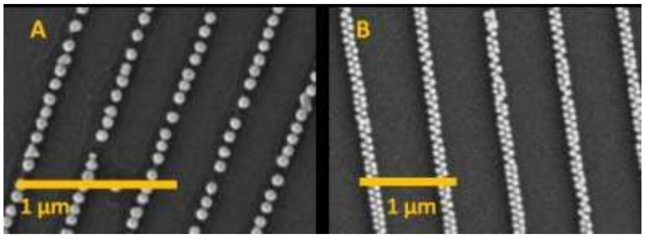


Figure 1. SEM images of two different arrays of gold nanoparticles, single-line (A) and double-line (B), upon colloid confinement with wrinkled surfaces of varying dimensions.

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COLL 97

Bandgap engineering of indium phosphide nanocrystal quantum dots through shell thickness and composition

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Fields ranging from imaging to telecommunications utilize the unique photophysical and electronic properties of nanocrystal quantum dots (NQDs). The development of new NQD compositions promises material properties optimized for specific applications, while also addressing material toxicity. Indium phosphide (InP) offers a "green" alternative to the traditional cadmium-based NQDs, but suffers from extreme susceptibility to oxidation. Coating InP cores with more stable shell materials significantly improves nanocrystal resistance to oxidation and photostability. We have investigated several new InP-based core-shell compositions, correlating our results with theoretical predictions of their optical and electronic properties. Specifically, we can tailor the InP core-shell QDs to a type-I, quasi-type-II, or type-II bandgap structure to achieve emission wavelengths ranging from 500-1300 nm depending on the shell material used (ZnS, ZnSe, CdS, or CdSe) and the thickness of the shell. Single molecule microscopy assessments of photobleaching and blinking are used to correlate NQD properties with shell thickness/composition.

COLL 98

Size-, charge- and chiral-selective transport through colloidal nanofrits

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To develop nanomaterials with controlled molecular transport, free-standing membranes (nanofrits) were prepared from colloidal solutions of nanospheres followed by an appropriate surface-modification. In one system, silica nanofits with varying nanopore size were evaluated for biomolecular separations. The fluxes of several generations of dendrimers were investigated in a proof-of-principle experiment to demonstrate the size-selectivity of our materials. For the protein diffusion studies, PEG chains were grafted onto the nanopore surface to minimize biofouling. A second system consisting of gold-coated nanofrits with a weak polyelectrolyte brush was investigated for the transport of

neutral and charged molecules. These pH- and ion-responsive brushes on the surface of the nanopores also exhibited variable degrees of swelling in response to cations in solution, thereby altering the nanopore size and charge. The third system was prepared by installing chiral recognition sites onto silica surfaces to prefer transport of one enantiomer of a diffusion probe through the nanopores.

COLL 99

Interface engineering on TiO_2 nanorods and its application in organic/inorganic hybrid solar cell

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In this study, we employed a two-step interface engineering method to optimize the replacement of insulating ligand oleic acid (OA) by conductive molecule 2-cyano-3-(5-(7-(thiophen-2-yl)-2,1,3-benzothiadiazol-4-yl)thiophen-2-yl)acrylic acid (W4) on TiO_2 nanorods. In first-step, we choose three different pyridine derivatives (pyridine, 2, 6-Lutidine, and 4-tert-butylpyridine (tBP)) as surfactants to replace the oleic acid on TiO_2 surface. The mechanism of removing OA and attaching effect for above three pyridine derivatives is investigated. At 70℃, we found the tBP has the best replacing effect for oleic acid as shown in **Table 1.**

Table 1. Composition of ligands on modified TiO_2 surface

Sample	Oleic Acid* (mol%)	Pyridine Derivatives* (mol%)	W4** (mol%)
TiO2-OA	3.06	-	-
TiO2-Pyridine	1.93	0.46	0.12
TiO2-2,6 Lutidine	1.80	2.27	0.06
TiO2-4-tert-butylpyridine	1.41	0.73	0.20

*** The molar ratio of oleic acid and pyridine derivatives were determined calculated by elemental analysis after the first-step interface engineering**
**** Amount of W4 was calibrated and calculated by absorption spectrum after second-step interface engineering**

After the introduction of conductive molecule W4 in second-step interface engineering, the amount of W4 on TiO_2-tBP is 3 time more than TiO_2-2, 6-Lutidine (0.06 mol% to 0.20 mol%). This effect also reveals on the device performance of P3HT/TiO_2 hybrid solar cell. The TiO_2-tBP-W4 device has the best performance with 1.6 times more than TiO_2-2, 6-Lutidine-W4 devices as shown in **Table 2.**

Table 2. The pgotovoltaic properties of different P3HT/TiO2-(surface modifier) devices

Sample	V_{OC} (V)	J_{SC} (mA/cm^2)	Fill Factor (%)	RS (Ohm-cm^2)	RSH (Ohm-cm^2)	PCE (%)
P3HT/TiO_2-Pyridine-W4	0.79	2.18	55.34	53	1964	0.95
P3HT/TiO_2-2, 6Lutidine-W4	0.78	1.40	48.48	81	2432	0.52
P3HT/TiO_2-4-tert-butylpyridine-W4	0.85	2.48	64.40	42	3921	1.36

COLL 100

Inkjet printed metal and metal oxide nanoparticle films for chemical sensing

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Chemical sensors have been fabricated by inkjet printing colloidal solutions of functionalized gold nanoparticles and unfunctionalized metal oxide nanoparticles onto polymer films. Chemiresistive properties of thiol-protected gold particles have been measured for sensor applications. Parameters that have been investigated include the effects of film thickness and aging of the sensors on sensitivity and reproducibility. Sensors have also been demonstrated for various printed metal oxide films, including zinc oxide. The photoluminescence and absorbance spectra of these films upon exposure to a variety of analytes have been measured and correlated to surface science experiments, including X-ray photoelectron spectroscopy and Raman spectroscopy. The effects of moisture and the reversibility of the response of the sensor films will be discussed.

COLL 101

Detection and degradation of chemical weapons models on mesoporous TiO_2 thin films

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Mesoporous TiO_2 thin films were investigated as sensors for chemical warfare agent (CWA) models. Synthesis was performed according to a literature procedure using P123 as a pore-generator. After forming a sol-gel and spin-coating a film onto silicon, the P123 was removed via calcification at up to 500 °C. Variations in experimental conditions for film formation included spin-coating rate, heating rate, and decomposition temperature. Film morphology was characterized with profilometry, water contact angle goniometry, and transmission electron microscopy (TEM). Sensor investigations were performed with mustard gas simulant chloromethyl phenyl sulfide (CMPS) or nerve agent model dimethyl methyl phosphonate (DMMP). After exposure to CMPS or DMMP vapor, the films were examined with infrared spectroscopy to determine whether binding or entrapment within the film occurred. Films with evidence of binding to CWA models were exposed to a medium pressure Hg lamp for up to 30 min to photochemically decompose the compound.

COLL 102

^{1}H NMR relaxation study of poly-vinyl pyrrolidone adsorption in zinc oxide colloidal dispersions

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Adsorbed macromolecules on the surface of colloidal particles are used to hinder the steric interaction between particles and engineer the material properties of colloidal dispersion, although the influence exerted by them are still not well understood. In order to determine the conformation in which the polyvinyl pyrrolidone macromolecules adsorb on the surface of ZnO nanoparticles, we present a study depends on solution-state nuclear magnetic resonance spectroscopy. Dynamic 1H NMR behavior of the colloidal dispersion is monitored through time-varying changes of macromolecules and of the solvent molecules. Both experiments are utilized by using well-defined magnetic field sequences to probe coupling between nuclear spins through T1 and T2 relaxation constants. Bound fractions of polymer in terms of respective macromolecule conformations (trains, loops and tails) and how they influence optical properties of ZnO colloids are obtained using this methodology.

COLL 103

Relating the radiative and non-radiative processes of CdTe and CdTe-ZnSe core-shell nanocrystals to their surface chemistry

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The surface chemistry of CdTe nanocrystals are less well understood than CdSe nanocrystals, but may be preferable to CdSe in some applications. For example, unlike CdSe, CdTe can retain fluorescence in water without a shell material. The surface of the CdTe nanocrystals plays an extremely important role for this property. We have examined the effects of having a Cd-rich vs a Te-rich surface in terms of the radiative

and non-radiative processes in controlling the fluorescence quantum yield of the nanoparticles – both as-prepared and upon ligand exchange for transferring them to water.

The fluorescence properties of CdTe can be improved by adding a shell material such as ZnSe. Here, the core-shell interface is particularly important in the resulting nanoparticle optical properties. We have also examined the radiative and non-radiative processes that affect these optical properties and propose a model of the extent of electron and hole trapping present in these nanoparticles.

COLL 104

Understanding photoluminescence intensity and lifetime fluctuations in individual NIR emitting nanocrystal quantum dots

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Our team has previously reported near complete suppression of Photoluminescence (PL) blinking in nanocrystal quantum dots (NQDs) in the visible spectral range with a core/thick-shell CdSe/CdS NQD system. NQDs capable of emitting blinking-free PL in the near-infrared (NIR) spectral range are highly desirable for applications ranging from bio-medical imaging to telecommunications. We now report on thick-shelled InP/CdS NQDs, which emit blinking free PL in the NIR (700 –1000 nm). Blinking suppression is studied as a function of shell thickness by analyzing the PL emission characteristics of many single InP/CdS NQDs. Specifically, utilizing time correlated single-photon counting techniques, we analyze the fluorescence lifetime intensity distribution of individual dots to understand the various blinking mechanisms involved. We discuss the effect of NQD band structure as it relates to blinking by comparing and contrasting this type-II system to CdSe/CdS NQDs with a quasi-type II band structure.

COLL 105

Unraveling the complexities of shell growth in thick-shell nanocrystal quantum dots: From synthesis optimization to complete suppression of blinking

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Previously, we showed for the first time that CdSe/CdS core/shell nanocrystal quantum dots (NQDs) comprising ultra-thick shells (number of shell monolayers, n, >10) grown by protracted successive ionic layer adsorption and reaction (SILAR) leads to remarkable photostability and significantly suppressed blinking behavior,[1,2] as well as suppressed non-radiative Auger recombination revealed as long biexciton lifetimes and efficient multiexciton emission.[3,4] The unique behavior of this core/shell system prompted us to assess correlations between specific physicochemical properties—*beyond shell thickness*—and functionality. Here, we demonstrate the ability of particle shape/faceting, crystalline phase, and core size to determine ensemble and single-particle optical properties (quantum yield/brightness, blinking, radiative lifetimes). Significantly, we show how reaction parameters (surface-stabilizing ligands, ligand:NQD ratio, choice of “inert” solvent, and modifications to the SILAR method itself) can be tuned to modify these function-dictating NQD physical properties. Lastly, we report an optimized synthetic approach that results in the complete suppression of blinking.

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COLL 106

Chemical transformations of nanosilver in biological tissue and the natural environment

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Nanosilver is manufactured in large volume as an antimicrobial agent in consumer and medical products, and is thus a high priority case for near-term environmental risk assessment. Several aspects of silver chemistry give rise to a complex environmental behavior worthy of systematic study -- it is stable in the short term, yet undergoes slow oxidative corrosion; its biological effects are often due to silver ion coexisting with the particles, the ion can be photochemically reduced back to elemental silver by sunlight, and silver also forms insoluble chloride phases that limit the free ion concentration in seawater or body fluids. This talk reviews the current state of knowledge of the chemical transformations of nanosilver in the environment and in biological systems, including the kinetics and mechanisms of oxidative dissolution, the active control of ion release rates, and the formation pathways for silver sulfides and selenides as potential low-bioavailability end states.

COLL 107

Metal and metal oxide nanoparticles in aqueous environments: Impacts of nanoparticle aging, surface coatings and size on aggregation and dissolution

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One important issue in understanding the environmental fate, transport, toxicity and occupational health hazards of nanoparticles is in characterizing the nature and state of nanoparticles in air, water or in vivo. For the nanoparticles of interest in these studies, metals and metal oxides, it can be asked: (i) will metal oxide and metal nanoparticles be present in air or water as isolated particles or in the form of aggregates?; (ii) will metal oxide and metal nanoparticles dissolve in aqueous solution or in vivo?; and (iii) under what conditions will metal oxide and metal nanoparticles aggregate or dissolve? As the size regime will be very different depending on the state of the nanoparticles, as dissolved ions, isolated nanoparticles or nanoparticle aggregates, these questions are important to address as it impacts the size regime that needs to be considered or modeled in for example, environmental transport or lung deposition models. Furthermore, the effect on biological systems including nanoparticle-biological interactions and toxicity will depend on the state of nanoparticles. In our studies, we have focused on the dissolution and aggregation behavior of several different metals and metal oxides in aqueous suspensions. In this talk, we present data on the role of nanoparticle aging, organic acids and size on the dissolution and aggregation of several metal-based nanoparticles including Cu, ZnO and TiO_2.

COLL 108

Effect of rhamnolipids on the dispersion of metal oxide nanoparticles in aqueous solution

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Metal oxide nanoparticles are becoming ubiquitous in industrial, manufacturing, and medical applications. However, the long-term impact of these nanoparticles on humans and the environment is unknown. One potential route of exposure is dissolution of nanoparticle aggregates into groundwater. Although such nanoparticles are generally hydrophobic in nature, their dispersion in aqueous media may be facilitated by dissolved dispersants such as naturally-occurring biosurfactants. This work considers the effects of metal oxide nanoparticle exposure to one class of naturally-occurring biosurfactants, the rhamnolipids, which are known to strongly adsorb to metal oxide surfaces. Dynamic light scattering and zeta potential measurements were used to investigate the effects of pH, surfactant concentration, and exposure time on nanoparticle suspension stability. A

correlation between the presence of rhamnolipids and an increase in nanoparticle suspension stability as well as a decrease in average aggregate size is observed.

COLL 109

Generation of silver nanoparticles from larger metal nanoparticles and macroscale metal objects visualized on functionalized TEM grid surfaces

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Detection of nanomaterials in natural environments is challenging and further complicated by the transformation of those materials during exposure, e.g. due to degradation or agglomeration. Recovery and subsequent characterization of the initial material is seldom possible. In order to assess the dynamics of nanoparticles under environmental exposure we use a platform-based system to tether nanoparticles to the surface so that one can directly observe transformations of the material with nanoscale resolution. The platform is robust and electron transparent allowing the use of multiple characterization techniques to understand how surface-bound particles are changing. By applying this approach to the investigation of silver nanoparticles we observed the generation of newly nucleated daughter particles in the vicinity of the deposited parent particles under mild environmental conditions (in air between 50-100% relative humidity). A three-stage mechanism for this transformation is proposed that led us to investigate similar behavior for macro-scale objects (e.g. wire, jewelry, and silverware). The fact that these macroscale objects produce nanoparticles suggests that naturally formed nanomaterials are produced by these objects and have gone undetected to date.

COLL 110

Atmospheric transformations of carbonaceous nanomaterials

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Engineered nanomaterials that are released to the atmosphere will be subject to transformations that could modify their fate, transport, bioavailability, and toxicity in the environment. Carbonaceous nanomaterials will probably become oxidized in the presence of ozone. The objective of this research is to determine the products of reactions of aerosolized C_{60} fullerenes with atmospherically relevant concentrations of ozone. Aerosolized C_{60} fullerenes are introduced into a smog chamber using a dry dispersion method, and batch reactions are carried out at ozone mixing ratios of 40-120 ppb. Aerosol samples from the chamber are collected for analysis by reflection

absorption infrared spectroscopy (RAIRS), liquid chromatography, and TEM. Infrared spectra of C_{60} aerosols indicate that the $C_{60}O$ epoxide and various carbonyl groups form at higher ozone concentrations. Results from complementary analytical methods verify the identities of epoxides and carbonyls and describe C60 aerosol size and morphology.

COLL 111

Sunlight and UVC mediated reactions of carbon nanotubes in the aquatic environment

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Photochemical transformation of nanomaterials released into environmental waters is likely to influence their ultimate fate and persistence. To this end, we have examined the photochemical reactivity of carbon nanotubes (SWNT) in aqueous media, and comparing their reactivity under sunlight and UVC (λ = 254 nm) light. Materials examined include (i) carboxylated single walled carbon nanotubes (SWNT-COOH) from Carbon Solutions; (ii) pristine SWNT from Southwest Nanotechnologies, which contain a high fraction of semiconducting (6,5) chiral tubes (SG65); (iii) partially oxidized (by acid-treatment) SG65 SWNTs and multi-walled CNTs from Nanolabs; and (iv) SWNTs functionalized with polyethylene oxide (SWNT-PEG) from Carbon Solutions. How functionalization affects photochemical reactivity will be reported, including changes in Raman, FTIR, and XPS spectra, TEM images, as well as generation and production rate of reactive oxygen species (ROS). In all experiments, ROS was detected by using molecular probes for singlet oxygen ($^1O_2$), superoxide anion ($O_2^{\cdot -}$), and hydroxyl radial ($\cdot OH$).

COLL 112

Surface functionalization of TiO_2 nanoparticles: Photo-stability and reactive oxygen species (ROS) generation

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One mechanism of toxicity of nominally “safe” materials such as TiO_2 is through the photocatalytic generation of reactive oxygen species (ROS). ROS production and ligand degradation can affect the bioavailability of these particles in aqueous organisms. We have investigated ROS generation by functionalized TiO_2 nanoparticles and its influence on aggregation, bioavailability, and toxicity measurements. Our measurements show that TiO_2 toxicity reaches a maximum for nanoparticles in an intermediate size regime, and is correlated with size-dependent changes in ROS generation. In an effort to reduce toxicity through control of surface ligands, we synthesized anatase nanoparticles of different sizes, functionalized them with different ligands, and examined the resulting ROS generation and ligand stability. Using a modular ligand containing a hydrophobic inner region and a hydrophilic outer region, we have synthesized water-stable nanoparticles having much-reduced ROS generation and thus reduced toxicity. These results suggest new strategies for making safer nanoparticles.

COLL 113

Electrochemical filtration reactive transport mechanism and kinetics

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An electrochemical carbon nanotube (CNT) filter has been reported to be effective for the adsorptive removal and oxidation of aqueous species. Here, we complete a detailed investigation of the reactive transport mechanism during electrochemical filtration. Similar to batch electrolysis; mass transfer, physical adsorption, and electron transfer are found to be three primary steps in the overall electrochemical filtration mechanism. Mass transfer was quantitatively examined and determined to be increased *6-fold* during electrochemical filtration as compared to batch electrochemistry. Physical adsorption of the organics onto the CNTs was evaluated using temperature-dependent batch experiments and fitted to the Langmuir isotherm. The electron transfer mechanism and kinetics were examined by challenging the electrochemical filter over a range of concentrations and direct electron transfer was determined to be the dominant oxidation mechanism. The maximum electron transfer rate is also observed to be affected by the polarity of the molecule indicating electromigration is also active.

COLL 114

In situ AFM studies of nano-TiO_2 and swelling clays

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The ability to predict the mobility of nanoparticles in the environment will require a detailed understanding of the specific interactions of these materials with the different components of soils and sediments. Adsorption on any soil component may inhibit aggregation and thereby affect mobility, but interactions with clay minerals will likely affect other soil properties such as permeability because of changes in the degree of swelling of these layered phyllosilicate minerals. Consequently, an understanding of the feedback processes by which the swelling properties of clay minerals affect - and are affected by- the adsorption of nanoparticles is needed for predictive models of the mobility of nanomaterials in the environment. In the present study, in situ atomic force microscopy (AFM) was used to monitor the changes in swelling properties of individual quasi-crystals of a clay mineral upon exposure to an aqueous suspension of TiO_2 nanoparticles. Comparisons of particles of different size and charge were used to investigate the extent to which these variables influence the nanoparticles' interactions with the clay mineral. The reversibility of adsorption under different conditions was probed by means of sequential changes to the composition of the fluid cell during imaging.

COLL 115

Surface property of gold nanoparticles determines their bioavailability, uptake and distribution in plants

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Gold nanoparticles (AuNPs) were functionalized with positively, neutrally and negatively charged surface groups, and used to determine their uptake and distribution in rice, ryegrass, radish and pumpkin plants. All three types of AuNPs were taken up by these plants, but both plant species and particle surface charges determined the extent of AuNP uptake and distribution. AuNPs(+) were readily taken up by plant roots, but more AuNPs(-) were transferred into shoots. KI/I_2 mixture was used to differentiate AuNPs adsorbed on the root surface from that internalized into the roots. AuNPs(+) were more easily washed off from the roots than AuNPs(-), suggesting most AuNPs(+) were attached to the root surface, not internalized into the roots. This study for the first time addressed the effect of AuNPs surface properties on their uptake and distribution in terrestrial plants, which has significant implications for nanotechnology applications in agriculture and food safety.

COLL 116

Abiological self-assembly: Predesigned metallacycles and metallacages via coordination

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Our latest results in coordination driven self-assebmly will be presented

COLL 117

Controlling nanoparticles with atomic precision: The case of gold

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Controlling nanoparticles with atomic precision has long been a major goal in nanoscience. In this talk, I will present a size-focusing methodology for synthesizing atomically precise gold nanoparticles protected by thiolates (i.e. $Au_n(SR)_m$, also called nanoclusters). Ultrasmall $Au_n(SR)_m$ nanoparticles (e.g. *n* of a few dozens) exhibit distinct quantum confinement effects and interesting electronic and optical properties that are fundamentally different than their larger counterparts-*fcc* crystalline nanoparticles. A few representative, size (*n*) specific $Au_n(SR)_m$ nanoparticles will be discussed in detail. Unlike *fcc* Au nanocrystals that possess translational symmetry, small $Au_n(SR)_m$ nanoclusters do not adopt *fcc* structure; indeed, new types of non-crystallographic structures have been discovered in X-ray crystallographic analyses on $Au_{25}(SR)_{18}$ and $Au_{38}(SR)_{24}$ nanoclusters. Experiment and theory have revealed quantized electronic structure and intrinsic magnetism in such nanoclusters. The transition from the quantum-confined state to metallic state occurs with increasing size (*n* of a few hundreds).

COLL 118

Ultrafast mixed balence nanoclusters

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This lecture will describe supramolecular mixed valence assemblies that exhibit rates of intramolcecular electron transfer on the “ultrafast” picosecond time scale. Trinuclear ruthenium clusters of the type, $[Ru_3O(OAc)_6(CO)(L)(pyS)]$ where L= 4-cyanopyridine, pyridine, and 4-dimethylaminopyridine, bound to Au nanoparticles (NPs) are electrochemically reduced to form mixed valence nanoclusters. Infrared spectroelectrochemical responses show dynamic coalescence of the ν(CO) region, indicating that electron transfer between Ru clusters attached *via* a π-conjugated bridge to NPs occurs on the vibrational timescale. Bloch simulation of IR ν(CO) spectra gives k_{et} on the order of 10^{11}- 10^{12} s^{-1}. Ground state electron transfer rates exhibit strong dependence on solvent dynamics. These results suggest that solvent dynamics control electron transfer, while solvent reorganization energy, λ_s, is surprisingly unimportant in determining ET rates. This behavior is consistent with supramolecular assemblies that lie on the nearly barrier-less, class II/III borderline of mixed valency.

COLL 119

Multi-component nanocrystal assembly: Routes to multifunctional nanomaterials and devices

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The synthesis of colloidal nanocrystals (NCs) with controlled crystal shape, structure and surface passivation provides ideal photonic, electronic and magnetic building blocks for the assembly of new NC thin films and devices. The NCs are "artificial atoms" with tunable electronic, and magnetic properties. This talk will briefly outline a modular approach to the self-organization of NC building blocks including combinations of semiconductor NCs (Quantum Dots), rare earth doped nanophosphors and magnetic NCs. We will show what is possible in the structural and functional characterization of two component and three componet assemblies and demonstrate the integration of NC superlattices in to think fim devices. The design space for new materials and devices expands dramatically with the creation binary and ternary NC superlattices (BNSLs & TNSLs). We will proivide specific examples as we organize differently sized FePt, CoPt3, Fe3O4, UO2, CoFe2O4, Au, Ag, Pd, and NaYF4:Re, LiGdF4:Re (Re=rare earths) nanocrystals among other systems into a rich array of multi-functional nanocomposites (metamaterials). Exploiting a novel methods of interfacial assembly and transfer we will show how assembly conditions can be pushed far from equilibrium resulting in oscillatory deposition of solid films with periodicity on both the nano and micro scales.

COLL 120

Peptide-directed synthesis and organization of nanoparticles: New structures and mechanistic insight

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A method for controlling the simultaneous synthesis and assembly of metallic nanoparticles will be presented. Particular focus will be given to how this method can be used to design new complex nanoparticle superstructues and tailor their structural metrics. In addition, new mechanistic insight into the simultaneous synthesis and assembly process will be detailed.

COLL 121

Microstructure and rheology of Pickering emulsion gels formed by droplet bridging

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Mixtures of immiscible liquids stabilized by solid particles are known as Pickering emulsions, and find important applications in foods, personal care products, oil recovery, and health care. The physicochemical properties of these multiphase mixtures and their correspondence to rheology carry important implications for the processing and shelf-life of their products and derivatives. In this talk we present a novel class of particle-stabilized emulsions that has been carefully designed such that liquid droplets are connected through a bridging particle monolayer, and index matching allows full 3D characterization of the emulsion by quantitative confocal microscopy. We find that droplet bridging results in highly stable and gel-like emulsions at droplet volume fractions well below the random close packing limit of spheres, with key rheological parameters determined solely by the solids volume fraction. We will discuss the microstructural origins of this rheological hallmark and its implications for the design of multiphase materials with gel-like rheology, and present new directions for future research.

COLL 122

Assembly of submicron colloidosomes with silica nanoparticles featuring a selective permeability

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We present a facile and straightforward method for the preparation of microcapsules with nanoparticle shells. These capsules, called colloidosomes, are prepared on the basis of Silica Ludox particles and stearic acid. In contrast to other known methods for the preparation of colloidosomes, here, capsule formation can be carried out at mild pH, ambient temperature with in-situ biomolecule loading and without the use of hazardous chemicals. The incorporation and release of BSA, lysozyme, fluorescine, luciferin and PEG into and from the capsules as well as the influence of these molecules on capsule formation has been studied. While small molecules are released almost instantaneously, molecules in the size of proteins are released over the course of several weeks. The results indicate that molecules that are negatively charged do not interfere with capsule formation and can be successfully incorporated into the capsules.

COLL 123

Using bijels for novel materials synthesis

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Bicontinuous interfacially jammed emulsion gels, or bijels, are a new class of soft materials. These are kinetically trapped, non-equilibrium configurations of immiscible fluid channels stabilized by an interfacial particle monolayer that jams the spinodal

interface, with the characteristic size of the fluid domains tuned solely through the solids volume fraction. These qualities make bijels excellent soft matter templates for novel materials synthesis. In this talk, we outline several strategies for the synthesis of macroporous, hierarchically porous, and composite materials using bijels as templates, and describe their vast potential for application in several fields including tissue engineering, catalysis, separations, and energy systems. Given the self-assembled nature of bijels, it follows that the physicochemical properties of the solid and fluid species are crucial for both bijel formation and the versatile materials processing routes that employ them. These consequential effects along with several novel examples of materials from bijel templates will be discussed.

COLL 124

Particle self-assembly in ionic liquid-based Pickering emulsions

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<script type="text/javascript"></script>

We report the experimental work of microparticle self-assembly in ionic liquid based Pickering emulsions, with emphases on the interfacial structure and the partition preference of particles. In ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate)-in-water Pickering emulsions, the polystyrene microparticles form monolayers at ionic liquid-water interfaces and are close-packed either on fully covered emulsion droplets or aggregated on partially covered droplets. The microparticles also exhibit partition preference in the dispersed and continuous phases and intriguingly, can even be transported across the ionic liquid-water interfaces. In oil (polydimethylsiloxane)-in-ionic liquid Pickering emulsions, a unique and new phenomenon is observed: the microparticles can form bridges between the oil droplets but avoid contact with the ionic liquid phase. The bridge formation inhibits individual droplet-droplet coalescence; however, due to low density and large volume (thus the buoyant effect), the aggregated oil droplets actually promote oil/ionic liquid phase separation and distress emulsion stability.

COLL 125

Toward stimulus-responsive control of foam and emulsion stability using thermoresponsive nanoparticles

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The physics and engineering of switchable stability in foams and emulsion systems depends of active control of the fluid/fluid interface. We utilize nanoparticles with designed surface chemistry to control the contact angle of the nanoparticle at the fluid/fluid interface, the free energy of attachment, ultimately the interfacial elasticity. Interrogation of the aggregation kinetics and rheology of the fluid/fluid interface enables elucidation into fundamental mechanisms of foam and emulsion stabilization.

Here, we discuss a new class of thermosensitive polymeric materials based on random copolymers which display a lower critical solution temperature (LCST) in water that is dependant on co-polymer ratio and ionic strength. Gold nanoparticles grafted with thermosensitive polymer brushes of these copolymers have switchable aggregation kinetics (k11) and interfacial elasticity (E*). We show the dependence of k11 and the complex interfacial modulus (E*) on environmental conditions such as salt concentration and temperature.

COLL 126

Formulation and characterization of magnetically responsive Pickering foams

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Soft materials, which respond to external stimuli, are on the leading edge of materials research. Foam and emulsion systems that can be controlled using UV light, temperature, and magnetic fields have recently been of interest to many researchers. We present an alternative class of magnetically responsive Pickering foams which remain stable until exposure to a gradient field. These foams are stabilized by hydrophobically modified cellulose with magnetic responsiveness imparted through the entrapment of carbonyl iron particles in the cellulose matrix. We have shown that this system remains stable for more than one week prior to exposure to a magnetic field and have evaluated the change in water fraction, collapse behavior, and foam viscoelastic properties with age. We established that the drainage and evolution of our foams occurs on a much longer time scale than surfactant stabilized foams, as expected. However, we also found that the response of the foam to a magnetic field is highly dependent upon the fraction of liquid in the foam films. We proposed two separate mechanisms of collapse, one for wet foams and one for dry foams. We then correlated the collapse behavior to the viscoelastic properties and magnetic susceptibility of the foam, both of which are dependent on the volume fraction of liquid in the foam films. Systems such as the one presented here can find application in a range of industrial and environmental settings that require controlled non-contact and on-demand defoaming.

COLL 127

Control over Pickering emulsion flocculation and rheology using polymer-grafted nanoparticles

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Pickering emulsion rheology is sensitive to droplet flocculation, with flocculated emulsions displaying higher storage and loss moduli than emulsions with the same dispersed phase volume fraction but individually dispersed droplets. When using polymer brush-grafted nanoparticles as emulsifiers, different emulsification conditions lead to different droplet flocculation states. When poly(2-(dimethylamino)ethyl methacrylate)-grafted silica nanoparticles are initially dispersed in the oil phase before homogenization, stable oil-in-water emulsions are produced with individually dispersed droplets. Suspending the same particles in the aqueous phase produces stable oil-in-water emulsions with flocculated droplets and higher moduli. Similarly, droplet flocculation can be controlled when using nanoparticles with poly(ethylene oxide) brushes. In this case, flocculation and emulsion rheology can be altered on demand by heating. Emulsions prepared at room temperature contain individually dispersed droplets that flocculate irreversibly upon heating and subsequent cooling back to room temperature. The result of this thermally triggered flocculation is an increase in moduli.

COLL 128

Particles as emulsion stabilizers: Influence of charge and roughness

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It has been known for more than a century that colloidal particles with the “right” wetting properties can adsorb to liquid interfaces and stabilize emulsions, much like surfactants or amphiphilic polymers do. Still, our fundamental understanding of the connection between particle properties and emulsion characteristics remains surprisingly poor. We can, for example, prepare an emulsion by mixing equal volumes of an oil phase and an aqueous particle dispersion; but even with complete knowledge of both liquids and all particle properties, current theory fails to predict reliably the stability and even the type (w/o or o/w) of the emulsion formed. In this presentation we will discuss the source of such difficulties and point out commonly overlooked effects of particle charge and surface roughness. We support our claims with experimental studies of the emulsion type and stability in systems that allow us to vary the particle charge and roughness *systematically* and *independently*.

COLL 129

Disjoining pressure expressions for thin films with multilayers of polymer coated Janus gold nanoparticles and monolayers of polymer coated gold nanopaticles at their interfaces

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Analytical disjoining pressure expressions for thin films separating two bulk polymeric materials with particles straddling the two interfaces are derived using a hybrid Hamaker-Lifshitz approach. This approach was previously derived in the case of two facing monolayers of polymer coated Janus gold nanoparticles (PJGNPs). Here instead we examine:

(a) Two facing three layers of PJGNPs, formed by particle self-assembly;

(b) Two facing monolayers of polymer coated gold particles, whose ligands are of a material different from the two bulk phases (considered as concentric spheres).

Cases (a) and (b) can take place in particle stabilized immiscible polymer blends. The first when particles are added in excess in the bulk of the drops, the second when the polymer ligands do not “like” both bulk polymers, hence the particles go at the interface.

The expressions take into account particle concentration, size and core materials and the presence of an intervening medium.

COLL 130

Interactions of proteins with ultrathin chitin films

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Chitin, as the second most abundant biopolymer, is of interest for drug delivery and tissue engineering. This work presents simple methods to produce amorphous and nanocrystalline ultrathin chitin films and explores their use as model substrates to study interactions with chitinase, lysozyme, and bovine serum albumin (BSA). Amorphous chitin films are prepared by spincoating trimethylsilyl chitin-chloroform-tetrachloroethane solutions onto quartz crystal microbalance with dissipation monitoring (QCM-D) sensors with subsequent regeneration of chitin by wet HCl vapor. Nanocrystalline chitin films are spincoated onto QCM-D sensors from aqueous suspensions. Results from QCM-D experiments for BSA show the substrates are suitable as biosensors, while the enzyme studies show the chitin can be degraded and that morphology affects the rate of degradation.

COLL 131

Surface modification of cellulose and lignin by adsorption of soy proteins

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The adsorption of the two main proteins in soy, glycinin and β-conglycinin, was studied by using quartz crystal microgravimetry, surface plasmon resonance, circular dichroism, and water contact angle measurements. The amounts of both globulins adsorbed from aqueous solutions of various pH and ionic strength were measured onto lignin and cellulose. While the adsorption on cellulose was drastically affected by salt addition little or no change was observed in the case of lignin substrates. In addition, adsorption of denatured proteins (mercaptoethanol or urea) was reduced (»50%). These observations indicate the relevance of hydrophobic interactions and the breaking the disulfide linkages in the macromolecules. Water contact angle measurements before and after protein adsorption supported our interpretation of the results in terms of the contribution of hydrophobic and hydrophilic aminoacids interacting with lignin and cellulose, respectively.

COLL 132

Injectable biomimetic hydrogels to direct neural stem/progenitor cell fate upon transplantation into the stroke-injured brain

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Stroke is a devastating injury that affects millions of people worldwide, and for which there is no therapeutic cure. Neural stem/progenitor cell transplantation is a promising approach to enable the replacement of dead or injured cells in the brain caused by stroke. However, current strategies are limited by cell death and uncontrolled differentiation upon transplantation. Our lab developed a physical blend of hyaluronan (HA) and methyl cellulose (MC) as a cell delivery vehicle and demonstrated significantly enhanced cell survival and distribution upon transplantation. To further enhance the cell survival of transplanted stem cells, we are immobilizing to HAMC both cell-adhesive peptides and growth factors known to promote cell survival and differentiation. We have specifically designed the immobilization chemistry to ensure peptide and growth factor bioactivity. We will report on these chemical modifications and the response of neural stem/progenitor cells in terms of viability and differentiation profile in culture.

COLL 133

Transport, binding and displacement of growth factors within starPEG-heparin hydrogels

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Multibiofunctional hydrogels offering spatiotemporal control over the presentation of growth factors and adhesion ligands are of particular interest in tissue engineering.

We refer to a recently introduced starPEG-heparin hydrogel platform and report data on uptake, association and delivery of potent and widely used growth factors, including FGF2, VEGF and BMP2.

It is demonstrated that the degree of crosslinking of the polymer network and affinity of the proteins to heparin determine their distribution within the gels. Selective desulfation of the heparin units was effective in increasing the release kinetics. Furthermore, chitosan was shown to be applicable as 'release booster' by displacing heparin-associated proteins.

The huge capacity of the gels for growth factors allowed for the combination of different effectors without interference of uptake or release over a wide range of physiologically relevant quantities.

The advantages of such systems are highlighted for example cases from angiogenic and neural tissue engineering.

COLL 134

Core-shell microgels as “smart” carriers for enzymes

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We present a thermodynamic study of lysozyme binding on a negatively charged core-shell microgel. Isothermal titration calorimetry (ITC) is used to investigate the temperature and salt dependence of protein binding. Our ITC analysis unequivocally shows that this process is driven by entropy. The addition of salt strongly decreases the binding affinity indicating significant electrostatic contributions to the adsorption process. However, at high salt concentrations substantial protein binding with unaltered entropies is still observed pointing to large contributions from hydrophobic interactions.

Furthermore, the calorimetric analysis suggests that protonation of lysozyme takes place upon binding. This is directly shown by analysis of the enzymatic activity of adsorbed lysozyme. It was found that the activity is enhanced about ~3.5 times indicating that lysozyme has taken up approximately one proton when entering the gel. The entire set of data demonstrates that core-shell microgels present “smart” colloidal carriers for lysozyme that enhance its activity.

COLL 135

Molecular recognition force spectroscopy study of a self-assembled enzymatic monolayer directly bound to a gold surface

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A self-assembled enzymatic monolayer of *Escherichia coli* dihydrofolate reductase (ecDHFR) was formed on an ultraflat gold surface through a single surface cysteine, C152, on the enzymes surface. The activity of the gold-immobilized ecDHFR as measured by radiographic analysis was found to be similar to that of the free enzyme in solution. Molecular recognition force spectroscopy was used to study the dissociation forces involved in the rupture of AFM probe-tethered methotrexate (MTX, a tight-binding inhibitor of DHFR) from the gold-immobilized enzyme. The rupture force was found to be 245 ± 110 pN. The enzymatic monolayer was then treated with free MTX and the interaction forces between the functionalized tip and surface significantly diminished to 40 ± 20 pN, suggesting the interaction was active-site specific. This work demonstrates the viability of direct enzymatic surface functionalization without the use of spacers, leading to new applications in the area of biomacromolecular force spectroscopy.

COLL 136

Chiral sum frequency generation spectroscopy: A probe for protein secondary structures and proton exchange at interfaces

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Characterization of protein secondary structures at interfaces is central in solving fundamental and engineering problems in biomedical and material sciences. However, it remains challenging because it requires a technique selective to both interfaces and secondary structures. Here, we use surface-specific chiral sum frequency generation (SFG) spectroscopy to obtain amide I and N-H stretch spectra of peptide backbone in various secondary structures at interfaces. We found that the spectra are unique to parallel beta-sheets, anti-parallel beta-sheets, alpha-helices, 3-10 helices, and random-coils, thus providing signatures to characterize these structures at interfaces. Moreover, the N-H/H-D stretch of peptide backbone is not interfered by the achiral water O-H/O-D

stretch, which allows probing kinetics of H-D exchange of protein backbone at interfaces in real time and in situ. Our results support that chiral SFG can identify secondary structures at interfaces, similar to the use of circular dichroism spectroscopy for characterizing secondary structures in bulk solution.

COLL 137

Structure and function analysis of surface-immobilized wildtype von Willebrand Factor and clinical von Willebrand Factor mutants

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von Willebrand Factor (VWF) is a soluble blood clotting protein. Previous studies in our lab have shown surface characteristics influence adsorbed structure and function of the platelet binding domain of VWF (A1 domain). Structural changes are also important in clinical VWF mutants. Here, we use surface analysis techniques to obtain greater detail about structural differences of VWF adsorbed onto different surfaces.

Near-edge x-ray absorption fine structure was used to identify differences in the amide backbone of A1 adsorbed to polystyrene, tissue culture polystyrene, and glass. Differences in the sum frequency generation amide spectra also suggested structural differences in adsorbed A1 on different surfaces. Time-of-flight secondary ion mass spectrometry data showed differences between clinical A1 mutants when adsorbed to different surfaces, as well as differences between the proteins when adsorbed to the same surface, suggesting conformational changes induced by surface adsorption may be different from changes caused by mutation.

COLL 138

Interface of covalently bonded phospholipids

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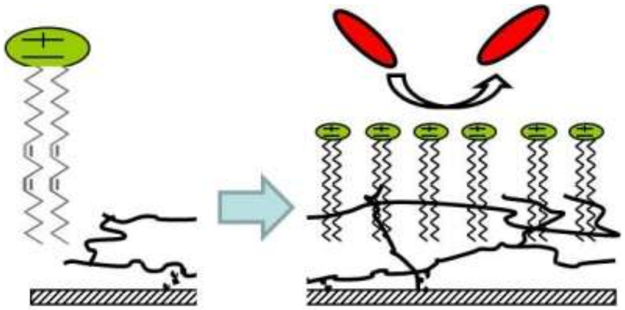
Surface anchored poly(methylhydrosiloxane) (PMHS) thin films were functionalized with 1,2-dilinoleoyl-sn-glycero-3-phosphorylcholine (18:2 Cis). The surface was characterized by X-ray photoelectron spectroscopy, contact angle measurements, atomic force microscopy, and scanning electron microscopy. The interface was very hydrophilic and repellent toward avidin, bovine serum albumin, bovine fibrinogen, lysozyme, and α-chymotrypsin adsorption (observed by normal scanning fluorescence)

at pH 7.4. Further possibilities of functionalization on the surface remain available owing to the formation of interfacial SiOH groups.



COLL 139

Functional peptides and polymers for drug and gene delivery

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Compared with conventional therapeutic systems, drug and gene delivery systems offer numerous advantages. Our studies were focused on the functional peptides and polymers for drug and gene delivery. To endow the delivery systems with active targeting property, studies have been carried out on the incorporation of various targeting ligands including particular cell penetrating peptide sequences, RGD sequence, transferrin, galactose, and folate to drug and gene delivery systems through covalent bonds and biotin-avidin interaction. To endow the delivery systems with stimuli responsibility, we designed and prepared various types of nanoparticulate drug delivery systems with stimuli responsibilities including pH, temperature, redox potential, and light sensitivities. These drug and gene delivery systems exhibited improved drug controlled release properties and enhanced gene transfection efficiencies. In addition, the targeted delivery to particular tissue and tumor cells could be achieved through incorporation of particular targeting ligands.

COLL 140

Cellular confinement in 3D suppresses focal adhesions and induces actomyosin-independent motility

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Cells migrating on two-dimensional (2D) substrates coordinate the formation of focalized substrate adhesions with cycles of cell protrusion and contraction; however, this mechanism may not accurately describe the movement of cells through 3D space. We sought to determine how 2D motility mechanisms adapt to more complex environments by using a microchannel-based approach to subject migrating cells to varying degrees of physical confinement. By simultaneously observing the movement of cells in both unrestricted 2D space and narrow microchannels, we demonstrate that physical confinement in 3D induces a distinctive mode of motility. Cells migrating in 3µm x 10µm microchannels exhibited a loss of dorsoventral polarity and moved at nearly constant velocity with a distinctive 'sliding' motion. Cells undergoing sliding motility did not generate lamellipodia, stress fibers or mature focal adhesions, and were not impeded by inhibitors of Rho GTPases, ROCK, myosin II or myosin light chain kinase. This work describes a distinctly non-mesenchymal mode of locomotion that is induced by confinement in 3D, and emphasizes that actomyosin-independent tumor cell migration may occur in physiological contexts.

COLL 141

Biomimetic membranes: Structure and dynamics and mechanisms of particle uptake

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The controlled transport of particles through cell-membranes is essential for proper functioning of all living organisms. The process in which living cells absorb molecules and nanoparticles is known as endocytosis. During this process the particles pass into the cell via “invagination” and subsequent “fission” of the cell-membrane. Because, bio-membranes are complex and direct investigations are difficult we developed an experimental model system to study transmembrane transport and the parameters which influence the mechanism.

Here we present a photon correlation spectroscopy (PCS) study of the uptake of nanoparticles by tailored block copolymer vesicles. The relaxation functions for a particle/vesicle mixture reveal the presence of free and bound particles. Both the experimental form factor and the effective diffusion coefficient of the resulting structures are consistently described by modeling by filled vesicles with about 10-20 particles under the examined conditions. The emerged picture is supported by fluorescence correlation spectroscopy (FCS) studies and cryo-TEM.

COLL 142

Hydration-induced reorganizations in multilamellar lipid mesophases

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Hydration-induced self-assembly of lipid amphiphiles producing organized membrane mesophases reflect an interplay between membrane material properties (e.g., elasticity, fluidity) and their dynamic interfacial interactions with water. Two generic manifestations of this phenomenon include (1) the formation of highly-oriented, multilamellar smectic membrane mesophases and (2) appearance of multilamellar cylindrical membrane phases or myelin figures obtained by controlled hydration of lipids from their nominally dehydrated mixtures. *First*, we examine how smectic coupling in multilamellar lipid membranes influences in-plane phase separation. We find that the two-dimensional (2D) intra-layer phase separation of lipids becomes coupled with the out-of-plane inter-planar smectic ordering, which propagates across hundreds of membrane lamellae producing long-range alignment of phase-separated domains in the third dimension. We postulate that this long range epitaxy is solvent-assisted, originating from the differences in the network of H-bonded water molecules at the aqueous interfaces of the domains and the surrounding phase. *Second,* probing the long-range dynamics of lipid myelinization, we find the existence of well-separated regimes of myelin growth, coiling, uncoiling, and retraction. A thermodynamic description of these regimes suggest these regimes to represent a distinct set of local equilibria, transitions between which appear to be effected by changes in water chemical potential. Co-authors Lobat Tayebi, Daryoosh Vashaee, Yicong Ma, Sunil Sinha, and Sean Gilmore are acknowledged. Funding from Basic Energy Sciences is acknowledged.

COLL 143

Artificial lipid bilayer platforms for ion channel screening

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We are working to develop artificial lipid bilayer platforms which allow the measurement of physiologically relevant ion channels quickly, easily, and inexpensively. In our initial work, we demonstrated the automated synthesis of lipid bilayer arrays. Our current work centers on measurement of the human cardiac potassium channel hERG (Kv11.1), rat TRPM8, and other physiologically relevant ion channels. In particular, our bilayer apparatus allows solution perfusion, enabling measurement of ensemble ion channel conductance in the presence of varying modulator concentrations, resulting in EC50 and IC50 values that match the literature. I will report on our progress to validate this platform with a number of physiologically relevant ion channels and develop a parallel and automated platform to perform these measurements with increased throughput. Such a platform may find use to increase productivity of conventional lipid bilayer studies as well as high throughput ion channel screening.

COLL 144

Patterning of nanometer-scale domains in lipid bilayers: Membrane "circuits"

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I will present new results where we use nanofabricated substrates that impose curvature to create dynamic sorting patterns of lipid domains that resemble the pixilated patterns of integrated circuits. A square lattice of hemisphere-like features, “bumps”, were fabricated by electron beam lithography of PMMA coated silicon wafers. A lipid multibilayer stack of DPPC: DOPC: cholesterol was deposited on the nanofabricated substrates using spin coating. This composition displays liquid-ordered (Lo)/liquid disordered (Ld) coexistence. The smallest 200 nm lattice sorted Lo phase into distinct interconnected networks of lines and rectangular shapes. The interconnectedness of the domain pattern decreased as the lattice spacing increased. Isolated circular domains, confined to one unit cell of the lattice, emerged in the pattern. These are essentially the “pixels”, or smallest addressable elements, and it will be shown that dynamic patterns of Lo phase are formed through placement and movement of these domain pixels.

COLL 145

Mechanical and dynamic mechanical analysis of asymmetric lipid bilayers

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While the asymmetric composition of the eukaryotic plasma membrane has long been recognized, there is no consensus as to its biological function. Here, we investigate the possibility that membrane asymmetry modulates the ability of membrane morphology to change by probing the mechanical properties of asymmetric membranes.

Asymmetric giant unilamellar vesicles (GUVs) are fabricated in multiphase microfluidic sheath flow using a double-emulsion format. Excess solvent from the organic phase is evaporated, producing bilayer lipid membranes. GUVs are produced with asymmetry in phosphatidylserine, phosphatidylethanolamine, and sphingomyelin compositions.

Mechanical properties of asymmetric GUVs are analyzed by micropipette aspiration and fluctuation analysis to find bending modulus, area expansion modulus, and intrinsic curvature as a function of lipid composition. In addition, a dual-beam optical trap is used to apply a dynamic force field to GUVs, allowing for dynamic mechanical analysis experiments that probe membrane viscoelastic (i.e. strain rate-dependent) properties.

COLL 146

Localization and regulation of bacterial proteins at curved membranes

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In this abstract we describe recent experimental progress that tests an evolutionarily conserved hypothesis for biomolecule localization at interfaces in bacteria and mitochondria. We explore how the curvature of the cytoplasmic membrane causes the spontaneous localization of domains of the intrinsically curved lipid, cardiolipin (CL) to region of large, negative curvature. We hypothesize that these domains function as landmarks for positioning and regulating the activity of amphipathic proteins in vivo. Using a combination of biochemical and physical chemical techniques we demonstrate that the *Escherichia coli* recombination repair enzyme, RecA binds to anionic phospholipids and co-localizes with CL to regions of large, negative curvature. These results suggest that anionic domains in membranes may control the polar localization of RecA in vivo. The lipid composition of the membrane regulates the DNA strand exchange activity of RecA, further suggesting that its interaction with the membrane may toggle the activity of this protein in vivo.

COLL 147

Probing the nature of ibuprofen confined in mesoporous media by neutron vibrational spectroscopy and first-principles calculations

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In this report, the nature of ibuprofen incorporated into mesoporous silicon dioxide or magnesium aluminometasilicate by sublimation and adsorption was investigated using neutron vibrational spectroscopy. Crystalline ibuprofen was the model drug compound. Neutron vibrational spectra of both bulk and nano-confined ibuprofen were compared with the simulated ibuprofen spectra using first-principles phonon calculations. The different character of the neutron vibrational spectra at lower frequencies for the nano-confined ibuprofen, compared to neat crystalline ibuprofen, infers that the overall structural order was markedly reduced once the ibuprofen molecules infiltrated the pores. Furthermore, the dimerization of ibuprofen molecules via hydrogen bonding between carboxylic acid groups was also inhibited, likely due to spatial constraints. Based on the attainable ibuprofen loadings by sublimation, the results suggest that nano-confined ibuprofen molecules were bound to the pore surfaces via hydrogen bonding between the carboxylic acid groups of ibuprofen and surface hydroxyl groups of the mesoporous media.

COLL 148

Tunable enhanced plasmonic nanostructures for enhanced sensing

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Gold nanosphere arrays with precisely controlled size and interspacing were fabricated by nanosphere lithography for applications in surface enhanced Raman scattering and metal enhanced fluorescence. We demonstrate that by etching 500 nm and 250 nm polystyrene spheres on a polyolefin surface using an oxygen plasma etcher, ordered bead arrays with sizes between 500 and 100 nm can be obtained. Integrating the polystyrene nanospheres onto our polyolefin shrink film, we can decrease our interparticle spacing by out 40%. In addition, by sonication of beads we can fabricate triangular nanopores with base sizes near 200nm, and maximum spacing of 150 . This can be shrunk to obtain sizes and spacings 40% smaller. We will deposit gold and silver nanoparticles into these pores for potential optical enhancements. The methods describe allow for tunable nanoparticle arrays at high resolution and low cost.

COLL 149

Application of surface-enhanced infrared and Raman spectroscopic analysis of aromatic amines

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Surface-enhanced Raman spectroscopy (SERS) has been studied to a much greater extent than surface-enhanced infrared analysis (SEIRA) because of the significantly greater signal enhancement factor of SERS and its wide variety of substrate choices. In this study, the feasibility of preparing a versatile substrate amenable to both techniques is investigated in order to optimize the synergistic powers of SERS and SEIRA for identifying trace levels of structurally similar aromatic amines. The analytes studied include known or suspected carcinogens such as 4-aminobiphenyl, 2-naphthylamine, o-toluidine, as well as melamine derivatives and their respective isomers. The substrate preparation procedures rely on the use of colloidal synthesis and electroless deposition techniques involving gold, silver, and copper. The reliability of correctly identifying the aromatic amines via spectral matching of SERS and SEIRA is evaluated by the Euclidian distance search algorithm and will be compared to the corresponding match indices based on NIST mass spectral library.

COLL 150

Controlling spatial localization of molecules for plasmon enhanced spectroscopy

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Focusing on local electromagnetic fields in plasmonic materials leads to enhanced signals for spectroscopy applications such as surface-enhanced Raman scattering. We use structural control to focus fields in plasmonic architectures. In order to take advantage of the optical antenna-like behavior of these materials, molecules of interest must be in the vicinity of the localized field. We are using spatial localization of surface functional groups to produce an asymmetrically functionalized nanoparticle, or Janus particle. This enables controlled assembly with other particles or templates such as polymers that provide a scaffold for organization. We also are using this process to direct Raman-active molecules into regions of the spatially-localized fields in order to tailor these nanoparticle assemblies for spectroscopic applications. The dependence of the yield of nanoparticle assemblies produced and the intensity of the Raman signals on different type of ligands and functionalization approaches will be discussed

COLL 151

Nanoparticle enhanced spectroscopy proteins in gel electrophoresis media: UV-visible, Raman and infra-red measurements

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In this paper we report results of UV-Visible, Raman and Infrared spectroscopy of nanoparticle containing electrophoresis media - namely, aqueous agarose and polyacrylamide gels with and without protein components. Our early results show promise for the detection and possible speciation of unlabeled proteins without their removal from the elcrophoresis media. Detection sensitivity is poorer than conventional plate reading with labeled proteins. But this situation may be further improved using immunological style sandwich type assays to improve the intimacy of contact between nanoparticles and target proteins.

COLL 152

Nanoparticle-enhanced detection of molecular displacements using the near-field of subwavelength optical waveguides

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Here we discuss recent results on the distance sensitivity of the near-field of subwavelength optical waveguides by measuring optical signals of fluorescent and plasmonic optical transmitters embedded in the evanescent field. By self-assembling

thin polymeric coatings on nanoscale optical fibers (< 200 nm diameters), we were able to map out the optical field intensity around the fibers as a function of distance. Through experiments and simulations we demonstrate sub-nm sensitivity to objects moving in the evanescent field and discuss the dielectric-plasmonic effects that appear to enhance the distance sensitivity. In addition, we demonstrate real-time monitoring of single molecular displacements by linking molecules between the plasmonic nanoparticles and waveguide surface and applying forces. The simple design and ease of obtaining optical feedback on molecular movement makes this platform ideal for ultrasensitive force sensing devices and high-throughput molecular analysis.

COLL 153

Rapid and sensitive detection of troponin I from human whole blood samples using silver nanoparticle films and microwave heating

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Cardiovascular diseases are among the leading causes of mortality in developed countries. The detection of TnI from human whole blood samples using Microwave-Accelerated and Metal-Enhanced Fluorescence (MA-MEF) technique, which is based on the combined use of low power microwave heating, silver nanoparticle films (SNFs) and fluorescence spectroscopy, is presented. The detection of TnI from buffer solutions and human whole blood samples on SNFs was carried out using fluorescence-based immunoassays at room temperature (control immunoassay, 2 hour total assay time) or using microwave heating (MA-MEF-based immunoassay, 1 minute). It was found that the lower detection limit for TnI detected from buffer solutions in the control immunoassay and MA-MEF-based immunoassay was 0.1 ng / ml and 0.005 ng / ml, respectively. The use of MA-MEF technique afforded for the detection of TnI from whole blood samples in 1 min with a lower detection limit was 0.05 ng/ml.

COLL 154

Single molecule surface enhanced Raman of poly (3-hexylthiophene-2, 5-diyl) and substrate dependence of surface enhanced Raman

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Poly(3-hexylthiophene-2,5-diyl) (P3HT) is widely used in organic photovoltaics because of its broad light absorption and relative good photostability. Raman spectroscopy has been used to study the morphology of the conjugate polymer thin in the presence of fullerene under various annealing and solvent conditions to reveal the structural changes of the polymer in a real device environment. This study uses nanotextured silver film as surface Plasmon source for single molecule Raman spectroscopy of single conjugate polymer. Our study indicates that P3HT shows extremely stable Raman

spectra with long lifetime in comparison to the R6G single molecule trajectories. Four kinds of solvent including chlorobenzene, dichloromethane, toluene, and tetrahydrofuran are used to help understand the solvent dependence and Raman signature of the conjugate polymer on nanotextured silver substrates. Raman spectra of ensemble and single molecules are compared. More than twenty single molecules were probed per solvent with their results indicating good agreement with the ensemble measurements. Our study shows that toluene showed the most Raman bands in its spectra but similar overall intensity was seen in the trajectories using all solvents, indicating solvent plays a critical role in defining the folding of the molecule on the surface. Time dependent Raman spectra were measured with 30 seconds per spectrum using a spectrometer with a nitrogen-cooled CCD camera. The spectra showed increases and decreases in various Raman band intensities independent of the solvent. Polarization effects were confirmed by varying the incident light polarization and help indicate the single molecule capability. We also present the fluorescence background of the silver substrate such as silver nanowires and the dependence of Raman signal of small molecules on the aggregation states of single nanowires and the changes in the polarization angle of incident light to reveal the relationship between the field enhanced fluorescence of silver and Raman.

COLL 155

Copper-benzotriazole nanofiber growth on copper from amine-based photoresist strippers

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Exposure of copper to amine-based photoresist strippers containing benzotriazole (BTAH) can result in the growth of thick films of Cu-BTAH nanofibers. For advanced semiconductor cleaning applications, the growth of insulating Cu-BTAH nanofiber films is unacceptable due to increased via resistance. With the ultimate goal of preventing these Cu-BTAH films, the growth of insulating Cu-BTAH films was investigated using a model photoresist stripper containing n-methylpyrrolidone, water, methanolamine, and BTAH. The growth of Cu-BTAH nanofibers from this model stripper occurs in two phases. In the first minute, an ultrathin Cu(I)-BTAH film forms. The bulk of this film growth occurs at Cu grain boundaries. Though not always observed, a second growth phase can occur in which a thick Cu(II)-BTAH film composed of nanofibers rapidly grows from the copper surface. Characterization of Cu-BZT nanofiber films, film growth from this system, and a possible mechanisms will be discussed.

COLL 156

Effect of counterion on aqueous inkjet dispersion's stability and performance

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Most Inkjet printers for home and office use aqueous pigment (cyan, magenta, yellow and black) dispersions instead of dyes for optical density improvement, waterfastness and ozone/light fastness. In order for aqueous dispersions to perform well in inkjet inks, the dispersions have to pass certain criteria such as heat aging stability in water and ink vehicles. The dispersions are considered colloidal particles therefore their stability and performance can be improved by surface treatment chemistry, treatment level and counterions. In this presentation we will illustrate the use of different counterions to tune dispersion's stability and performance on uncoated plain paper and offer possible explanations based on Zeta potential titration and conductivity titration results.

COLL 157

Polymer-directed orientation of shaped nanocrystals

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Shaped nanoparticles present unique building blocks for the fabrication of electromagnetic materials, but are challenging to organize into hierarchical arrangements that possess specific orientations. Here we present a facile self-assembly approach to arrange polymer-grafted metal nanocubes into arrays of one-dimensional plasmonic strings that possess tunable orientation and electromagnetic properties. We engineer the non-specific nanoparticle interactions that modulate the relative strengths of attractive van der Waals and repulsive steric forces by addressing simple parameters such as polymer chain length, rigidity, and grafting density. We demonstrate this by fabricating a nanoparticle thin-film that switches from one nanoparticle orientation (edge-connected) to another (face-connected). The observed change in optical response is consistent with electric field calculations and demonstrates the potential of nanoparticle self-assembly for creating designer plasmonic materials.

COLL 158

Transport and the retention of nanoparticles in sand filters in municipal water treatment facilities: The role of surface active agents and filter sand biofilm

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Nanoparticles (NPs) are manufactured in a wide range of industries and their application for consumer products is increasing. Questions have been raised whether they can be removed by traditional water treatment procedure once they are released into surface or groundwater. This study aims at: (1) investigating the potential retention and transport of NPs in sand filters at water treatment facilities (WTF); (2) exploring the

role of dispersant and capping agents, which are commonly added during the manufacturing of NPs, (3) understanding the influence of biofilm in a biological filtration media, which covers the surface of the sand surface in the filtration system. Three types of commonly used NPs, CeO_2, TiO_2 and Ag were studied with bare surface and in the presence of surfactant. Filter sand and water from prefiltration stage of WTF were obtained. The water was collected prior to the sand filter and was characterized in terms of pH, total organic carbon, conductivity, turbidity, phosphate, sulfate and nitrate. The stability of different NPs was investigated by studying the particle size distribution with time and the EMP/Zeta potential in water. NPs Breakthrough was obtained from column studies with three different sand surfaces to investigate role of sand surface and biofilm. All the experiments were conducted using NPs with and without surfactant and the stabilization mechanism of surfactant was discussed. The data was used to build a predictive computational fluid dynamic model that has practical significance to evaluate the interaction of NPs and the traditional sand filtration system in WTFs.

COLL 159

Liquid-solid extraction of metallic cations by cationic amphiphiles

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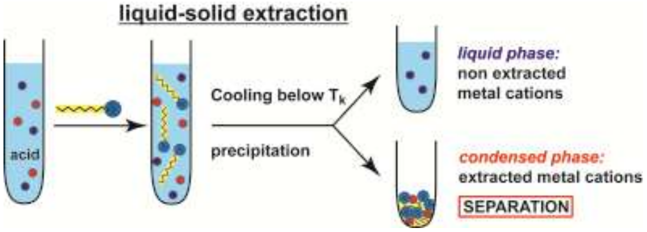
On the large scale, selective metal ion separation is conducted in a liquid-liquid extraction process through an emulsion mixing of hydrophobic complexants in an organic phase and ions in acidic water. However, we demonstrate that liquid-solid extraction, where the final state of the separation is a solid phase containing the extracted ions, is also suitable for the separation of cations. In liquid-solid extraction, the selective precipitation of metal ions from an aqueous salt mixture occurs in the presence of a cationic surfactant, below its Krafft temperature (see Figure 1) [1]. By computing the free energy, we were able to identify the interactions between the surfactant micelle surface and the ions [2]. We demonstrated also that the hydrophibicity of the anionic complex is of importance to tune the selectivity of liquid/solid extraction.



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[2] W. Müller et al, *Langmuir* submitted

COLL 160

Structure of redox active core dendrimers in polar and non-polar solvents

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Dendrimers with redox core have application in nanoscale devices like artificial receptors, electrical switching due to their electron accepting, electron donating, shifting and storing capability. Structure activity relationships have shown to control the redox processes in dendrimers. In this study we have used rigid G2-benzyl ether dendrimers to represent hydrophobic interior of protein and reduced Iron-sulfur redox ($Fe_4S_4^{-2}$) cluster at their core. We perform MD simulations to monitor the influence of different surface groups on the structure of the dendrimers, in solvents of different polarity. We found that surface groups and solvent interactions change the folding pathway and dynamics of the equilibrium conformation due to the steric hindrance. Moreover, the symmetry and position of the core is significantly affected by the polarity of the solvent used. Also a change in solvent accessibility of the core is is more prominently observed in non-polar solvents.

COLL 161

J-Aggregation and two-photon absorption enhancement of polymer-templated porphyrin derivatives

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Supramolecular structures based on organized assemblies of macrocyclic chromophores, particularly porphyrin-based dyes, have attracted widespread interest as components of molecular devices with potential applications in molecular electronics, artificial light harvesting, and pharmacology. We report the formation of J-aggregates of two porphyrin-based dyes, 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (TSPP) and an amino tris-sulfonate analog (ATSPP) in water using a functionalized norbornene-based homopolymer, synthesized by ring opening metathesis polymerization (ROMP). Ionic interactions of the cationic side chains (ammonium groups) of the polymer under acidic conditions with the negatively charged sulfonate groups of the porphyrins facilitated polymer template enhanced J-aggregation of the porphyrin dyes. J-aggregation behavior was investigated photophysically by UV-vis absorption along with steady-state and time-resolved fluorescence studies. Two-photon absorption (2PA) was

enhanced by about an order of magnitude for the J-aggregated TSPP relative to its free base. Significantly, the 2PA cross section of the polymer-templated TSPP J-aggregate was up to three times higher than the J-aggregated TSPP in the absence of the polymer template while the 2PA cross section for polymer-templated J-aggregates of ATSPP increased substantially, up to ca. 10,000 GM, suggesting a prominent role of polymer-templating to facilitate porphyrin aggregation and greatly enhance nonlinear absorption.

COLL 162

How the effects of pyridine on nanocrystal photoluminescence vary with nanocrystal shape

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Colloidal nanocrystals are solution-processable chromophores with size-tunable properties and potential for use in electronic applications, including photovoltaic solar cells. Researchers have incorporated nanocrystals with a variety of shapes into photovoltaics. The charge transport properties of nanocrystal-based photovoltaics are increased when nanocrystals with elongated shapes (e.g., nanorods, tetrapods) are used.

The surfaces of colloidal nanocrystals are covered with ligands. Exchanging these surface ligands with small molecules (e.g., alkylamines, alkanethiols, etc.) has been shown to alter nanocrystal photoluminescence. Although researchers use nanocrystals with different shapes in various applications, it is not known whether ligand effects on nanocrystal photoluminescence vary with nanocrystal shape. We report that exchanging CdSe nanosphere ligands with pyridine and dimethylaminopyridine quenches the nanosphere photoluminescence, as reported by other groups. However, pyridine does not significantly quench nanobelt photoluminescence. We discuss these effects in terms of the differences in the surface structure and composition of nanospheres and nanobelts.

COLL 163

Do nanoarchitectured electrode pore geometries influence electrochemical capacitance?

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A wide variety of porous carbons have been studied as electrodes in electrochemical capacitors, but it is not clear whether ordered pore geometries are preferable to disordered ones in nanoarchitectured electrodes in order to discharge greater capacitances or to exhibit increased rate capabilities. We hypothesize that electrode

pore geometries do not alter the magnitude of discharge capacitance, when all other physical and electrochemical characteristics of the electrode are comparable. In this study, we fabricate and compare the discharge capacitances of carbon nanofoams and carbon inverse opals—carbon nanoarchitectures with aperiodic and three-dimensionally ordered macropores, respectively. Both carbon nanofoams and carbon inverse opals have similar electrochemical surface areas, surface chemistries, and electronic conductivities. The electrochemical surface areas of carbon inverse opal papers are too variable yet to draw definitive conclusions, but preliminary electrochemical evidence indicates that both pore geometries discharge similar magnitudes of capacitance and have similar dielectric relaxation times.

COLL 164

Transparent organosilicate films with thermally insulating and UV-blocking properties based on silica/titania hybrid hollow colloidal shells

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In this study, we propose transparent organosilicate films with thermally insulating and UV-blocking properties based on silica/titania hybrid hollow shells (SiO_2/TiO_2 HHSs). SiO_2/TiO_2 HHSs are the attractive candidates to save energy as one of effective insulating materials due to low thermal conductivity originating from hollow inner space as well as the excellent UV-block characteristics of TiO_2 shells. The hollow silica shells (HSSs) were first prepared using poly(acrylic acid) (PAA) colloidal aggregates as templates, tetraethyl orthosilicate (TEOS) as a silica precursor, and ammonia hydroxide as a catalyst based on the modified Stöber method. TiO_2 shells were then coated on the surfaces of HSSs using titanium tetrabutoxide as a titania precursor. The PAA@SiO_2/TiO_2 core@multi-shell colloidal nanoparticles prepared were washed with distilled water to remove the PAA templates, leaving behind SiO_2/TiO_2 HHSs. The average diameter of SiO_2/TiO_2 HHSs was varied from 30 to 100 nm. The organosilicate matrices were also prepared by the sol-gel reaction with TEOS, methyltrimethoxysilane, and dimethyldimethoxysilane as silica sources along with hydrochloric acid as a catalyst. The SiO_2/TiO_2 HHSs mixed with organosilicate matrices were deposited on glass substrates to realize thermally insulating and UV-blocking layers. The SiO_2/TiO_2 HHS-coated glasses show excellent heat- and UV-blocking capabilities, yet maintaining high transparency.

COLL 165

Preparation and characterization challenges to understanding environmental and biological impacts of nanoparticles

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The use of engineered nanoparticles in research and in consumer products engenders a growing need to understand their properties and behaviors as they are synthesized, applied and evolve (or age) in a particular environment. There is an increasing awareness of the need to understand the health, safety and environmental impact of nanoparticles in their snthesized form and as they evolve through application or environmental interaction. It is also recognized the reports on the properties of nanoparticles are sometimes based on inadequate characterization. This talk will provide examples of measurement issues and challenges we have faced in understanding and characterizing various types of nanoparticles. Topics include: the importance of surface characteriation; effects of synthesis and handling details on particle properties; influence of solution conditions on particle aging and chemical state; and characterization challenges associated with time, insitu versus ex situ measurement, probe damage, and particle extraction from solution.

COLL 166

XPS characterization of functionalized gold nanoparticles

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Nanomaterials exhibit unique surface properties. Thus, there is a need to develop rigorous and detailed surface analysis methods for their characterization. The surface chemistries of carboxylic acid terminated self-assembled monolayers (COOH-SAMs) on Au nanoparticle (AuNP) surfaces were characterized with XPS. As the AuNP diameter decreased and SAM chain length increased, the XPS atomic C/Au ratio on the surface increased. As the XPS C/Au atomic ratio depends on the SAM structure as well as the curved nature of the AuNPs, special XPS data analysis methods must be developed to accurately analyze SAM covered AuNPs. Simulated Electron Spectra for Surface Analysis (SESSA) was used for this purpose. Quantities such as SAM density, thickness, surface roughness, etc. were tuned in SESSA to optimize agreement between simulated and experimental XPS compositions. In addition to the COOH-SAMs, amine and ethylene glycol terminated SAMs on AuNPs were also characterized.

COLL 167

Coherent vibrational and electronic spectroscopy of engineered and natural nanoparticles

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Understanding the physical and chemical processes occurring at the surfaces of nanoparticles is important for understanding, controlling, and predicting how nanoparticles interact with the environment. This presentation will show how nonlinar optical coherent electronic and vibrational probes access the surfaces of engineered and natural nanoparticles directly, in real time and space, at room temperature, under aqueous solution and flow conditions or at one atmosphere of air, and without the necessity of external labels. Example are presented that focus on nm-sized CdSe quantum dots as an example of engineered nanoparticles and on highly size resolved organic aerosol particles from tropical and boreal forests as an example of natural particles.

COLL 168

Citrate coatings on metal nanoparticles: A computational study

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The nature of the interactions of coatings with the surfaces of metallic nanoparticles is poorly understood. Experimental evidence suggests that citrate coatings are not continuous, thus allowing solutions to have direct interaction with the surface of a metallic nanoparticle, which may have an impact on the fate of these materials in the environment.

The purpose of this research is to use *ab initio* quantum chemical approaches to understand the nature of the interactions between silver nanoparticles and a citrate coating. Density Functional Theory (DFT) methodologies were used along with a robust basis set to predict the interactions between citrate and the surface of silver nanoparticles. Binding energies for citrate-silver nanoparticle interactions were calculated for common crystallographic surfaces of face centered cubic (FCC) silver. Multiple citrate molecules were sorbed to the test surfaces to assess the extent of the coating of citrate on surfaces of metallic silver.

COLL 169

Identification, characterization and determination of nanoparticles by ICP-MS: Challenges and limitations

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The lack of reliable methods to determine nanoparticle identity, characteristics and concentrations in environmental samples at environmentally relevant concentrations is one of the most significant gaps in environmental nanosciences.

Inductively coupled plasma mass spectrometry (ICP-MS) is a multielemental-specific technique, which is used routinely for the quantification of the element content of nanoparticles and nanomaterials. However, novel approaches based on the use of ICP-MS are also emerging. Direct analysis based on single particle detection and hyphenation of flow field flow fractionation (FFFF) techniques to ICP-MS are two of the most promising ones. Whereas FFFF-ICP-MS allows the separation and quantification of nanoparticles according to their size, single particle detection ICP-MS provides information about soluble and nanoparticle forms of an element, size distributions, and number and mass concentration without previous separation. State of the art of these methodologies in the field of nanoscience will be presented, discussing their performance, challenges and limitations.

COLL 170

Silver nanoparticle metrology, chemistry and materials science for predicting environmental transformations

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The perspectives chemists and materials scientists have provided to assessing the potential risks silver nanoparticles pose on environmental health and safety (EHS) has had a significant impact in recent years. This talk will present recent findings on how the silver nanoparticle surface interacts and reacts with its surrounding environment, including environmental waters, with the aim of better predicting what environmental compartments might be at greatest risk. The three main topics will be: 1) role and limits of metrology in understanding and characterizing transformations of silver nanoparticles, 2) a potential mechanism for the nevironment to form incidental silver nanoparticles by humic acis reducing silver ions, and 3) UV light-induced photo-oxidation of silver nanoparticles. By understanding how to characterize silver

nanoparticle structures and properties, those structures and properties can then be related to activities and potential transformations that enable better prediction of how silver nanoparticles might behave if released into the environment. Such predictions would be a useful guide to both nanoEHS researchers and science-based regulatory policy.

COLL 171

Effect of photolysis on the stability of silver nanoparticles and their surface coatings in natural organic matrices

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The objective of this study was to determine the effect of solar irradiation on the aggregation kinetics of silver nanoparticles. Silver nanoparticles with different stabilization coatings were exposed to simulated sunlight by UVA irradiation, and the impact on the irradiation was investigated in solutions with and without natural organic material. The two particle types investigated were those coated with a citrate coating and those coated with a Polyvinylpyrrolidone (PVP). Advanced analytical techniques were employed to characterize the nanoparticles before and after UVA irradiation. Field flow fractionation interfaced to inductively coupled plasma mass spectrometry (FFF-ICP-MS) provides a methos to determine size and elemental compositions of nanoparticles at environmentally relevant concentrations (parts-per-billion). This research has implications for predicting the fate of silver nanoparticles in the environment, suggesting humic substances and photolysis will play critical roles in the stability of nanoparticles in the environment.

COLL 172

New insights into adsorption properties of metal (hydr)oxide nanoparticles: Electrochemical effects

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A mechanistic understanding of the adsorption properties of metal oxide nanoparticles (NPs) in aqueous media is the most important step towards both the understanding of their role, transport, and fate in the environment and the realization of their new chemistry in different technological areas including environmental remediation. So far, the adsorption on NPs from aqueous solutions has commonly been interpreted by using surface complexation models within the so-called *chemical* concept. At variance with this, we show that the *electrochemical* reactivity contributes to the adsorption performance of semiconducting metal (hydr)oxide NPs. The chemical system studied—hematite (α-Fe2O3) NPs interacting with naturally-occurred carbonate/CO2—has direct

relevance to environmental remediation, wastewater treatment, clean and renewable energy production, and (bio)geochemical processes. Using in situ FTIR spectroscopy, we discover that a variation in the electrical potential of these NPs affects the composition and structure of the Helmholtz layer and hence and the electric potential distribution across the interface. The structural and electronic characteristics of the interface are correlated with each other, and a new framework that takes into consideration the semiconductor part of the double layer is suggested for the adsorption modeling. The outcomes of the research conceptually broaden the aquatic chemistry of metal oxide NPs providing new insights into the fundamentals.

COLL 173

Modular surface functionalization of metal oxide nanoparticles toward the study of their environmental fate and transport

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The environmental fate of nanoparticles is influenced by organic ligands bound to their surfaces. Differences in ligand-nanoparticle binding motifs can confound investigation of the influence of organic ligand properties on nanoparticle fate. We therefore developed a strategy to modularly functionalize metal oxide nanoparticles using a citric acid derivative bearing an alkyne group. This ligand forms stable, multi-dentate complexes to metal oxide nanoparticles and enables subsequent functionalization via the Cu(I)-catalyzed azide-alkyne cycloaddition reaction. We demonstrated the broad utility of this strategy by functionalizing metal oxide nanoparticulate films. For environmental fate studies, we functionalized colloidally suspended TiO_2 nanoparticles with poly(ethylene glycol) ligands bearing neutral, cationic, and anionic head groups. We investigated nanoparticle aggregation by dynamic light scattering and nanoparticle attachment to humic substances by QCM-D. This strategy enables the effects of varying nanoparticle surface functionalization on environmental fate processes to be understood without the confounding influence of differing surface-binding motifs.

COLL 174

Studies of colloidal nanocrystals in liquids using the transmission electron microscope

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This talk will present our recent work on the study of colloidal nanocrystals in a fluid using the TEM. We have studied the motion of nanocrystals, the trajectories for the

growth of individual particles, and the formation of nanocrystal arrays as the liquid evaporates. In each case, the ability to observe the behavior of single particles offers new physical insights.

COLL 175

Photoswitchable plasmonic nanoparticle clusters

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We assemble and characterize metal nanoparticle aggregates that incorporate photoswitchable biomolecules as stimulus-responsive linkers. The interparticle plasmonic coupling is tunable upon exposure to light, yielding fully reversible photoswitchable nanoclusters. We investigate the thermodynamics and kinetics of the assembly processes and describe our work using these particles in photoswitchable and phototriggered biosensor applications.

COLL 176

Coherent plasmonic and plexcitonic complexes: Lineshape engineering “from the bottom up”

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While our abilities to assemble nanoparticles using functional linker molecules have been greatly advanced, determining specific nanoscale geometries that may yield interesting optical properties at the macroscale remains an enticing challenge. Manipulating optical and electromagnetic properties through strong near-field coupling of plasmon resonant structures has been shown to be an important and potentially useful direction of research. In our talk, we will discuss how coherent properties of closely coupled metallic nanoscale systems give rise to unusual and controlled optical lineshapes, how we can create these structures using combinations of chemical and clean-room fabrication methods, and how optical characterization at the level of individual nanocomplexes provides detailed information relating nanoscale structure to coherent optical properties.

COLL 177

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

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We place single molecules and larger groups into precisely controlled environments on surfaces. The monolayer matrices and the inserted molecules 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 controlled chemical patterning 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 178

"Striped" nanoparticles and cell, the tale of two interacting self-assemblying systems

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In this talk I will discuss a novel physical chemistry phenomenon that we have recently discovered and that we are studying in depth: when nanoparticles coated with structured self-assembled monolayers (composed of molecularly-thin striped domains of alternating composition – hereafter called 'striped' NPs) interact with fluid lipid bilayers, there exists a driving force for the fusion of these two systems. Studies with both lipid bilayers and cell membranes show that when similar particles coated with similar mixture of ligand molecules but with no structure on the ligand shell are exposed to lipid bilayers or cell membrane no noteworthy interaction takes place. Hence the structure present in the ligand shell of striped NPs is the true key to this novel form of interaction between these two self-assembly systems.

Preliminary results indicate that the fusion ultimately increases inter- and intra-molecular order within the lipid bilayer. This ordering is a key to the driving force for the fusion. This phenomenon has consequences in many fields. First, at the fundamental level, it evidences that when self-assembled (SA) systems under different order constrains interact, the outcome can be unexpected and not captured by the current knowledge. This is often the case in nature where a cell's life cycle strongly relies on interactions involving different SA systems. Morphological similarities between our striped NPs and cell penetrating peptides (CPP) suggest that our preliminary results illustrate deep physical principles that regulate such interactions. Second, the fusion process depends critically on the lipid bilayer fluidity, composition, geometry, and integrity. All of these topics will be discussed in the presentation.

COLL 179

Multiplexed labeling and signal amplification in diagnostic magnetic resonance

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The use of magnetic materials is expected to afford significant advances in cell separation, diagnostics, and therapy of scant cell population. We describe a set of highly sensitive and multiplexable magnetic tagging method that amplifies the loading of magnetic nanoprobes (MNPs) onto targeted cells. The methods utilize oligonucleotides, copper-free click chemistry, and supramolecular interaction as the binding agents between the functionalized antibody and the modified MNP. We validated the method by surface plasmon resonance measurements, labeling of specific growth factor receptor, and detection of human cancer cells. The efficiency of these methods was demonstrated by profiling various cancer markers of interest (HER2/*neu*, EpCAM, and EGFR), each of which exhibit varying abundance levels, on a panel of cancer cell lines. Not only did this method allow multiplexed analysis, but it was also capable of detecting multiple markers in a *single* sample containing only a small number of cells.

COLL 180

Surface engineering of iron oxide nanoparticles for targeted cancer therapy

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The success of a therapeutic superparamagnetic iron oxide nanoparticle (SPION) largely relies on the proper design of its core to ensure MRI detectability and more critically, of its coating to render the ability to bypass physiological and cellular barriers. Strategies to bypass the physiological barriers involve tuning surface chemistry of the nanoparticles to maximize blood half-life and facilitate the navigation in the body. Strategies to bypass cellular barriers include the use of targeting agents to maximize uptake of the nanoparticle by cancer cells, and employing materials that promote desired intracellular trafficking, maximize the loading, and enable controlled drug release. In this talk, we will discuss the primary design parameters in developing therapeutic SPIONs with a focus on surface coating design to overcome the barriers imposed by the body's defense system and provide examples of how these design parameters have been implemented to produce therapeutic SPIONs for specific therapeutic applications.

COLL 181

Enhancing microRNA inhibition and detection using polyvalent DNA-functionalized gold nanoparticles

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Gold nanoparticles densely surface-functionalized with oligonucleotides (DNA-Au NPs) are hybrid materials with novel bioactivities. These nanoconjugates have unique physicochemical properties that enable them to address many challenges associated with both molecular biodetection of low abundance microRNAs (miRNAs) and miRNA-based gene regulation in cancer. We show herein that DNA-Au NPs selectively enhance RNase H activity while inhibiting general nucleases that are normally present in serum. We have investigated the nanomaterial surface chemistry to uncover the mechanism of selective RNase H activation and found that the high DNA density of DNA-Au NPs is responsible for their unusual behavior. These nanoconjugates were applied successfully to inhibit the growth of prostate cancer cells. And endogenous miRNAs have been quantitatively demonstrated by a novel scanometric-based miRNA profiling technology (Scano-miR). Scano-miR allows simultaneous quantification of all known miRNAs with the ability to detect femtomolar concentrations of miRNA in serum and identify single nucleotide polymorphisms (SNP).

COLL 182

Ultrabright fluorescent silica particles for detection of epithelial cancers

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We have recently reported self-assembly of ultra-bright fluorescent colloidal mesoporous (nanoporous) silica particles. As an example of brightness, 40nm silica particles with encapsulated rhodamine 6G dye are ~30 times brighter than ~20-30nm coated water-dispersible quantum dots (green CdSe Zn/S).

Here we present the functionalization of those particles with folic acid. The procedure keeps high fluorescent brightness of the silica particles. Since the majority of epithelial cancers have overexpressed folic acid receptors on the cell surface, we use the particles to identify cancer cells for the example of human cervical cancer. Primary cells derived from three cancer patients and three healthy individuals were used for study *in-vitro*. We demonstrate that statistically significant ($p>0.05$) difference between cancer (a mix of malignant and precancerous) and normal cells is observed after 15 min of cell

incubation with particles. The particles are internalized with the help of folic receptor as expected based on the known action of these receptors.

COLL 183

Toward an all-in-one nanovehicle for cancer therapy: Surface modification of metal nanoparticles

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The goal of this project is to develop a multi-purpose nanovehicle for targeted imaging and treatment of solid tissue tumors. Nanoparticles (NPs) are assembled with a paramagnetic core to facilitate magnetic resonance imaging and a gold coating to which thiol-terminated poly(ethylene glycol)-biotin (PEG) is attached. Avidin is linked to the biotin terminus of the PEG to provide multivalent attachment sites for additional biotinylated molecules in different combinations. Targeting of the nanoplatform is achieved by monoclonal antibodies (mAb) directed against tumor-specific biomarkers. The flexibility of assembly allows for various antibodies and/or anti-tumor therapeutics to be exchanged without the need to synthesize the nanovehicle from scratch for each application. As a proof-of-concept we have developed our NP to target pancreatic adenocarcinoma with boron neutron capture therapy. This presentation will outline the surface chemical modification strategy with the system. We will highlight the characterization of the nanoparticles following modification steps using a battery of analytical methods such as infrared and UV-visible spectroscopies, magnetic resonance relaxivity studies, dynamic light scattering, and transmission electron microscopy.

COLL 184

Engineering nanoparticle interactions with cells via synergies in biochemistry and physical chemistry

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Nanoparticles are of interest in oncology for delivery of drugs or vaccines or as agents for imaging or direct therapeutic stimulation in tumors. However, achieving the full potential of nanomaterials in cancer diagnosis and treatment will require a better understanding of how to control nanoparticle-cell interactions. We have been exploring how surface chemistry of nanoparticles and particle functionalization influences interactions with the cell membrane, internalization of nanoparticles, and biological responses to nanoparticles in vitro and in vivo. Examples of two strategies for mediating cell-nanoparticle interactions will be presented, one based on modulating the physical

chemistry of nanoparticle-cell interactions via the design of organic ligand-protected gold nanoparticles, and a second based on bioconjugation strategies to anchor nanoparticles to cell membranes in ways that either promote or prevent nanoparticle internalization.

COLL 185

Multicompartmental nanocarriers for cancer theranostics

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Conventional cancer therapy involves potent chemotherapeutics with severe systemic side effects. Furthermore these treatment regimens are not effective especially at advanced stages. Sophisticated nanomaterials may serve as vectors for cancer therapy with potentially greater efficacy and low systemic toxicity. Here we manufacture such nanocarriers by electrohydrodynamic co-jetting, allowing for compartmentalization of various functionalities including imaging modalities and drugs. Specifically we demonstrate a multicompartmental nanocarrier capable of sensing endosomal pH and subsequently releasing nucleic acids for gene delivery and silencing, as well as drugs. We also demonstrate that these nanoparticles can specifically target to cancer cells and deliver their payload *in vitro*. These particles demonstrate their potential as multifunctional carriers capable of theranostics.

COLL 186

WITHDRAWN

COLL 187

Targeted delivery of non-covalently biofunctionalized dendrimer nanocarriers for multimodal imaging and therapy in oncology

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Our recent success in targeted delivery of chemically self-assembled antibody nanorings with antiCD3 single-chain antibodies to $CD3^+$ T-leukemia cells has enabled us to extend their applications in oncology. Herein, we report a convenient method to

non-covalently biofunctionalize bis-methotrexate conjugated PAMAM-G5 dendrimers with dihydrofolate reductase by simple mixing. Modular construction and reversible assembly are unique advantages of these nanocarriers and, provide a promising novel drug delivery system for enhanced detection and treatment.

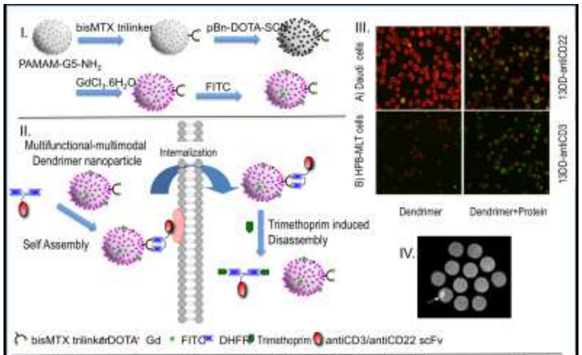

Figure 1: (I) Construction and (II)application of biofunctionalized dendrimer nanoparticles in targeted delivery; (III) A) DHFR$_2$-CD22 fusion proteins delivering nanoparticles to Daudi cells (Human Burkitt's lymphoma cell line); B) DHFR$_2$-CD3 fusion proteins delivering nanoparticles to HPB-MLT cells (T Leukemia cell line) and (IV)their imaging by MRI

COLL 188

Influences of salt etched polyelectrolyte multilayers on the conformation of adsorbed fibronectin and cell growth

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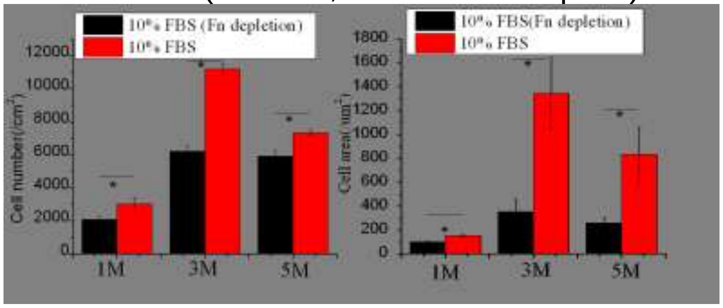
ATR was used to detect the conformation of fibronectin and BSA adsorbed on the salt treated PEI(PSS/PDDA)$_7$ multilayers. It was found that the conformation of BSA and fibronectin adsorbed on 3M NaCl etched multilayers was mostly reserved, but was significantly changed on 1M NaCl etched multilayers

BSA	**α-helix**%	**β-sheet%**	**β-turn**%
Native	52-58	35-36	5-8
1M	35.61	36.38	28.01
3M	50.09	28.28	21.63
5M	43.55	23.44	33.01
Fibronectin	**β-sheet%**	**β-turn**%	**Random coil%**
Native	34.9-38.8	31.5-33.8	29.8-31.7
1M	25.38	35.07	39.55
3M	27.95	46.17	25.88
5M	23.34	40.39	36.27

. To correlate the fibronectin adsorption and conformation change with cell growth behaviors, human vascular smooth muscle cells (VSMCs) were seeded on the salt etched PEMs (25k/well, 24 well culture plate) in 10% serum and 10% Fn depletion



. Both the cell numbers and cell spreading areas were significantly smaller in the Fn depletion serum than the normal one, especially on the 3M NaCl etched PEMs, confirming that Fn plays an important role in mediating VSMC adhesion on the salt etched PEMs. The conformation change correlates very well with the relative RGD activity of Fn and cell adhesion behaviors, and thus can better explore the mechanism of cell-biomaterial interactions.

COLL 189

Peptide adsorption and function at pendant PEO brush layers

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Surfaces coated with pendant hydrophilic polymers such as polyethylene oxide (PEO) in a brush conformation are generally biocompatible and protein-repellent. However, theory predicts that small polypeptides can integrate into an otherwise non-fouling brush layer, if the peptide diameter is less than the brush chain spacing. In addition, such integrated peptides are protected from competitive elution by larger proteins. We describe experiments with nisin, a small (3.4 kDa) antimicrobial peptide, loaded into brush layers made with PEO-based triblocks on various substrates. Several techniques, including ellipsometry, XPS, TOF-SIMS, optical waveguide lightmode spectroscopy (OWLS), and antimicrobial assays indicate that nisin integrates into PEO brush layers in multi-layer quantities, without loss of antimicrobial activity. Fibrinogen does not elute entrapped nisin or adsorb at the nisin-loaded brush. A fundamental understanding of the mechanisms of peptide integration into PEO brush layers will enable novel approaches for drug delivery and bioactive, functional surface coatings for biomedical devices.

COLL 190

Lysozyme transport in PHEMA gels

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Protein binding in hydrogels adversely affects their performance and usage in several biomedical applications including contact lenses. Here, we focus on understanding and modeling transport of lysozyme, the most abundant tear fluid protein, in hydrogels of poly-hydroxylethyl methacrylate (p-HEMA), a common contact lens material. Protein uptake experiments with gels of different thicknesses showed a time scale increase as the square of the thickness suggesting diffusion control transport. A Fickian model was fitted to the uptake data to obtain a lysozyme diffusivity of $1.92 \times 10^{-16} \pm 6.3 \times 10^{-17}$ m^2/s. A large fraction of protein is adsorbed in the gel and a subsequent Langmuir binding isotherm was obtained. Uptake of lysozyme was found to be reversible and release profiles were accurately predicted without any additional parameters, thus validating the model. This model could assist in lens development of lens cleaning protocols and applications related to protein binding in several biomaterials.

COLL 191

Interactions of proteins with gold surfaces investigated by atomistic multilevel simulations

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Protein-inorganic surface interactions are of paramount importance in fields as diverse as biomaterials and nanobioelectronics. Gold surfaces are particularly relevant for applications (e.g., contacts in bioelectronics, nanoparticles for nanobiotechology). Atomistic modeling of such interactions can help to reveal the basic physicochemical principles governing protein-surface binding. However, deriving an accurate computational description of protein-metal interactions is particularly challenging because it requires treating a diverse range of contributions (e.g. weak dative bonds, image charge interactions) that must be correctly balanced.

We have developed a sequential multiscale modeling scheme to study protein-gold interactions at various levels, from *ab initio* to rigid protein-surface docking [1]. In this contribution, this scheme will be presented together with a comparison with available experimental data [2]. Insights into protein-gold interfaces from our simulations will be also discussed.

[1] Calzolari et al. *J. Am. Chem. Soc.* **2010** , *132*, 4790; Kokh et al. *J. Chem.Theor. Comp.* **2010** , 6, 1753; DiFelice&Corni*, J. Phys. Chem.Lett.* **2011** , 2, 1510.

[2] Cohavi et al. *Chem.Europ.J.* **2011** , 17, 1327; Calzolai et al. *NanoLett.* **2010** , 10, 3101

COLL 192

Interactions of apolipoprotein AI, AII, and HDL with polyurethane and modified polyurethane surfaces

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Lipoproteins are highly surface active blood constituents that have, surprisingly, been largely overlooked in the context of blood contacting materials and devices, despite the fact that their role in atherogenesis and other clinical manifestations is widely recognized. We have shown previously that apolipoprotein AI (apo AI), the major protein component of the high density lipoprotein (HDL) particle, is adsorbed extensively from plasma and blood to materials with a wide range of surface properties. In the work to be presented here we investigated the interactions of apo AI, apo AII (the second most abundant protein component of HDL), and the HDL particle itself with two surfaces: a "standard" segmented polyurethane and a polyurethane modified with polyethylene oxide to render it protein resistant. Experiments in buffer and plasma using radiolabeling and SDS-PAGE/immunoblotting methods showed differential adsorption behaviour of these species with respect both to one another and to the two contrasting surfaces.

COLL 193

Evaluation of the real-time protein adsorption kinetics on albumin binding surfaces by dynamic in situ spectroscopic ellipsometry

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Functionalized surfaces with an affinity for albumin over competing serum proteins were prepared by immobilizing linear peptides and small chemical ligands (SCL), with albumin binding properties, on silanized silicon surfaces. Our work has documented low platelet adsorption on albumin-binding surfaces when evaluated under static conditions, and under conditions of shear. The amount of adsorbed platelets was noted to correlate with low levels of surface adsorbed fibrinogen. vWF was undetectable. It appears that surface passivity by albumin-binding surfaces is conferred by the ability of surface bound albumin to either impede the co-adsorption of competing proteins. In this study, the real time adsorption of human serum albumin (HSA) from a single- and multi-component system was monitored by dynamic ellipsometry. The experimentally

obtained time-dependent adsorption data was analyzed by two models: (a) pseudo first order and (b) a biphasic kinetic model that accounted for the formation of tightly and loosely bound complexes. The biphasic kinetic model was noted to better fit the experimental data and the binding constants were determined by non-linear regression analyses. The net forward rate constant (k_1) for the tightly bound complex formation was distinctively higher for surfaces functionalized with peptides (~0.014 min^{-1}) when compared to surfaces functionalized with SCL surface (~10^{-3} min^{-1}).

[figure 1]

COLL 194

Self-assembly of caseins and their interaction with interfaces

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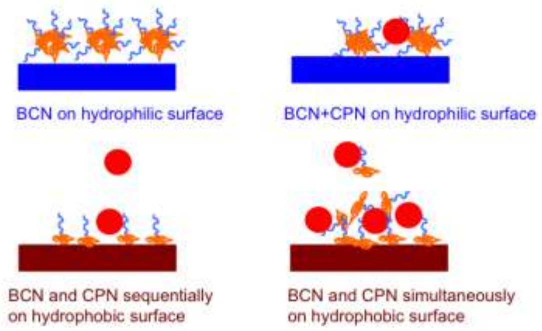
The biological roles of casein molecules include the sequestration of amorphous calcium phosphate, as calcium phosphate nanoclusters (CPN), to form stable complexes in milk. Here, the most amphiphilic of the calcium binding caseins, β-casein, play a particular important role. The adsorption of β-casein is of relevance for biomineralisation and has been studied by ellipsometry, surface force measurements, neutron reflectivity, and wetting force measurements.The common model emerging from these studies is that the protein forms a monolayer at hydrophobic surfaces, with the “hydrophobic” part of the protein sticking to the surface and the highly charged N-terminal portion protruding into the solution. On hydrophilic surfaces the protein is suggested to adsorb as micellar type of aggregates. These observations can be related to the β-casein's ability to self-assembly in bulk solution. Recent results on the co-adsorption of calcium phosphate nanoclusters (CPN) and β-casein at hydrophobized and hydrophilic silica-water interfaces will be discussed. The structural characteristics of the adsorbed layer, determined by neutron reflectivity showed that the calcium phosphate nanoclusters profoundly affected the rate of adsorption and structure of the interface compared to the adsorption of β-casein alone. For the hydrophobic interface the effects depended on the point at which the nanoclusters were added. It is proposed that the nanoclusters become surface active because whole β-casein molecules can replace one or more of the hydrophilic peptides in the shell of the nanoclusters.



COLL 195

Site-oriented His-tag proteins on solid substrates: Optimizing biofunctional surfaces

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The purpose of this presentation is to discuss experimental results on site-oriented chemical adsorption, induced by modifying the substrate with Ni(II) in combination with recombinant His-tag proteins (antigens and enzymes) used to design novel biofunctional surfaces. To this end, the presentation covers from the expression, purification and characterization of the recombinant proteins up to the surface biorecognition capabilities. The substrate modification is based on the formation of amino terminated SAMs either on gold or silica to anchor nitrilotriacetic acid (NTA) that strongly interacts with Ni(II). His-tagged proteins remove water molecules from NTA-Ni chelate leading to a stable octahedral complex on the substrate. However, physical protein adsorption also takes place which is mostly desorbed upon dilution at high degree of surface coverage. The biofunctional surface shows a good biological response as monitored by direct electrochemical methods. The proposed strategy provides a simple way to prepare reusable biofunctional surfaces on different substrates.

COLL 196

Molecular structure of *sil1p* R5 segment biosilicification protein complex with silica by solid-state NMR

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Diatoms produce proteins known as silaffins which precipitate silica out of silicic acid under ambient conditions in a process called biosilicification. *Sil1p* is a silaffin with several segments, each of which have the same biosilicification property. R5 is one such peptide segment, with a known sequence of SSKKSGSYSGSKGSKRRIL. The precipitation occurs as a complex. We look at the structure of R5 as a free peptide and when formed in a complex with silica in the solid state by NMR. Both 1-D and 2-D PDSD NMR methods with ^{13}C and ^{15}N selective labeling were used to obtain NMR chemical shifts. The phi and psi angles backbone torsion angles were determined using TALOS+ to give a model structure for the free peptide and the peptide-silica complex.

COLL 197

Poly(trimethylene carbonate) molecular weight affects protein adsorption, enzymatic activity and macrophage behaviour

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Poly(trimethylene carbonate) degrades *in vivo* by macrophage mediated enzymatic degradation, which occurs at a higher rate on 100kDa pTMC surfaces compared to 60kDa pTMC surfaces. It is hypothesized that this higher degradation rate is caused by greater macrophage attachment or higher enzymatic activity, possibly due to a difference in adsorbed protein present on the two pTMC surfaces. *In vitro* degradation of 100kDa and 60kDa pTMC disks incubated in cholesterol esterase and lipase showed a higher rate of degradation of the 100kDa pTMC. Macrophages were cultured on discs of 60kDa and 100kDa pTMC and TCPS. Over time, macrophage number significantly decreased on the 60kDa pTMC and TCPS surfaces. A higher quantity of fibrinogen was found to adsorb to the 60kDa pTMC surface. These results suggest that differences in pTMC degradation are due to both macrophage attachment and enzymatic activity and that higher fibrinogen adsorption may be associated with lower macrophage attachment.

COLL 198

High-resolution secondary ion mass spectrometry reveals the cholesterol and lipid distribution within the plasma membranes of fibroblast cells

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Microdomains enriched with cholesterol and sphingolipids, which are referred to as lipid rafts, are believed to be present in the plasma membrane and mediate important cellular functions. Functional tests, biochemical assays, biophysical measurements, and fluorescence microscopy have provided valuable information about cell membrane organization. Yet, no consensus exists on the sizes and locations of compositionally distinct domains in the plasma membrane. A direct method to image specific lipid molecules is required to unambiguously establish the distributions of cholesterol and sphingolipids in the plasma membrane. To this aim, we have used high-resolution secondary ion mass spectrometry to chemically image the distributions of metabolically incorporated ^{15}N-sphingolipids and ^{18}O-cholesterol in the plasma membranes of intact fibroblast cells with approximately 90 nm lateral resolution. We show that lipids within the plasma membrane are spatially organized on length scales that range from two hundred nanometers to a few micrometers.

COLL 199

Distinct mechanisms regulating calcium signals at the plasma membrane and endoplasmic reticulum in response to mechanical stimulation

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Mechanical environment plays pivotal roles in regulating stem cell commitment and functions. However, it remains unclear on how mechanical stimuli are transmitted into biochemical signals in stem cells. In this study, we investigated the molecular and biophysical mechanisms by which mechanical forces regulate Ca^{2+} signaling in human mesenchymal stem cells (HMSCs), integrating genetically encoded Ca^{2+} biosensor based on fluorescence resonance energy transfer (FRET) and optical laser tweezers. Laser-tweezer-traction of the cell membrane induces intracellular Ca^{2+} oscillations caused by Ca^{2+} release from endoplasmic reticulum (ER) in the absence of extracellular Ca^{2+}. These force-induced Ca^{2+} oscillations produced by ER Ca^{2+} release are mediated not only by the mechanical support of cytoskeleton and actomyosin contractility, but also by mechanosensitive Ca^{2+} channels on the plasma membrane, specifically TRPM7. When the ER Ca^{2+} release is inhibited and the extracellular Ca^{2+} level is restored, laser-tweezer-traction of the cell can induce the intracellular Ca^{2+} increase, which is mediated by the cytoskeletal structure but not actomyosin contractility. Taken together, our results indicate that active actomyosin contractility regulated by MLCK and myosin II is essential for the force transmission into the deep intracellular organelles but dispensable for the mechanical regulation of plasma membrane channels.

COLL 200

Single-molecule study of membrane and membrane protein dynamics

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Many membrane proteins are responsible for transporting various chemical species in and out of cell membranes. However, it is difficult to directly probe the conformational dynamics of membrane proteins, especially the large-scale motions related to function. In this talk, an example will be given to show that fluorescence fluctuations of individual protein molecules could be used to reveal functionally relevant motions of membrane proteins. In addition, examples will be presented to show how peptide binding affects the dynamics of individual lipids in model membranes.

COLL 201

Field directed assembly and fusion of vescicles

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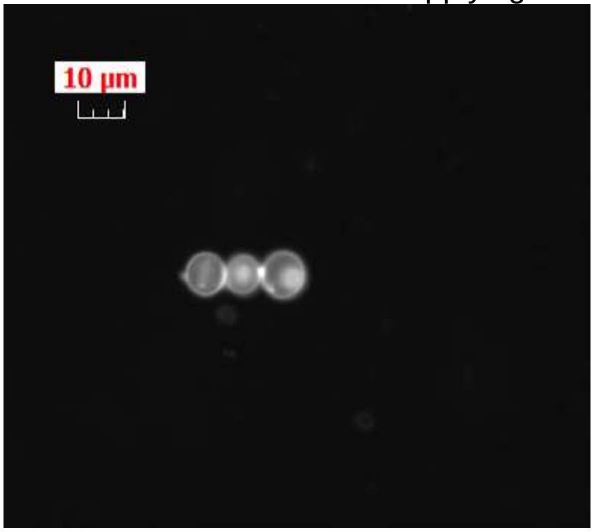
Giant unilamellar vescicles (GUVs) can be directed into chain-like structures by placing the GUVs in a ferrofluid and applying an external magnetic field.



Lipid transfer between vescicles and membrane stifness changes can be easily monitored with and without the presence of a magnetic field. Here we present the use of a photopatterning and electroformation technique to generate ten micron sized vescicles. The subsequent alignment and deformation of these soft colloids under varying hydrodynamic flows will be presented.

COLL 202

Transport and adsorption of hydrophobic molecular ions at cell membranes: Real time observations through nonlinear light scattering

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The adsorption and transport of a modest size hydrophobic molecular ion (~ 360 Da MW) at the membranes of *E.Coli* bacteria, a cell with two membranes, and the Murine Erythroleukemia (MEL) cell has been observed with real time resolution using the nonlinear light scattering approach Second Harmonic Generation.

It is observed that the hydrophobic cation Malachite Green 1) adsorbs onto the *E.Coli* outer membrane with a much higher density than the inner membrane, reflecting the effect of the negative charges of the polysaccharide hairs at the outer membrane, 2) transports through the *E.Coli* outer membrane with a rate one order of magnitude faster than the inner membrane, demonstrating the effectiveness of the ion transport porins in the outer membrane, 3) transports through the *E.Coli* membranes much faster than a neutral molecule of similar size, illustrating the effect of ion channels, and 4) adsorbs onto but does not penetrate through the MEL cell membrane which is more tightly packed and lacks ion channels for molecular ion transport. The adsorption and transport of hydrophobic ions at the cell membrane are also greatly affected by the salt content of the solvent. It is observed that the salt ionic strength and ion specificity affect molecular adsorption depending on the nature, either charge or hydrophobic force dominated, of the molecule-surface interactions.

COLL 203

Implant induced blood-brain barrier disruption, new methods for the characterization and modulation of barrier function

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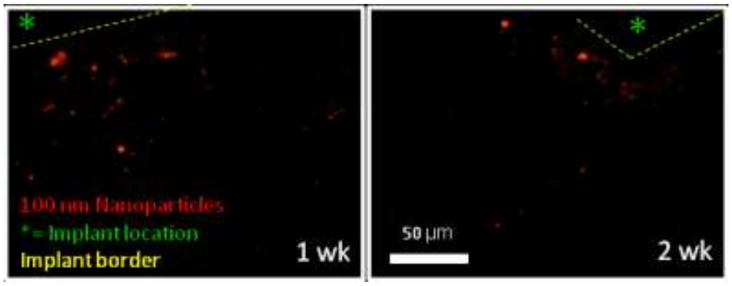
Long-term utility of neural electrodes is limited due to the biological response to the implanted material. Hallmarks of the brain foreign body response (FBR) are the hypertrophy and hyperproliferation of reactive astrocytes that form a glial scar, the presence of microglia and recruitment of macrophages, local neuronal degeneration, and leakage of the blood-brain barrier (BBB). The latter is a newly identified complication of the FBR and involves disruption of membrane junctions. We have developed new methods to alter and examine barrier function near electrodes. Using nanoparticulate tracers we have probed the size of BBB leakage, showing barrier permeability to particles as large as 500 nm, an order of magnitude larger than previously measured.



Electrodes modified to deliver genes via a layer-by-layer approach allow us to isolate the local effects of molecules that we have previously characterized using global genetic knockout models, including MCP-1 and thrombospondin-2, on BBB dynamics.

COLL 204

Exciton coupled membrane permeable fluorescent probes for phosphatidylserine

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Phosphatidylserine (PS), an anionic lipid with the amino acid L-serine in the hydrophilic head group is present predominantly in the inner leaflet of mammalian cell membranes and could reach concentrations of up to 30% of the total lipid content. Disruption of the asymmetry of phosphatidylserine in which it translocates from the inner to the outer leaflet and gets surface exposed occurs with the onset of diseases like cancer and Alzheimer's and when cells become apoptotic. We have developed novel fluorescent protein probes employing the C2 domain of lactadherin in which two small fluorescent molecules such as NBD (nitorbenzodioxazole) are attached to adjacent cysteines (Lact-C2-Cys-NBD probe) or lysines (Lact-C2-Lys-NBD probe) to target PS. The unqiue properties of the Lact-C2-NBD probes are: (1) the NBD molecules are proximal and exciton coupled with a red fluorescence (680 nm maximum) when the probes are not PS bound, (2) the NBD molecules become distal when the probes bind PS and exhibit a green fluorescence (540 nm maximum) characteristic of individual NBD molecules without exciton coupling, (3) they are membrane permeable as they can bind to PS in the outer and inner leaflets of DOPC/DOPS vesicle and cell membranes of live prostate cells without the addition of any membrane permeabilizing or PS translocating reagents, and (4) they have excellent phtostability. Significant aspects of this research will be presented.

COLL 205

Nanoplasmonics for manipulating photon emission statistics of Individual core/shell nanocrystal quantum dots

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Plasmonic fields associated with metallic nanostructures are known to greatly modify photoluminescence (PL) emission and decay dynamics of nearby nanoemitters such as semiconductor nanocrystal quantum dots (NQDs) through plasmonic enhancement and quenching. Here, we demonstrate that plasmonic interaction can also be used to *manipulate photon emission statistics* of NQDs. Specifically, we show that sub-Poissonian statistics (antibunching) of photons emitted from individual core-shell NQDs can be transformed into super-Poissonian statistics (photon-bunching) when they are coupled with localized plasmons of a rough silver surface. More interestingly, we also show that photon emission statistics can undergo a transition from bunching to anti-bunching to Poissonian limited statistics, with increasing exciton population. We analyzed the processes involved and determined the conditions required for the manifestation of this phenomenon. Our analysis reveals the way to utilize this phenomenon as a new novel approach toward plasmonic manipulation on photon emission statistics.

COLL 206

Au stabilized Ag nanoplates for enhancement of SPR spectroscopy

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Ag nanoparticles (NPs) possess an extremely high enhancement effect for the detection sensitivity in surface plasmon resonance (SPR) spectroscopy. One of the fundamental issues impeding the further development of Ag enhancer for SPR is the lack of stability of Ag NPs. We present a novel method to stabilize Ag nanoplates by depositing a thin Au layer on the plates in solution instead of etching the plates. The coated structures maintain the plasmonic property of original Ag nanoplates. Thanks to the thin gold layer, Ag@Au nanoplates now can be stored in water, PBS buffer or H_2O_2 solution for several days without any changes. The deposited Au layer also makes the post-modification of Ag nanoplates efficient and easy to manipulate. A layer of protein-nanoplate complexes are formed after flow-injection of biotinylated Ag@Au nanoplates, which has led to 20-fold increase in the SPR resonance angle shift compared with that enhanced by Au NPs.

COLL 207

Multiplexed SERS detection using internally etched silica-coated gold nanoparticles

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Internally etched silica-coated gold nanoparticles are synthesized for the direct and multiplexed detection of thiophenol (TP), 4-methoxythiophenol (4-MTP), 2-naphthalenethiol (2-NT), and 4-aminothiophenol (4-ATP). Molecular fingerprint identification is achieved using surface enhanced Raman scattering (SERS). After the synthesis and characterization of these nanomaterials, SERS detection of TP, 4-MTP, 2-NT, and 4-ATP are evaluated as a function of time and degree of etching as indicated by changes in the plasmonic properties of the nanostructures. The blue shift in the plasmon and a single extinction band in these data indicate that silica etching occurs near the metal core while preserving the optical stability of the nanostructures, resulting in predictable and multiplexed SERS detection of the targeted molecules.

COLL 208

Versatile design of metal nanoarchitectures for photonic applications

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Optical properties resulting from dipole moments in nanoparticles (NPs) assembled in a periodic or cluster architecture enable exploration of metamaterial, near field enhancement, and narrow band resonances. It is a long-standing challenge to fabricate architectures using high throughput methods with tunable properties at optical frequencies. Standard lithographic techniques to produce metal nanoarchitectures are typically not easily translated into large-area production. In contrast, techniques involving directed self-organization can be inexpensive and scalable. Here synergistic research on (i) design of optical structures, (ii) fabrication using self-organization processes on polymer surfaces that serve as both low-cost substrates and allow for selective chemical functionalization for NP cluster assembly and thermally responsive optical properties, and (iii) correltations between optical properties and NP arrangement will be presented. Surface enhanced Raman scattering measurements on chemically assembled NP systems are found to achieve reproducible, high signal enhancements from point to point across the sample surface.

COLL 209

Nanoparticle enhanced TERS imaging

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Optical microscopy of biological systems is useful for detecting various structures with varying chemical or structural contrasts. In the past, fluorescent tags have been useful as imaging probes of biomolecules. An alternative is to use optical properties of nanoparticles for contrast and detection. The local electromagnetic fields gained from the excitation of conduction band electronics of metal nanostructures can be used to enhance Raman scattering from molecules in close proximity. This effect, the electromagnetic enhancement responsible for surface-enhanced Raman scattering (SERS), thus provides a sensitive probe of chemical environments. We have coupled tip-enhanced Raman scattering (TERS) with nanoparticle probes to obtain chemical, structural, and spatial information simultaneously. In protein-ligand interactions, our results show signal enhancements from both the ligand, bound to a nanoparticle probe, and the target protein, thus demonstrating this environmental sensitivity. We are exploring these effects to distinguish the differences in protein binding interactions, as well as investigating receptors in cellular membranes.

COLL 210

Novel and easy-to-use tip-enhanced Raman spectroscopy on opaque substrates with a micro-sized mirror and a silver-nanowire tip

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Surface chemical analysis at nanoscale in ambient conditions is challenging but important for the field of microelectronics, materials science, and life science. A novel and easy-to-use system for tip-enhanced Raman spectroscopy (TERS) was proposed by integrating atomic force microscopy (AFM), confocal microscopy, and a micro-sized mirror. Silver nanowires mounted on AFM tips were used to locally enhance the Raman scattering, which avoids signal interference from silicon tips, and also insures an excellent yield of TERS-active tips. The Raman enhancement observed on mechanically exfoliated graphene flakes on oxidized silicon wafer allows quick chemical analysis from a nanoscale region, and thus enable chemical mapping beyond the diffraction limit. Compared with other TERS geometries, the inserted mirror between a sample and the objective lens of the confocal microscope not only allows analysis on large or opaque samples, but also simplifies the alignment processes of the setup.

COLL 211

Versatile and highly sensitive solution dispersible surface-enhanced Raman scattering substrates prepared by on-wire lithography

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In addition to increasing their sensitivity, many recent developments in the preparation and study of surface enhanced Raman scattering (SERS) substrates have focused on improving their versatility for a wide range of applications and detection environments. Since most SERS substrates are limited to use on the surfaces they were fabricated on, one important step towards increased versatility is the synthesis of solution dispersible SERS structures that can be used in solution, dropcast on arbitrary surfaces, or deposited and functionalized in the traditional way. However, methods to produce tunable, highly sensitive, solution dispersible SERS hotspots in high yield are still extremely limited. Here, we will discuss recent advances in the use of on-wire lithography (OWL) to fabricate gold nanorod dimers that overcome these challenges to produce a highly sensitive and versatile SERS platform with both fundamental and applied examples of their potential as solution processable analytical tools.

COLL 212

Dispersant-dependence of the resonance Raman spectra and excitation profiles for aqueous SWCNT solutions

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Single-wall carbon nanotubes (SWCNTs) are well known for their unique mechanical, electronic and optical properties; properties which are dependent on the SWCNT chirality, length and especially local environment. Recently, SWCNTs have received attention as components in nanomedicine applications, because they can be modified to include targeting or therapeutic agents, and because they can be observed once uptaken by cells due to the strong resonance Raman and/or fluorescence signal. However, as the SWCNT properties are strongly influenced by their environment, a detailed, careful spectral analysis is necessary to ensure comparability between studies and technical quality. In this work, we show the dispersant depedence of the resonance Raman spectra and excitation profiles for commercially-available SWCNTs dispersed using several bio-compatible dispersants. Other characterization methods will include optical absorbance and photoluminescence. Items to consider when designing an in vivo or in vitro study around the resonance Raman signal from the SWCNTs will be highlighted.

COLL 213

Bulk preparation and stability of Janus emulsions

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Complex triple Janus emulsions of (silicon oil + vegtable oil)/water/vegetable oil/silicon oil were prepared in a one-step bulk process and their morphology investigated by optical microscopy. The destabilization of these complex emulsions involved a combination of coalescence induced change from creaming to sedimentation.

COLL 214

Emulsions stabilized by lyotropic liquid crystalline phase: Gel-like properties and transparency control

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Liquid crystalline (LC) phases such as cubic (I_1) and hexagonal (H_1) phases have viscoelastic properties so that we can obtain gel-like emulsions by employing such liquid crystals as a continuous phase. Since such liquid crystalline phases have relatively high reflactive indices, it is known that transparent emulsions can be obtained at a certain surfactant concentration in the aqueous (continuous) phase.[1] In this contribution our recent rheological results for the O/LC and W/LC emulsions will be presented. Also transparency control of the O/LCemulsions through adjusting refractive indices of both aqueous (continuous) and oil (dispersed) phases are presented. The emulsions show gel properties (G' overcomes G'' in a range of frequency measured) and become transparent by choosing surfactant composition and glycerol additions due to contrast matching. Temperature also affect the transparency.

COLL 215

Control of nanostructural organisation at the air-water interface from poly(ethylene imine)/SDS and poly(2-ethyl-2-oxazoline)/SDS mixtures

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The spontaneous formation of multilayer structures from polymer/surfactant mixtures presents many opportunities for novel practical applications. The occurrence and scope of multilayer formation is governed by many factors, including the concentrations of each component, solution pH, polymer composition, molecular weight and architecture. In order to study the effects of these parameters in more detail, we have synthesized a series of well-defined poly(2-ethyl-2-oxazoline) (PEtOx), linear poly(ethylene imine) (LPEI) and branched poly(ethylene imine) (bPEI) samples containing from six to forty nitrogen atoms and studied the self-assembly at the air-water interface from their mixtures with sodium dodecyl sulfate (SDS) using surface tension and neutron reflectivity. The results obtained were used to identify the optimal conditions for multilayer formation. Recent neutron reflectivity experiments with $LPEI_{6-40}$ have allowed us to bridge the gap between our earlier studies of short-chain oligoamines (ethylenediamine to pentaethylenehexamine) and their high molecular weight counterparts (2 – 25 kDa).

COLL 216

Cationic surfactants adsorption on different hydrophobic/hydrophilic charged polymer surfaces: A comparative study

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The adsorption of cationic surfactants ($C_{12}TAB$, $C_{14}TAB$, $C_{16}TAB$, $C_{18}TAB$, DPC, CPC) on different polymer surfaces (cellulose, PET, polystyrene) was investigated with the aim to improve the understanding of the role of surfactant molecular structure, surfactant concentration and polymer properties on the adsorption process.

The hydrophobic/ hydrophilic properties of the polymer surfaces were examined by the contact angle measurements. Streaming potential studies provided insight into the polymer swelling kinetics and enabled pH-dependant characterization of surface properties. Surfactant adsorption was visualized by streaming potential measurements, while the adsorption isotherms were measured for surfactant concentrations up to 0.1 × critical micellar concentration. The amount of non-adsorbed surfactant in liquid phase was determined by charge titration measurements.

Both the surfactant structure and polymer character influence the adsorption process, while the contribution of polymer is dominant. The hydrophobic interactions are of a substantial importance.

COLL 217

Surfactant sculpting of photocurable monomers into hierarchically organized biomimetic materials

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A defining feature of biological materials is the hierarchical organization of structure and composition. This design paradigm avoids vexing tradeoffs between competing properties by independently optimizing each property at separate levels of the

hierarchy. Herein we describe a facile method that faithfully reproduces this hierarchical organization in synthetic polymers. It consists of a photocurable monomer and water. To this quasi-two-component system we add surfactants that sculpt the interface into the desired shape. The resulting structures are then solidified by crosslinking with UV light. Drawing from the rich phase behavior of oil/water/surfactant systems, we demonstrate complex biomimetic morphologies over many length scales ranging from several mm down to 100 nm. Quantitative image analysis reveals fractal morphologies with at least four distinct levels of hierarchy, which depended most strongly on surfactant tail length and oil viscosity. The observed morphologies resemble neural networks, biofilms, honeycombs, keratin flakes, vascular structures, and spongy bone.

COLL 218

Self-assembly of helical microtubules directly visualized by optical microscopy in real-time

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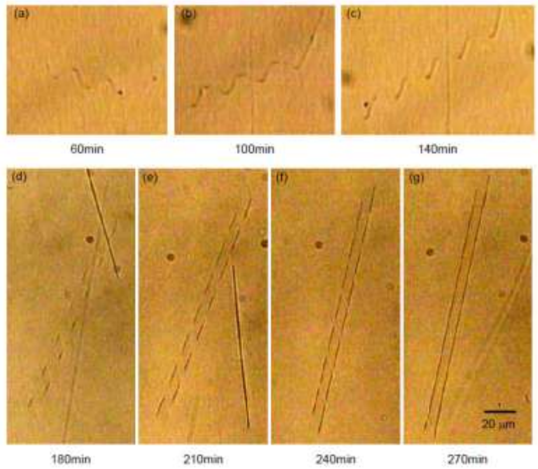
The assembly and growth of helical tubules by amphiphilic peptides or surfactants is a topic of great relevance to soft matter physics (e.g., the connection between molecular chirality and self-assembly) and to biological structures (e.g., tubules are believed to be intermediate structures in the formation of gallstones). The pathway for forming tubules from an initial state of vesicles or micelles has been studied theoretically, but has not been directly visualized in real-time. In the current study, we demonstrate the formation of tubule structures in aqueous systems consisting of the single-tailed diacetylenic surfactant, 10,12- pentacosadiynoic acid (PCDA) upon the addition of a short-chain alcohol. PCDA tubules can be conveniently prepared over a range of sizes from nano to micro. We focus on micron sized tubules because their assembly process can be directly captured by optical microscopy. The step-wise process involves a nucleation of helical microribbons from nanoscale vesicles. These ribbons then fold and re-arrange into closed tubules. In many cases, tubules further re-arrange into plate-like structures. A notable aspect of the above system is that the surfactant is achiral; yet, the tubules are formed from helical ribbons. Our studies offer new insights into tubule formation that will be valuable in clarifying and refining theoretical models for these fascinating structures.



COLL 219

Microstructural transformations in concentrated, charged vesicle suspensions: The crowding hypothesis

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Charged unilamellar vesicles in a concentrated suspension can deflate and transition to a bilamellar state. We propose that the driving force for this deflation-induced transition is the repulsive electrostatic pressure between the charged vesicles. To directly examine the role of concentration and electrostatics on this transition, we study the time evolution of cationic vesicle suspensions at different surfactant and salt concentrations using CryoTEM imaging. We find that above a critical concentration, charged vesicles in a suspension can experience '*crowding*' due to overlap of their electrical double layers that can result in a microstructural transformation, depending upon the salt concentration and vesicle size.

COLL 220

Mechanisms of interactions of mixed surfactant systems with stratum corneum: Monitoring drying stress and lipid rigidity

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It is known that the harshness of surfactants in cleansers can cause damage to skin proteins and lipids, leading to after-wash tightness, dryness, irritation, and itchiness. Anionic surfactants can bind to stratum corneum proteins which lead to transient swelling and hyper-hydration. The subsequent drying stresses that develop in stratum corneum (SC) are crucial for its barrier function, and can also cause dry skin damage. A recent study conducted by Dauskardt et.al., has shown the effect of water treatment/moisture changes on drying stresses generated in stratum corneum. Surfactant interactions with skin can vary significantly, depending upon the nature of their functional head group and pH. In this study, we have compared the effects of single and mixed surfactant systems, consisting of commonly used anionic-zwitterionic surfactants (SLES-Betaine), on the drying stress behavior of stratum corneum. The macroscopic effects of surfactant treatment are correlated with the fundamental properties of stratum corneum proteins/lipids using Confocal Raman microscopy, specifically through the lipid rigidity parameter. A specific mixed surfactant ratio was found to give the least drying stress and lipid interactions. The beneficial effects of a mixed system are proposed to be due to a change in CMC and mixed micelle size as well as potential for lipid interaction.

COLL 221

Fluoroalkyl polyethylene glycols for perfluorocarbon microemulsion and double emulsion

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Perfluorocarbons (PFCs) are chemically and biologically inert, highly gas-dissolving, highly fluidic, and with low surface tension. Their unique properties have triggered various applications such as oxygen delivery, diagnosis, and lubrication. However, PFCs are immiscible with aqueous media, hence fluorosurfactants are required to make PFC microemulsion and double emulsion for practical applications. In this study, methoxy polyethylene glycols (MPEGs) end-functionalized with various perfluoroalkyl groups were synthesized by reacting different types of perfluoroacid chlorides with various low-MW amino-MPEGs via amide linkage. According to the ratios of hydrophilic to fluorophilic groups balance (HFB) for these PFC microemulsions obtained, an empirical formula was applied to calculate the HFB values which can be used to design the structure of fluorosurfactant for the preparation of PFC microemulsion and double emulsion. A variety of PFCs such as perfluorooctyl bromide and perfluoroepentane, and perfluoropolyether were examined for this study.

COLL 222

Steric stabilization of self-assembled cubic lyotropic liquid crystalline nanoparticles: High throughput evaluation of alternative classes of steric stabilizers

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Nanostructured lyotropic liquid crystalline colloidal particles (i.e. cubosomes) are gaining interest in applications such as drug delivery and imaging agent encapsulation systems. It is therefore essential that the stability and integrity of these nanoparticles is maintained over time. This study investigates alternative stabilization agents to the extensively used Pluronic F127, which imparts a steric barrier to prevent aggregation of cubosomes. Using high throughput methodologies in preparation and characterization of monoolein and phytantriol dispersions, we were able to rapidly assess the performance of a wide range of non-ionic (Pluronic, Myrj) and custom stabilizers (i.e. PEG-SA-Phytantriol copolymer). It is shown Pluronic F108 is superior to Pluronic F127 as a monoolein cubosome stabilizer, preserving the double diamond (Pn3m) cubic phase typically observed with bulk monoolein, while providing equivalent colloidal stability.

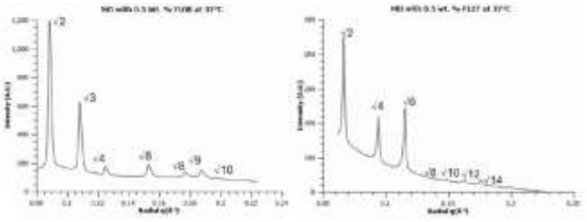

Fig 1. Small angle diffraction data (SAXS) and assigned Bragg reflections obtained for Pluronic F108 (left) and F127 (right) stabilised monoolein nanoparticles at 0.5 wt. %, displaying Pn3m and Im3m cubic phases respectively

The stabilization of phytantriol dispersions by Myrj 59 was also equivalent to Pluronic F127 at lower stabilizer concentrations, while preserving the internal nanostructure.

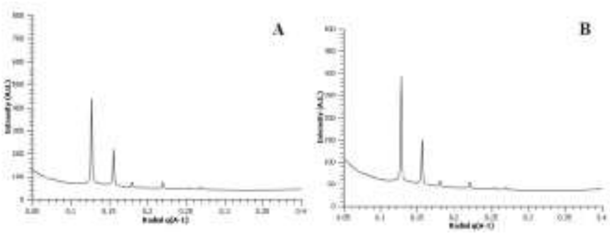

Fig 2. SAXS diffraction patterns and assigned Bragg reflections obtained for A) Pluronic F127 (left) and B) Myrj 59 (right) stabilised phytantriol nanoparticles at 1.0 wt. % and 0.1 wt. % respectively, both showing the Pn3m cubic phase

COLL 223

Health effects following environmental exposures to nanomaterials: Toxicological principles

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The large scale production of some nanomaterials has led to concerns about their release into the environment and exposure-related outcomes in humans and environmental receptor species. However, exposure concentrations in air, soil, and water are largely unknown, as are the chemical and structural transformations that may occur after release. Physicochemical changes may also continue following uptake by an organism. The nanoparticle surface likely interacts in a dynamic way with biological constituents and these interactions may determine response outcome; however, such processes have not been well-described. Quantitative data about tissue- and cell-specific accumulation patterns and how long the materials persist after realistic exposures is also missing. Such information will help us to understand response mechanisms at realistic exposure concentrations and durations. These challenges – and overcoming them – provide ample opportunity for cooperative research programs between materials scientists and biologists in order to protect human and environmental health.

COLL 224

Impact of engineered nanomaterials on biological and environmental systems

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Nanotechnology is most commonly driven by the increasing importance of very small particles in a variety of applications. These applications mainly reside in technologies stemming from the electronic or optical sensing approaches. With the advent of surface functionaliation on very small particulates, however, gave way to the birth of nanomedicine and nanotoxicology. Our research continues to investigate the interface between the hydrophobic nature of inorganic nanostructures and the hydrophilic nature of biology. As part of the R&D in biological applications, we also study the unintended implications of engineered nanomaterials. Particles are carefully selected in groups of similar physicochemical properties, characterized as they transform over time, and exposed to mammalian and bacterial systems. Properties such as particle size, surface charge, and chemical composition are related to specific pathway-specific biological responses such as apoptotic, oxidative stress, or other immune or inflammatory events. Results of these studies provide insights on how engineered nanomaterial features influence cellular responses and thereby outline possible approaches for developing and applying predictive models for biological responses caused by exposure to nanomaterials.

COLL 225

Impact of TiO_2 nanoparticles on bacterial biofilm formation

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Toward elucidating the implications of nanoparticles released into the environment, this work aims at understanding the impact of TiO_2 nanoparticles on bacterial cell function of biofilm formation. Non-pathogenic bacteria *Shewanella oneidensis* were exposed to TiO_2 nanoparticles, chosen based on their common use in consumer products, with varied exposure concentrations and times. Standard microbiological assays were performed, including colony counting and growth curve analysis, to determine bacterial viability and replication post-nanoparticle exposure. Though all nanoparticles cause a similar decrease in viability, this work reveals a concentration-dependent decrease in the doubling rate of *S. oneidensis*. Biofilm formation and characteristics were also examined after nanoparticle exposure using quartz crystal microbalance (QCM). Understanding of nanoparticle impacts on critical bacteria functions allows us to gain a mechanistic understanding of toxicity and guides us towards design rules for creating safe nanomaterials.

COLL 226

Interactions of well-defined nanomaterials with environmentally relevant microbial pathogens

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While several manufactured engineered nanomaterials (ENMs) are currently in the market, there are concerns that the uniformity in particle size, shape, and morphology of a given sample is often poor. This makes understanding the reactivity and behavior of ENMs in the environment difficult since the reactivity of ENMs is highly dependent on size, shape and morphology. Our group has thus focused on developing straightforward synthetic procedures for the production of well-defined metallic, bimetallic and metal oxide nanoparticles in high yield. Electrochemical, x-ray, and surface probe microscopy are a few of the fundamental techniques used to characterize our ENMs. The presentation will focus on understanding the mechanisms by which ENMs interact with microbial pathogens common in the environment, and to obtain a fundamental understanding of how these interactions are influenced by environmental factors. We will also discuss the effect of interactions of microbial pathogens with biomolecules at the interface of well-defined ENMs.

COLL 227

Mechanism of airborne engineered nanoparticle toxicity in alveolar cells at the air interface

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The increasing use of engineered nanoparticles (NPs) in industrial and medical applications is expected to increase unintended environmental or occupational exposures and intended medical or direct consumer exposures. The physical and chemical properties of the NP engage and activate distinct proteins and cellular pathways that, in turn, govern the fate of the NP and its impact on the cell and ultimately on human health. The relationships between particle properties and these complex cellular processes and response are still unclear. Airborne NPs that enter the respiratory tract are likely to be deposited in the alveolar region. To preserve inhaled NP properties that are presented to alveolar cells *in vivo*, we study cells grown and exposed to aerosolized NPs at the air-liquid interface (ALI). Here we present our findings, providing realistic relationships between airborne particle properties and their cellular fate and response. This work is funded by NIEHS grant 1RC2ES018786-01 (G.O.).

COLL 228

Chemical and morphological transformations of silver nanowires in aqueous media

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Metal nanowires have a diverse range of anticipated applications but there is limited information on the fate of nanowires in the environment. We studied the colloidal stability and oxidation rates of silver nanowires (Ag NW) with two lengths and two surface coatings in different aqueous solutions, including conditions relevant to studies of toxicity to *Daphnia magna*, an aquatic organism that is an indicator for ecosystem health. While poly(vinylpyrrolidone) (PVP) and aluminosilica (SiO_2) coatings prevent NW aggregation in ultrapure water, rates of aggregation and settling were increased in the presence of dissolved inorganic and ionic ions. In stirred anaerobic solutions, morphological changes, including nanowire fusing, was the dominant transformation. In aerobic solutions, silver oxidation releasing dissolved Ag^+ occurred for all coatings. Rates of Ag^+ release cannot explain observed differences in observed Ag NW toxicity to *Daphnia*, suggesting toxicity is controlled by a complex mix of colloidal and chemical processes in solution.

COLL 229

Molecular-level interactions of nanomaterials and their surface chemistries with Daphnia magna: Using genomic biomarkers as an indication of chronic toxicological impacts

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Most studies on the environmental impacts of nanomaterials focus on acute lethal doses of a nanomaterial which provides little information as to how the nanomaterial may be interacting with the organism at the molecular level or the potential long-term impacts of a lower realistic exposure. This presentation will discuss changes in gene expression induced by exposure to sub-lethal concentrations of nanomaterials as an indicator of molecular-level interactions of nanomaterials with Daphnia magna. Genomic data can also be used as a sensitive indicator of how nanomaterials may be affecting specific physiological systems within Daphnia and how the chemistry of a nanomaterial may change these impacts. The use of molecular interactions as indicators of higher level or longer-term impacts of exposure will also be discussed. The ultimate goal of this research is to provide a potential high-throughput method to evaluate nanomaterials for environmental safety and to suggest ways to make safer nanomaterials.

COLL 230

Alterations in physical state of silver nanoparticles exposed to synthetic human stomach fluid

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The bioavailability of ingested silver nanoparticles (AgNPs) depends in large part on initial particle size, shape and surface coating, properties which will influence aggregation, solubility and chemical composition during transit of the gastrointestinal tract. Citrate-stabilized AgNPs were exposed to synthetic human stomach fluid (SSF) (pH 1.5) and changes in size, shape, zeta potential, hydrodynamic diameter and chemical composition were determined during a 1 hr exposure period using Surface Plasmon Resonance (SPR), High Resolution Transmission Electron Microscopy/ Energy Dispersive X-ray Spectroscopy (TEM/EDS), Dynamic Light Scattering (DLS) and X-ray Powder Diffraction (XRD). Exposure of AgNPs produced a rapid decrease in the SPR peak at 414 nm and the appearance of a broad absorbance peak in the near infrared (NIR) spectral region. During exposure to SSF, changes in zeta potential, aggregation and morphology of the particles were also observed as well as production of silver chloride which appeared physically associated with particle aggregates.

COLL 231

Assessing nano-bio interactions at the interface of engineered nanoparticle and model cell membrane

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There has been a growing interest in understanding the nano-bio interface interactions related to the toxicity of engineered nanoparticles (ENPs). In this presentation, we present two methods to assess the integrity of lipid bilayers, used as model biomembranes, upon exposure to ENPs. In the first method, we quantify the leakage of a fluorescent dye (by fluorometry) pre-loaded to hollow spherical lipid bilayers (i.e., liposomes, size = 100 nm) that are impermeable to the selected dye when intact. The second method is electrophysiology that relies on detecting electrical currents passing through lipid bilayers formed on an aperture (~150 μm in diameter) that divides two electrolyte reservoirs. Electrodes are placed into the reservoirs to monitor the current burst across the lipid bilayer which is resistant to conductance when integral. Using the methods, we examine ENPs' physicochemical characteristics (e.g., surface functionalities, charge, shape, core compositions) on the lipid bilayer disruption.

COLL 232

Carbon nanotubes for chemical sensing

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The organization and functionalization of carbon nanotubes (CNTs) has been used to create sensory devices that provide changes in chemical resistance in response to a target analyte. The advantages of chemiresistive sensors include the following: (1) Small changes in resistance can be measured with high precision and inexpensive electronics. (2) Resistivity sensors have very low power requirements. (3) Resistive materials are readily integrated into many different structures, ranging from integrated circuits to fabrics. (4) The simplicity of a resistive measurement is ideal for the formation of cross-reactive array (e-nose or e-tongue) devices. Restricted geometries created by nanostructures impart superior sensitivity to chemical sensors. This presentation will detail our latest results for the creation of CNT sensory systems with specific responses to chemicals including, explosives, ketones, and ethylene by the incorporation of recognition elements.

COLL 233

Peptide-polymer amphiphiles in the assembly of enzyme-responsive micellar nanoparticles

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Herein, we describe enzyme-directed assembly of fluorogenic micellar nanoparticles generating amplified detectable signals unique to the particles. These micelles are assembled from peptide-polymer amphiphiles (PPAs) labeled with combinations of FRET pairs. This is achieved by labeling otherwise similar block copolymer amphiphiles with each of the dyes. When mixed together, signals from the FRET-pairs can be utilized to detect particle assembly and hence enzymatic activity. Furthermore, we show FRET signals within the shell of the assembled micelles can be used to measure particle stability (critical aggregation concentration) and enable a determination of intraparticle distances between amphiphiles in the micellar aggregates leading to elucidation of the packing arrangement of amphiphilic copolymers within the micelles.

COLL 234

Single molecule arrays

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We have developed single molecule microarrays for sensitive detection of proteins and nucleic acids. These arrays enable digital counting of single analyte molecules resulting in ultrasensitive measurements. This approach has been applied to a variety of clinical problems where conventional methods lack the sensitivity necessary to detect the relevant molecules of interest.

COLL 235

Epidermal electronics

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Recent work on materials, mechanics principles and designs layouts have produced routes to electronic systems with thicknesses (~30 microns), effective elastic moduli (<150 kPa), bending stiffnesses (<1 nN·m) and areal mass densities (< 3.8 mg/cm2) matched to the epidermis. Laminating such devices onto the skin leads to conformal contact, intimate integration and adequate adhesion based on van der Waals interactions alone, in a manner that is mechanically invisible to the user. Functional components range from monitors of elecrophysiological signals, to temperature and strain sensors, to transistors, light emitting diodes, photodetectors and a variety of elements capable of radio frequency operation, including inductors, capacitors,

oscillators and rectifying diodes. This talk describes advances in the materials for these systems, with applications in multimodal physiological status and cognitive state monitoring.

COLL 236

Co-opting Moore's Law: Vaccines, medicines and interfacially-active particles made on a wafer

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In 1965, Gordon Moore, co-founder of Intel, described the trend that the number of components in integrated circuits had doubled every year since 1958. This trend has continued to today, enabled by advances in photolithography which has taken the minimum feature size of transistors down from about 10 microns in 1970 to 0.045 microns (45 nm) today. In biological terms, this corresponds from the size of a red blood cell to the size of a single virus particle! This top-down nano-fabrication technology from the semiconductor industry is, for the first time, in the size range to be relevant for the design of medicines, vaccines and interfacially active Janus particles. This lecture will describe the design, synthesis and efficacy of organic nano- and micro-particles using a top-down nano-fabrication technique called PRINT (Particle Replication in Non-wetting Templates). Examples described will include the design of PRINT particles useful as vaccines targeted chemotherapy agents.

COLL 237

Mechanochemicallly-induced interfacial bonding formation between 8-hydroxyquinoline and hydroxyapatite nanocrystals

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Th nanocomposite formed by hydroxyapatite nanocrystal (HAp) and 8-hydroxyquinoline (8Hq) was fabricated by a mechanochemical milling process. The crystallinity and nanostructure of HAp were preserved with the process. Th photoluminescence peak at around 500 nm newly appeared due to the charge transfer (CT) transition with the process, suggesting that 8Hq molecules covalently bound to the Ca^{2+} ions of HAp. The interfacial bonding structures were calculated by a DV-Xa molecular orbital method to find the formation between the Ca^{2+} ions and the O atoms of 8Hq. When 8Hq approached to the Ca^{2+} in the HAp simplified by CaO cluster, the difference between

HOMO and LUMO energy was larger as compared to that of 8Hq. The character of HOMO in 8Hq dominantly composed of O 2p orbital, whereas 30 % of HOMO of 8Hq/CaO was O 2p orbital of CaO. Thus, the interfacial covalent bonding effectively affected the new transitions to show the efficient green luminescence.

COLL 238

Microwave-accelerated surface modification of metal nanoparticles with self assembled monolayers of alkanethiols

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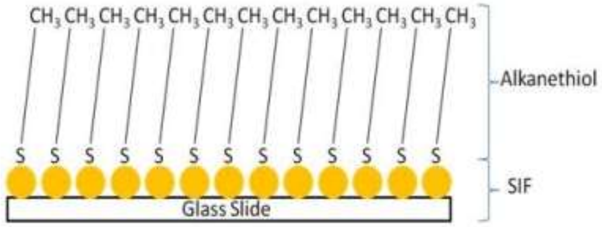
Self-assembled monolayers (SAMs) of alkane thiols are regularly employed in the preparation of engineered plasmonic surfaces. However, the preparation of SAMs on plasmonic surfaces can take up to 24 hours. In this work, we present out initial findings for reducing the preparation time down to 10 minutes using low power microwave heating. In this regard, we employed a model alkane thiol (1- Undecanethiol, UDET) to modify the surfaces of Silver Island Films (SIFs). We exposed a 0.1 mM UDET solution placed on SIFs to low power microwave heating for 5-45 minutes and carried out the identical experiment at room temperature for 3 hours. Raman spectroscopy (the presence of C-S bond) and contact angle measurements (40° and 100° before and after surface modification, respectively) revealed that SAMs of UDET were formed on SIFs in 10 minutes using microwave heating, a significant improvement over room temperature surface modification procedure.



COLL 239

Preparation of plasmonic nanoparticle-coated PMMA assay platforms for microwave-accelerated bioassays

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It was previously shown that surface modification of plastic substrates can lead to an increase in surface functionality. In this work, we have investigated the deposition of

metal-nanoparticles onto surface functionalized poly(methyl methacrylate) (PMMA) discs that can potentially be used in microwave-accelerated bioassays. The diameter of PMMA discs were adjusted to 5 cm, which is significantly smaller than the wavelength of microwaves at 2.45 GHz (12.2 cm) to avoid charge buildup and subsequent destruction of the PMMA discs. We have studied several techniques for the preparation of PMMA assay platforms and found that the polymerization of the monomer, methyl methacrylate, results in clear and optically transparent PMMA discs. The absorbance of the disc was obtained before surface modification and after coating of the silver nanostructures. An increase in absorption at 450 nm was due to the attachment of the metal-nanoparticles on the modified PMMA discs.

COLL 240

Multifunctional plasmonic shell-magnetic core nanoparticles for targeted diagnostics, isolations and photothermal treatment of tumor cells

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Cancer disease presents greatest challenges in public health care and global economy due to the fact that deaths and disability from cancer cost nearly 1 trillion dollars a year. Current treatment based on surgery, radiation therapy, and chemotherapy are often associated with severe side effects . As a result, new approaches to treat cancer that do not rely on traditional therapeutic regimes, is very important for public health as well as global economy . Here we report multifunctional plasmonic shell –magnetic core nanotechnology-driven approach for targeted early detection, isolation and photothermal treatment of cancer cells.

COLL 241

Microfluidic synthesis of molecularly imprinted polymer: Biosensor applications

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In nanotechnology, there are a lot of efforts for developing smaller and more compact devices to meet our growing demands in miniaturization. To improve the performance of nanodevices, there are many challenges for chemists to synthesize novel materials and particles since nano technology is a part of the chemical domain, which produces new materials at the molecular level. New synthetic approaches such as microfluidic synthesis have gotten a great attention to develop novel materials/particles/polymers at the nano- or micro-scales. Microfluidic approach allows us to produce materials with specific advantages that can't be achieved through conventional synthetic routes. We present here a microfluidic synthesis of molecularly imprinted polymeric (MIP) system in colloidal phases that were provided by “molecular imprinting technique. The molecular imprinting method is a general protocol for the creation of synthetic receptor sites with

specific molecular recognition functions for bio or chemical sensors in cross-linked network polymers. Synthesis of high affinity receptor sites in MIPs systems is a key contribute to achieve high performance in their molecular recognition functions.

COLL 242

Determination of binding properties of protein/Au conjugates and protein/Au conjugate Ag sandwiches using calorimetry

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The research herein is focused on the investigation of characterizing Au nanoparticle conjugates. The size and concentration of nanoparticles will be determined through the use of extinction coefficients via UV-Vis spectrophotometry as according to literature. The binding of IgG and a-IgG to Au nanoparticles and Ag(Au/IgG – a-IgG/Au)Ag “sandwiches” will be probed using isothermal titration calorimetry (ITC). In turn this data will allow for preliminary information regarding the biochemical thermodynamic parameters (ΔG, ΔH, and ΔS) to be understood, providing insight into the binding properties of nanoparticles with protein. To further characterize the Au conjugates and gold conjugates/Ag “sandwiches,” their SERS enhancement will be determined.

COLL 243

Investigation of stability in Ag nanoparticle solutions using Monte Carlo simulations and zeta-sizer measurements

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Characterization of the silver nanoparticles in solution will begin with the determination of their SERS activity. In addition, the stability of the nanoparticles will be tested using zeta potential in which pH and ionic strength are varied, and their resulting effect on surface charge of nanoparticles investigated. Furthermore, the electrostatic repulsion, van der Waals attractions and the effect of steric interactions will be studied. The effect of pH and concentration on zeta-potential will be optimized to maximize solution stability. To complement the zeta potential data Monte Carlo simulations will be used to determine the meta-stable state (the aggregation dynamics, essentially) of these nanoparticles, in addition to their size and shape. By combining theoretical insights with data collected experimentally, the nature of the stability of the silver nanoparticles may be better understood.

COLL 244

Surface properties and liquid crystal alignment behavior of well-ordered poly(oxyethylene)/poly(3-hexylthiophene) blend films

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In this study, in order to utilize the photoluminescent property of a conjugated polymer and the liquid crystal (LC) aligning property of a well-ordered comb-like poly(oxyethylene), we investigated blend surfaces of poly(3-hexylthiophene) (P3HT) and poly[oxy(*n*-decylsulfonyl methyl)ethylene] (CH_3-10SE) mixtures. The morphology, compositions, and wettabilities of these blend surfaces were systematically analyzed as a function of the blend composition and were correlated with the alignment behavior of nematic LC on the blend surfaces. Therefore, we found that CH_3-10SE part with a well-ordered side chain structure predominantly affects the both of wettability and LC alignment behavior of the blend films while there was no clear association between the wettability and the LC alignment behavior.

COLL 245

Design and modification of porous materials for the reactive removal of ammonia

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The use of porous materials for the removal of toxic industrial chemicals is of particular interest for filtration purposes, because of their high surface area leading to a large number of reactive sites. In this study, nucleophilic aminolysis of esters was targeted for the removal of ammonia. Two distinct materials were designed for this chemistry: zirconium hydroxide modified with surface bound carbonate groups, and MCM-41 infused with poly(butyl acrylate) running through its pores. The results show a significant increase of the modified materials' capacity for ammonia over the unperturbed materials. Zirconium hydroxide has already been shown to have acid-gas removal capabilities. Conversely, the MCM-41 material has a narrow range of capabilities and would need to be engineered with other materials for broad range use.

COLL 246

Rotational and translational motion of nanocomposites

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We report on the dynamics of clusters made through the combination of spherical particles. Clusters present ideal model systems to study the motion of objects with complex shape. The translational and rotational diffusion coefficients of particle doublets, triplets and quadruplets could be determined by a combination of regular polarized dynamic light scattering (DLS) and depolarized dynamic light scattering (DDLS) because their overall dimensions were below 400 nm. The translation dynamics was found to be largely decoupled from the rotational motion. Knowing the exact geometry of the assemblies, we apply a hydrodynamic model, in which the surface of the clusters is represented as a shell of small friction elements, for calculating the diffusion coefficient for objects with complex shapes. We present a quantitative comparison of the theoretical predictions with the results obtained by DDLS.

COLL 247

Formation and characterization of polyamide 6/SiO2 nanocomposites via sol-gel technique

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Several polyamide 6/SiO_2 nanocomposites with varying amount of SiO_2 were prepared using sol-gel technique. These nanocomposites were formed in situ by hydrolysis and condensation of TEOS and 88% formic acid was used as a solvent for nylon 6. The microstructure development during thermally –induced crystallization has been carried out with a combination of differential scanning calorimetry (DSC), FTIR and solid-state NMR spectroscopy. IR spectroscopy and wide angle diffraction (WAXS) were used to determine the crystal form of nylon 6 at room temperature. DSC and FTIR spectroscopy showed a decrease in crystallinity with increasing TEOS loading as compared to neat polyamide 6. Scanning electron microscopy (SEM) and Transmission Electron Microscopy (TEM) was used to determine the particle size. We plan to investigate crystallization kinetics, water absorption, thermal stability and mechanical properties of these nanocomposites with increasing SiO_2 content and results also will be reported.

COLL 248

Optoelectronic properties of metal-semiconductor nanocomposites in strongly coupled regime

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Several chemical routes to CdSe/CdS core-shell nanocrystals (NCs) with each of them leading to different shape of nanocrystals were developed. Also a simple chemical method for growing Au domains onto CdS nanorods and CdSe/CdS NCs in oleylamine

was developed. The size of Au NCs can be precisely tuned by adjusting the temperature of the reaction mixture, while the shape of Au/CdS nano-composites (matchstick or barbells) is controllable via the reaction rate. All of the aforementioned nanocomposites had semiconductor emission quenched and further study is necessary to determine whether a significantly wider band gap shell material can prevent fast transfer of excited carriers from semiconductor into metal domains.

COLL 249

“Host-guest” interactions between amphiphilic invertible polymers and insoluble cyclohexasilane in polar and non-polar solvents

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“Host-guest” interactions between amphiphilic invertible macromolecules based on PEG and sebacic acid, and potential precursor for electronic materials, cyclohexasilane (Si_6H_{12}) in acetonitrile (neither a solvent for cyclohexasilane, nor supporting micellization of amphiphilic invertible macromolecules) and toluene (supporting polymer micellization solvent for cyclohexasilane) have been investigated.

In benzene, upon addition of Si_6H_{12} to amphiphilic polymer solution, the ^{1}H NMR study revealed i. interaction between Si_6H_{12} and oxygen-containing functional groups of the polymer and ii. rising additional interaction between cyclohexasilane and hydrophobic polymeric domains formed upon self-assembly.

In acetonitrile, despite the extended conformation of the macromolecules and absence of self-assembled polymeric domains, an macromolecular amphiphilicity itself contributes to localizing Si_6H_{12} by AIP and enables Lewis acid-base interaction between Si_6H_{12} and the AIP carbonyl groups. The obtained results demonstrate an interesting phenomenon that insoluble Si_6H_{12} can be localized by AIP macromolecules in a medium which does not support formation of polymeric domains.

COLL 250

XPS imaging and depth profiling of PMMA/PVC blends

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Recent developments in XPS instrumentation have made it possible to examine the surface and in-depth concentration mapping of phase separation of simple polymer blends. Previously, the preferential segregation of one component in the vertical direction was determined via angle-resolved analysis but with no spatial resolution to detect surface domain formation. The large sample surface area limited lateral resolution and depth information was restricted to about the top 100 nanometers. Instrumentation recently acquired by our laboratory possesses a monochromatic X-ray source with a 10 micrometer spot size and imaging capability. In addition, a dual neutralization system and C-60 ion gun allows for true depth-profiling. Polymethyl methacrylate (PMMA)/poly vinyl chloride (PVC) blends of various weight percent compositions were prepared as solvent cast films using MEK. The three dimensional phase concentrations are quantified using surface and in-depth analysis and the results compared to previous work from this laboratory.

COLL 251

Preparation of nanoporous freestanding ultrathin films by polymer blend phase separation

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Polystyrene (PS)/poly(methyl methacrylate) (PMMA) blend was spin-casted onto the poly(vinyl alcohol) (PVA)-coated substrate to prepare an ultrathin film (thickness < 100nm), where PVA was introduced as a sacrificial layer to achieve freestanding. The effect of substrate surface energy on phase separation morphology was investigated foremost. By means of freestanding, the bottom side of the film was first observed and comparable to the top side of films. AFM and SEM technologies were used for morphology (topography and cross section) characterization. In all cases, there found no significant morphological differences between top and bottom side. The nanoporous structure was exhibited on the resulting films after solvent etching. The size of nanopores and the magnitude of nanopores penetrating the films was investigated and found controllable by various preparation conditions. It was concluded that the phase separation behavior of polymer blend within ultrathin films is different from that within bulk ones.

COLL 252

Role of oxygen vacancies on NO reduction on rutile TiO_2(110)-1×1

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The reactivity of NO on rutile TiO_2(110)-1×1 surface was systematically investigated using temperature-programmed desorption (TPD) to understand the role of oxygen

vacancies (V_O's) in NO reduction. For this purpose, we compared two TiO_2(110)-1×1 surfaces with (r-TiO_2(110)) and without (p-TiO_2(110)) oxygen vacancies. The vacancy concentration was carefully characterized by the integrated area of the 500 K-H_2O desorption peak in H_2O TPD and was measured to be about 5 % for r-TiO_2(110). Our NO TPD results indicate that NO is reduced to N_2O and N_2 on both TiO_2(110) surfaces with three distinct desorption peaks up to the substrate temperature of 400 K. N_2O desorption peak maxima are found to appear at 180 K, 270 K and 415 K, while N_2 desorption peak is only resolved at 270 K. Interestingly, our results further indicate that the integrated amount of reaction products such as N_2O and N_2 from NO is higher on r-TiO_2(110) than on p-TiO_2(110). Although the detailed mechanism of NO reduction on TiO_2(110) is still unclear, our results generally suggest that the defects such as oxygen vacancies and Ti^{3+} interstitials on r-TiO_2(110) surface interact preferentially with NO to enhance the yield of reduction into N_2O and N_2.

COLL 253

Quantification of thiolated surface species on gold nanoparticles using ICP-OES and ICP-MS

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In this study, prototypical thiolated ligands were conjugated on gold nanoparticles (AuNPs), and packing density was measured on an ensemble-averaged basis using inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). The effects of sample preparation, including centrifugation and digestion, as well as AuNP size and concentration, on recovery were investigated. Detection limits as well as practical limits of quantification for Au and S were compared for the two ICP-based methods. These preliminary data provide fundamental information on the advantages and limitations of ICP-based analyses of conjugated AuNPs and will be applied to future work focusing on other ligands of interest as well as hyphenation of ICP-MS with size-selective techniques and optimization for single-particle analysis.

COLL 254

Synthesis and characterization of smart nanohydrogels containing a magnetic Fe3O_4 core

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This paper reports a novel method to synthesis magnetic stimuli-sensitive latex nano-particles made with magnetite/poly(N-isopropylacrylamide-co-acrylic acid) (Fe_3O_4/P(NIPAAm-co-AAc)). The iron oxide (Fe_3O_4) was functionalized with AAc to form a stabilized suspended core, which served as the nuclei sites for further polymerization with NIPAAm and AAc monomers. The P(NIPAAm-co-AAc) shell layer exhibited thermo-sensitive (ascribed from NIPAAm) properties. The Fe_3O_4 inclusion to the latex nano-particles was confirmed using the TEM, FTIR, XPS, XRD, and TGA analyses. The latex nano-particles contained 2.25% (by weight) of Fe_3O_4. The diameters were approximately 200-400 nm with a lower critical solution temperature of 35°C. The novel magnetic stimuli-responsive latex nano-particles have potential use in numerous fields, such as catalyst supports, protein immobilization, cancer therapy, target drug delivery systems, and other biomedical applications.

COLL 255

WITHDRAWN

COLL 256

Surface modification of MWCNT and preparation of MWCNT-Au nanoparticles composites

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Facile synthetic route to decorate carbon nanotubes (MWCNTs) with gold nanoparticles is presented via a simple chemical reduction process using β-diketone and sodium citrate at room temperature. Pristine- and surface-modified MWCNTs were comparatively utilized for the preparation of MWCNT-Au-nanoparticles nanohybrid. Gold nanoparticles on the surfaces of MWCNTs were produced *in situ*, and more importantly all the solutions were aqueous phase-based. The surfaces of MWCNTs were functionalized with thiol groups through several steps including oxidation. The shape of the prepared gold nanocrystals on the –SH functionalized MWCNTs was spherical and the diameter of the particles was in the range of ~2 nm. It was found that thiolated MWCNTs were densely decorated with Au nanparticles, while pristine MWCNTs were not.

It was also found that gold nanoparticles were successfully prepared when MWCNT-PANI (polyaniline) composites were utilized, indicating that MWCNT-PANI composites played a role as a reducing agent for the reduction of gold precursor. The average size of Au nanoparticles was 20 nm, and it was easily controlled by just varying the concentration of MWCNT-PANI.

COLL 257

Facile one step synthesis of flower-shaped silver colloids using pulsed proton beam

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A new aqueous solution phase method is presented for the synthesis of “flower-like” silver nanomaterials using pulsed proton beam irradiation process at room temperature. It was observed that the morphology of the prepared silver crystals was easily controlled by varying the number of exposures to the pulsed proton beam. As the number of exposures to the pulsed proton beam was increased, the gradual structural change of synthesized silver colloids from sharp-edged and smooth-surfaced flower shape to blunt- edged and rough-surfaced structure was observed. The synthesized flower-like silver nanocrystals exhibited excellent surface enhanced Raman scattering (SERS) signals, which were attributed to the rough microstructures on the surface of the synthesized Ag crystals.

COLL 258

Monolayer protected gold clusters for targeted drug delivery and imaging

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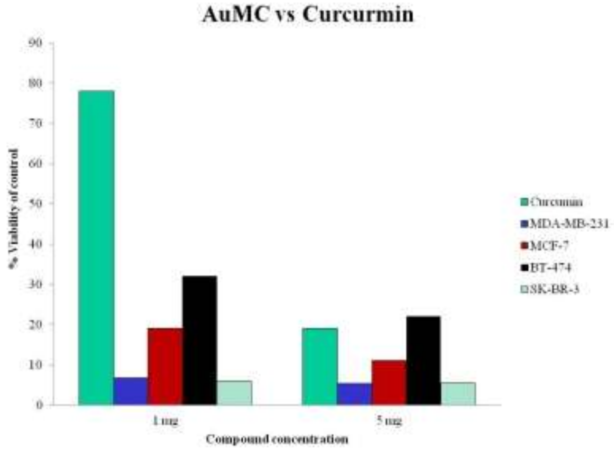
New synthesis strategies for nanoparticle-based material in which there is controlled spatial ordering of ligand is of continued interest for targeted drug delivery. Current drugs lack the much needed selectivity, specificity and sensitivity. Novel gold clusters synthesized with a coumarin based dye and doxorubicin dihydrochloride were studied. Two-photon cross-sections were measured inorder to probe their use as biological imaging agents. Dye labeled gold clusters has higher two photon cross-sections. Results using cytotoxicity, apoptotic morphological changes test and DNA fragmentation indicate their efficacy. Testing them on normal breast cells, testing their activity against different types of cancer and their efficacy on the enzymes that regulate cancer growth pathway is underway. Besides, increasing the cluster uptake by varying size (1nm) and composition of the cluster(cis-Platin based analogs) are being probed



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COLL 259

Programming multi-component self-assembly with side chain shape

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Conjugated diyne units introduce distinct "kinks" in the side chains of 1,5-substituted anthracene derivatives. These kinks place shape constraints on molecule packing and monolayer packing density. Diyne kinks positioned near side chain center allow (nearly) optimal packing of identical alkadiyne side chains. Such alkadiyne side chains are "shape self-complementary". By contrast, placement of the diyne kink far from side chain center inhibits packing of identical side chains, rendering these alkadiyne chains "shape self-repulsive". Employing pairs of molecules, each outfitted with shape self-repulsive, but pairwise shape- complementary, we have successfully prepared compositionally patterned two-component, and even, four-component self-assembled monolayers (SAMs).

COLL 260

Self-assembly and growth of triazole based nanostructures and their interactions with mammalian cells

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In this work, we have examined the growth and self-assembly of triazole derivatives and the binding affinity of those assemblies with metal nanoparticles and quantum dots was investigated. It was found that the triazole moiety played a significant role not only in the formation of the assemblies but also in binding to the nanoparticles. In general, depending upon the substituent chain length, the sizes of the assemblies were found to be in the range of 500 nm to 1mm. The assemblies efficiently bound to gold nanoparticles, as well as CdS nanoparticles. The binding of the nanoparticles to the assemblies was confirmed by absorbance, fluorescence as well as infra-red spectroscopy. Upon binding to the assemblies, the nanoparticles showed a red-shifts in fluorescence and absorbance spectra. Further, we examined the potential of the nanocomposites for antibacterial applications, where in it was found that the assemblies were potent against the gram negative bacteria e-coli. We also examined their interactions with mammalian cells. The nanocomposites were found to attach to the

macrophages. In particular, the immunological response of the mouse macrophages was examined in the presence of the formed nanocomposites.

COLL 261

Fabrication of carbon microcapsules containing silicon nanoparticles: Carbon nanotubes nanocomposite for anode in lithium ion battery

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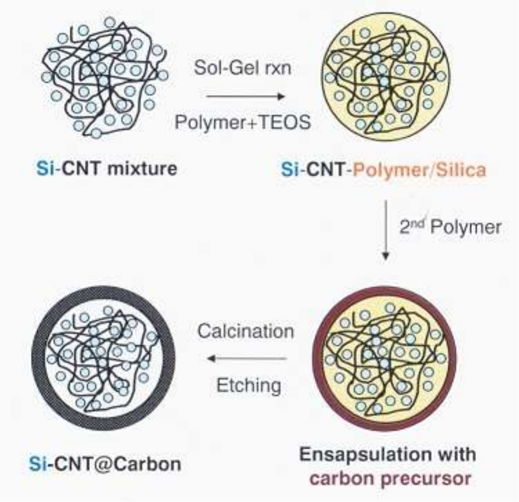
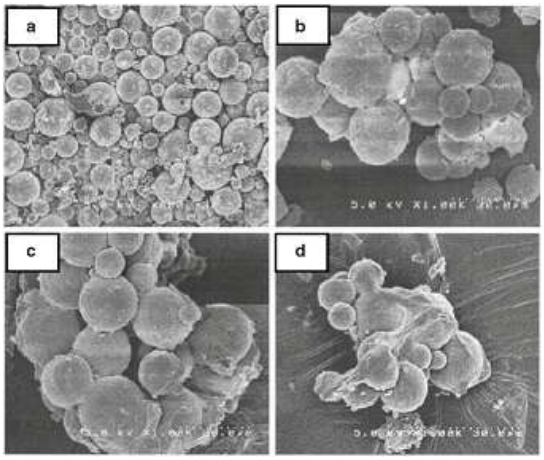
Carbon microcapsules containing silicon nanoparticles–carbon nanotubes nanocomposite have been fabricated by a surfactant mediated sol–gel method followed by a carbonization process. To obtain Si-CNT nanocomposites with spherical morphologies, a silica precursor (TEOS) and polymer (PMMA) mixture was employed as a structure-directing medium. Thus the Si-CNT/Silica-Polymer microspheres were prepared by an sol–gel method. Then a carbon precursor polypyrrole (PPy) was incorporated onto the surfaces of preexisting Si-CNT/silica-polymer to generate Si-CNT/Silica-Polymer@PPy microspheres. Subsequent thermal treatment of the precursor followed by wet etching of silica produced Si-CNT@C microcapsules.



The intermediate silica/polymer must disappear during the carbonization and etching process resulting in the formation of an internal free space. The carbon precursor polymer should transform to carbon shell to encapsulate remaining Si-CNT nanocomposites. Therefore, hollow carbon microcapsules containing Si-CNT nanocomposites could be obtained (Si-CNT@C).



These final materials were employed for anode performance improvement in lithium ion battery. The cyclic performances of these Si-CNT@C microcapsules were measured.

COLL 262

Enzyme cascade reactions inside polymer vesicles to fight oxidative stress

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Oxidative stress plays a significant role in the pathogenesis of many diseases, such as arthritis or cancer. Efforts to reduce oxidative stress by direct administration of antioxidant enzymes were not successful due to the low bioavailability of the enzymes. A step further was achieved by encapsulation of superoxide dismutase (SOD) inside polymeric vesicles to protect the enzyme from proteolytic attack, and thus increase its bioavailability,[1] but the system did not cope with the formation of H_2O_2.[2]

Here, we develop the concept by simultaneously encapsulating a couple of enzymes, superoxide dismutase and lactoperoxidase acting in tandem. Superoxide radicals and related H_2O_2 are detoxified inside the polymer vesicles due to the *in situ* cascade reaction. Simultaneous encapsulation of enzymes during the process of vesicles formation has been established by fluorescence correlation spectroscopy and fluorescence cross correlation spectroscopy. To evaluate the efficiency for therapeutic applications, we studied the internalization and the activity of vesicles containing the combination of enzymes in different cell lines (THP-1 and HeLa cells). Flow cytometry and confocal laser scanning microscopy clearly point to an efficient candidate for enzyme-based antioxidant therapy.

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COLL 263

Mechanistic studies of the simultaneous synthesis and assembly of gold nanoparticle double helices

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Our previous work has demonstrated that carefully designed peptide-conjugate molecules can direct the synthesis and self-assembly of complex and well-ordered nanoparticle superstructures. Here, we detail recent studies that probe the mechanism of the synthesis and assembly of gold nanoparticle double-helical structures using C_{12}-PEP_{Au} ($[C_{11}H_{23}CO]$-AYSSGAPPMPPF). Specifically, we show that 1) it is critical that the peptide conjugates be well-dispersed (not assembled) at the outset of the reaction; 2) gold seed particles must be present at the outset of the reaction; and 3) gold particles and peptides assemble together in a simultaneous fashion. The differences between our methodology and conventional template-based nanoparticle assembly methodologies will be highlighted, and the aspects of our methodology that allow one to design and prepare exquisitely complex and incredibly well-ordered nanoparticle superstructures will be discussed.

COLL 264

Microwave-assisted isomerization of terminal alkenes catalyzed by alkanethiolate-capped Pd nanoparticles

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This study presents the isomerization of a variety of alkenes utilizing dodecanethiolate-capped Pd nanoparticles employing a microwave reactor. Sodium borohyride is selected as a source of hydrogen gas. The results indicate that microwave energy in conjunction with low heat provides an effective means for the isomerization in terms of yield, specificity, and reaction time. In the case of 3-methylpent-1-ene, a reaction time of 10 min with the temperature at 40 °C yields ~95% conversion to 3-methylpent-2-ene. The reactions of 1-pentene and 1-octene also results in similar rates of conversion and specificity. For isoprenol, a reaction time of 10 minutes with the temperature at 50 °C yields ~46% conversion to prenol. This is more efficient than the presently known

isomerization of isoprenol, which takes 100 hours of reaction time at temperature of 60-100 °C to produce a 61% yield.

This study shows in general that Pd nanoparticles with high organic percentages and smaller core diameters display higher catalytic efficiencies. Furthermore, the characterization of Pd nanoparticles by transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and ^{1}H NMR prior to and after the reaction is done to study the effect of microwave irradiation on the overall stability of nanoparticle catalysts. Visual clues and the resulting yields suggest that the nanoparticles tend to aggregate and become less effective as catalysts with higher temperature.

COLL 265

Oriented fluorophore luminescent solar concentrators

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Luminescent solar concentrators (LSCs) use fluorescent waveguides to collect sunlight over a relatively large area, concentrating it onto a small area of high efficiency photovoltaic cells. Compared to mirror- and lens-based concentrators, LSCs have higher theoretical concentration factors, can collect both diffuse and specular sunlight without the need for solar tracking, and deliver bandgap-matched photons. However device efficiencies reported to date have been too low for practical applications, primarily as a result of self-absorption and escape-cone losses. This poster reports progress toward the development of LSCs based on oriented fluorophores – a strategy to reduce escape losses by preferentially confining emission to the plane of the device. Results are presented from prototype devices incorporating fluorescent dye cascades covering the visible spectrum with an oriented terminal red fluorophore, along with a detailed statistical model of photon transport which rigorously accounts for photon polarization.

COLL 266

Organic-vapor-liquid-solid deposition of organic semiconductor films with an impinging jet

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A method for rapid, mass-efficient deposition of highly crystalline organic films under near ambient conditions of pressure and temperature is reported based on delivery of an organic precursor via an impinging gas jet to a substrate coated by a thin liquid solvent layer. Films of several organic semiconductors were deposited by sublimation into a flow of carrier gas directed at substrates coated by a solvent, and growth kinetics were followed *in situ* with optical microscopy. A fluid dynamics model is applied to account for the gas phase transport and aggregation, and the results compared to experiment. The combination of gas jet delivery with an organic-vapor-liquid-solid growth mechanism leads to larger crystals and lower nucleation densities than on bare surfaces, with markedly different nucleation and growth kinetics. An explanation based on enhanced solution-phase diffusivity and a larger critical nucleus size in the liquid layer is proposed to account for the differences.

COLL 267

Surface modification of polypyrrole and poly(3,4-ethylenedioxythiophene) films for sensing and control of bio-adhesion

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Some electronically conducting polymers undergo a reaction with thiols that results in covalent attachment to the polymer backbone. In the cases of polypyrrole and poly(3,4-ethylenedioxythiophene), this reaction irreversibly reduces the polymers, but can have a dramatic effect on the surface properties. For example, fluorinated thiols can dramatically increase the water contact angle of the films to the point where they become nearly superhydrophobic. Control over the location (through patterning) and extent of reaction (though exposure time) limits the loss of film electroactivity, but this is challenging with volatile thiols. Careful control of reaction parameters can influence the rate of reaction and provides some insights into the reaction mechanism. The reaction may be used to attach “molecular devices” to the film surfaces or to influence the adsorption of proteins or the adhesion of cells.

COLL 268

Understanding nanosilver bioperformance: The chemical transformation of nanosilver in biological systems

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Colloidal nanosilver is manufactured at high volume for incorporation into consumer and medical products as an antimicrobial agent. Under physiological conditions, silver can undergo complex chemical transformations that determine the performance and safety of nanosilver products. Here we present a systematic study of nanosilver biotransformation under well-defined conditions. We focus on the chemical aspects of transformation pathways, including oxidative dissolution, Ag^+ precipitation and complexation, reaction with sulfur and selenium, and UV photoreduction. In vitro experiments are designed under simplified but biologically relevant chemical conditions to investigate the effect of thiol compounds, ascorbic acid, and chloride. Finally, nanosilver its biotransformation will be studied using a reconstructed skin model.

COLL 269

Determining α-synuclein conformation on gold nanoparticles

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Gold nanoparticles (Au NPs) are known to be able to act as a platform for the adsorption of proteins. This adsorption of proteins onto Au NPs was also shown to be dynamic with a constant exchange of proteins between the hard and soft corona. This non-random adsorption signifies that the resultant protein conformation might have changed, which can have severe effects on the functioning of proteins. However, limited information and methods exist for probing and understanding protein folding on NPs due to its complexity. Using a controlled protease digestion method, we show that the conformation of α-synuclein bound to Au NPs can be deduced. We also show results of the possible influence of Au NPs sizes on α-synuclein conformation. This of important significance for the use of Au NPs in therapeutics as the knowledge learnt allows us to control and even fine tune α-synuclein binding and hence its possible regulation.

COLL 270

Molecular origins of surfactant-mediated stabilization of protein drugs

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Loss of activity through aggregation and surface-induced denaturation is a significant problem in the production, formulation and administration of therapeutic proteins. Surfactants are commonly used to stabilize proteins against aggregation and adsorption loss to minimize these detrimental effects and associated costs. However, the effectiveness of a surfactant strongly depends on its mechanism(s) of action as well as properties of the protein and interfaces present. We have suggested a mechanism for protein-mediated rate of surfactant adsorption that can be used to quantify parameters governing surfactant-protein interactions and surfactant action at interfaces. The kinetics of surface tension depression were recorded for selected surfactants (poloxamer 188, polysorbates 20 and 80) in the presence of lysozyme at different surfactant concentrations and temperatures, and analyzed with reference to that mechanism. Quantifying protein effects on surfactant action at the air-water interface in this way will provide information useful for defining a desired mode of surfactant stabilization.

COLL 271

Transition between emergent collective behaviors of nanomotors triggered by equilibrium shift

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Emergent behaviors based on self-organizing process is widely observed in many living systems. Here we report a silver orthophosphate microparticle system showing such emergent behavior in aqueous medium. Transition between two behavioral patterns, namely “exclusion” and “schooling”, is triggered by the shift of chemical equilibrium in response to different stimuli. The transition can be explained by a self-diffusiophoretic mechanism. The reported system is an initial step in designing artificial “intelligent” synthetic micro- or nanomachines that can communicate and work collectively in response to external stimuli. It is among the few examples of nanomotors that are based on reversible non-redox reactions, and demonstrates new design principles for nanomotor systems.

COLL 272

Direct evidences and structural characterizations of the thread assembly formed by nonamphiphilic lyotropic liquid crystals

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The assembly structure of nonamphiphilic lyotropic liquid crystals (chromonic LC) is intriguing because mesogens require nonmaphiphilic structures, yet self-assemble in water. Here, we report the use of NMR spectroscopy to characterize the molecular conformation of nonamphiphilic molecule disodium cromoglycate (5'DSCG), when it exits mainly as monomers, and also the intermolecular distances between specific protons, when 5'DSCG exists as oligomers and polymers in water. NOESY study revealed the molecular conformation of 5'DSCG to be a bent structure at low

concentration. Long range NOE of 5'DSCG supported thread model and eliminated stacking model. This work showed the details of the self-assembly of nonamphiphlic molecules that are known for nearly 5000 years.

COLL 273

Development of electrochemical materials for conducting materials

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The development of electro-chemical materials is indispensable for the advancement of electronic equipment. The chemistry of flux for electronic equipments will be discussed.

COLL 274

Synthesis and multilayering of novel pseudo-polyelectrolytes into thin films

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Strong (SPE) and weak polyelectrolytes (WPE) have been well documented in the realm of multilayering. However, multilayering with a pseudo-polyelectrolyte (pPE) is a fairly recent branch of these systems. To date, only two known pPE that have been multilayered. We have been able introduce another pPE, into this promising field; poly(4-vinylbenzeneboronic acid) (PVBBA). In addition, a fourth pPE, poly(4-vinylperbenzoic acid) (PVPBA), is being examined. As previously reported, for pPE's only a very narrow range of assembly pH's is accessible. A linear growth in absorbance readings was observed for these multilayered systems of PVBBA at pH's 11, 11.5, and 12. In addition, we have investigated the WPE, poly(4-vinylbenzoic acid) (PVBA). Multilayered systems for PVBA were produced at pHs 6, 7, 8, 9, 10, and 11. This latter system will help us understand multilayered films created with PVPBA, in which the systems have the potential of producing a strongly antimicrobial surface.

COLL 275

Synthesis and transformation of gold-silver composite nanoparticles

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We report the highly simple synthetic strategy to prepare solid silver-core gold-shell nanoparticles possessing tunable absorption properties. The diameters of the cores and thickness of the shells are easily controlled by the molar ratio of silver to gold salt solutions at room temperature. These nanoparticles exhibit broad, strong absorbance from visible to near infrared. Subsequently, the systematic transformation of the core-shell particles to anisotropic structures is achieved under visible light irradiation. The resulting anisotropic nanoparticles exhibit a higher surface area to volume ratio, and much strong and broader absorption band as a function of the roughness. The tunable, strong absorption band and high surface area of these anisotropic nanoparticles may be beneficial for potential applications including catalytic reactions, optical devices, and photothermal systems.

COLL 276

Chiral permselectivity in nanoporous colloidal nanofrits surface-modified with chiral moieties

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Robust free-standing membranes (nanofrits) composed of silica spheres of diameter 350nm are covalently surface-modified with the goal of achieving chiral-selective transport within the nanopores. Surface modifiers are carefully chosen on the basis of their capability to provide a difference in non-covalent binding energy (e.g. H-bonding, van der Waals interactions) with each diffusing enantiomer and/or by an enantiomer's preferential inclusion into a cavity (e.g. chiral calixarenes). Flux plots of pure enantiomers of a chiral probe molecule are studied and compared as the functionality of the selectand moieties is varied. To enhance the number of chiral recognition sites per unit surface area, polymer brushes of the small molecule modifiers are grown via ATRP from a surface-bound initiator. The transport properties are likewise investigated as a function of both polymer identity and brush length (controlled by varying the polymerization time).

COLL 277

Light-enhanced catalytic activities of various gold nanoparticles

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Various gold nanoparticles possessing tunable absorption bands in visible range were prepared and used in reduction and coupling reactions under light irradiation. Since gold nanoparticles have shown an ability to absorb light energy and convert it into heat, the irradiation of these gold nanoparticles with solar light can raise temperature of reaction media without any electrical thermal input. We have evaluated the photothermal heating efficiency of water in the presence of various gold nanoparticles upon light irradiation.

Subsequently, these nanoparticles are employed in the chemical reactions in the presence and absence of light irradiation to examine their catalytic efficiency as a function of absorption property. In general, light irradiation enhances the reaction rate and yield in the presence of gold nanoparticles due to the higher photon-to-heat conversion property.

COLL 278

Improving the corrosion resistance of buried steel by using Polyaniline coats

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The work investigates improving the corrosion resistance of buried steel rods by coating it with polyaniline (PANi). Buried steel has many industrial applications especially in petroleum oil transportation between countries construction of large metallic buildings, bridges, tanks, pipelines, etc. Compared to metallic coats PANI is not only environmentally friendly but also it is less expensive. The galvanostatic technique was used in forming the PANi layer. The formed PANi layer was investigated for its corrosion resistance while couples with stainless steel cathode and buried in sand containing known amounts of moisture, NaCl and sulphuric acid (H_2SO_4) using the potentiodynamic examination test. In addition investigation for the characteristics of the formed layer using X-ray Photoelectron Spectroscopy (XPS) and Ellipsometric analysis was carried out. The results show that coating steel with PANi layer can improve its corrosion resistance against NaCl, H_2SO_4 and water by a factor up to 1.88, 1.89 and 1.56 respectively.

COLL 279

Selective sulfuration at the corner sites of a silver nanocrystal and its use in stabilization of the shape

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We developed a new approach to site-selective sulfuration at the corner sites of Ag nanocrystals including triangular nanoplates and nanocubes. The reaction simply involved mixing an aqueous suspension of the Ag nanocrystals with an aqueous solution of polysulfide at room temperature. As a precursor to elemental S, polysulfide is highly soluble in water and can directly react with elemental Ag upon contact to generate Ag_2S in the absence of oxygen. The reaction was easily initiated at the corner sites and then pushed toward the center. By controlling the reaction time and/or the amount of polysulfide added, the reaction could be confined to the corner sites only,

generating Ag-Ag_2S hybrid nanocrystals with greatly improved stability against aging at 80 and 100 °C in air than their counterparts made of pure Ag.

Figure 1. Ag-Ag_2S triangular hybrid nanoplate.

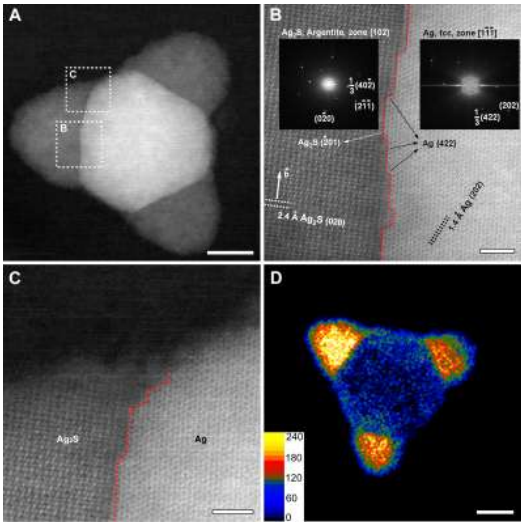
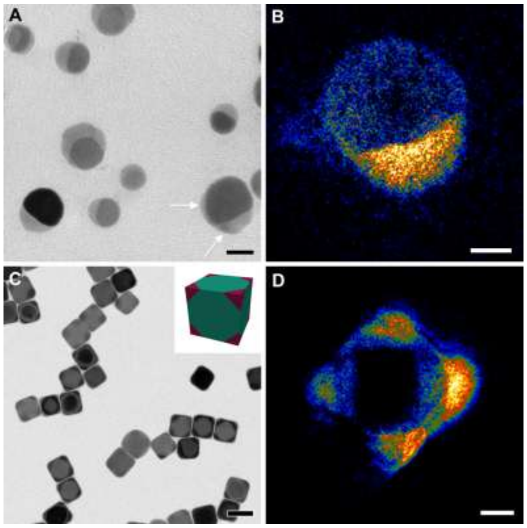


Figure 2. Sulfuration of Ag circular disks lacking sharp corners and Ag nanocubes with sharp corners.



COLL 280

Nanoparticle superlattices: Self-assembly and molecular filtration

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We perform combined experimental and theoretical studies of self-assembled coloidal nanoparticles. First, we explore the transport of small molecules acrosee membranes formed by 5 nm diameter Au nanoparticles ligated with dodecanethiol [1]. We show that molecules with cross-sections smaller than 2 nm can pass through the membranes, but their rejection rate depends on the net molecular charge. Using atomistic molecular dynamics simulations, we show that the molecular passage is related to the presence of nm-sized pores formed between nanoparticles due to fluctations of their parameters. Second, we study microscopic self-assembly principles of regular and truncated Pt nanocubes ligated with octylamine, which are observed to form sc and fcc superlattices, respectively [2]. Our simulations show that charge polarization of the ligated Pt core could lead to Coulombic attraction between the corners of truncated nanocubes.

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[2] Chan, H.; Demorti, A.; Vukovic, L.; Kral, P.; Petit, C. (in preparation)

COLL 281

2D oriented attachment growth of silver nanoplates

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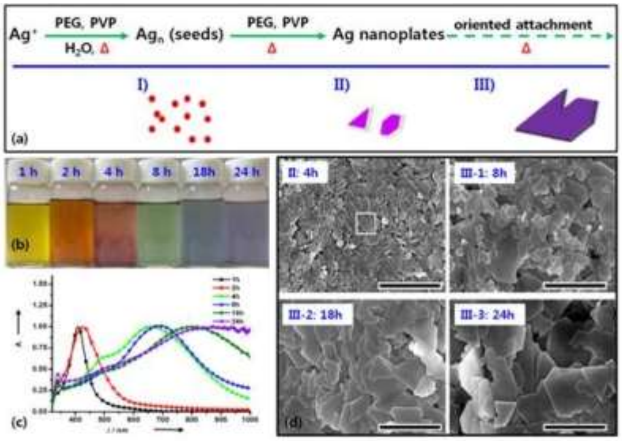
Ag nanoplates have received intensive attention due to their potential applications in molecular detection, optoelectronics and sensing etc. At present, many methods have been available for generating Ag nanoplate with different sizes and shapes. Such methods and modified versions thereof, usually involved the use of citrate as a capping agent, which can selectively bind to {111} facets maintaining a plate-like shape, or the use of weak reducing agents to achieve kinetic control for generating a planar structure. Here we reported a novel 2D oriented attachment growth of Ag nanoplates using polyethylene glycol (PEG) as a solvent as well as a reducing agent, in the presence of PVP. In our modified polyol method, the nucleation and seed stage occurred in the aqueous solution, and the 2D oriented attachment growth stage occurred in the PEG environment through evaporation of water.



COLL 282

Haze control of the Ag nanowire-based transparent electrode film

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Recently, Ag nanowires are under intense research interest because they can be a strong candidate material for next generation flexible transparent electrode replacing indium thin oxide (ITO) thin film electrodes. Ag nanowire based transparent electrode film exhibit excellent electrical and optical properties (<150 Ω/□ at >90% transmittance). In addition, Ag nanowire based transparent electrode film can be produced by simple roll coating process and their flexibility exceeds ITO based transparent films. However, the haze issues associated with the reflection from metallic Ag nanowire surface has been one of the remaining issues for commercial success.

In this presentation, we report a study on the haze properties of Ag nanowire transparent electrode films with respect to the nanowire width, length, the assembly structure and the addition of surfactants.

COLL 283

Highly conductive flexible transparent electrode using silver nanowires and conducting polymer

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As displays become larger and solar cells become cheaper, there is an increasing need for low-cost transparent electrodes. Intensive effort has been made to replace ITO (Indium Tin Oxide) based transparent electrode with cheap and flexible ones. Among those, silver nanowires have got limelight because of its great conductivity and flexibility.

Even though the electric property of the Ag nanowire based transparent electrode surpassed ITO, the optical property needs to be improved (lower transmittance, higher haze). Here, we reported transparent electrode based on Ag nanowires and conducting polymer to improve optical properties. The Ag nanowires are coated onto PET films and the resulting transparent electrode film shows 200 ohm/□ resistance and > 90% optical transmittance.

COLL 284

Site specific deposition of Ag on the corners of Pt cube

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Novel heterostructured nanoparticle was synthesized by the deposition of Ag on Pt cube by overcoming lattice mismatch, where Ag deposition preferentially occurred at corners of Pt cube. HRTEM image and EDX line-scan profiles on a single Pt cube with Ag deposits confirm the preferential deposition of Ag at corners of Pt cube. The mechanism of such site specific deposition of Ag was discussed in relation to I^- (shape forming agent) and succinate (organic protective agent). Negative circumstance formed by I^- and succinate accumulate Ag^+ around Pt seeds. Accumulated Ag^+ adsorb on Pt{111} of truncated cube because Pt{100} is preoccupied by I^- and succinate resulting in site specific deposition of Ag on corners of Pt cube. Such controlled deposition of second component on shape-regulated core will lead to unique physical and chemical properties not realized so far; e.g., masking or creating active sites at the corner as a catalyst model.

COLL 285

Chiral nematic phase of nonamphiphilic lyotropic liquid crystals

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Unlike conventional colloidal science that large relies on hydrophobic-hydrophilic separation of amphiphilic molecules, the molecular interactions are not clear for how certain nonamphiphilic molecules can form assembly and unusual liquid crystals in water. Here, we present the synthesis of three stereoisomers, and the study of the structure-assembly correlation. We discovered that the enantiomers 5'DSCG-(*R,R*)-diviol and 5'DSCG-(*S,S*)-diviol formed liquid cystals while the achiral 5'DSCG-*meso*-diviol did not. Conformation of each stereoisomer in monomer form and in assemblies was characterized by multi-dimensional NMR. Cryogenic transmission electron microscopy revealed a more flexible assembly formed by chiral 5'DSCG-diviol than by 5'DSCG. This study demonstrates that the nonamphiphilic colloidal science is governed by complex molecular interactions with a similar sophistication as those observed in polymorphism. We will also discuss the use of this new knowledge to enable the fabrication of new soft materials.

COLL 286

Imprinted nonporous silica nanoparticles for saccharide adsorption without diffusion resistance

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The synthesis of submicron silica particles by precipitation in ammonia-containing aqueous ethanol solutions (the Stöber process) was first reported nearly four decades ago. The resulting particles (“Stöber particles”) are nonporous and their ease of synthesis has led to many promising applications. Here we report the synthesis of Stöber particles in the presence of a glucose-based surfactant (n-octyl-β-D-glucopyranoside, C8G1) with the goal imprinting the surface with adsorption sites selective towards glucose. Various ratios of C8G1 and cetyltrimethylammonium bromide (CTAB) are used to identify the ratio giving the best conditions for enhanced glucose binding. The effectiveness of imprinting is also investigated as a function of the time of surfactant addition. The synthesized particles are characterized using nitrogen adsorption and SEM. The adsorption of glucose and xylose on these particles is measured and compared using depletion measurements from aqueous solutions analyzed by ATR-FTIR and HPLC.

COLL 287

Self-orientation of anisotropic inorganic nanoparticles arrested within a polymer film

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The spatial distribution and organization of nanoparticles (NPs) within polymer films are important parameters to control in the fabrication of functional nanocomposites. We demonstrate that anisotropic NPs within a polymer film are capable of self-assembly into superstructures that possess well-defined interparticle orientations. We synthesized cube-shaped nanoparticles grafted with hydrophilic polymers. When introduced into a hydrophobic polymer matrix, these nanocubes behave as a single fluid phase and undergo phase segregation in the spinodal regime, forming to form periodic NP domains. Interparticle orientation within these domains can be predicted by free energy calculations and tuned through parameters such as grafted polymer chain length. We have also observed that other anisotropic NP shapes exhibit similar phase segregation behavior, but adopt different orientations.

COLL 288

Systematic study of silver nanoplates: Synthesis, characterization, and stabilization

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In this presentation, we have carried out systematic studies on the synthesis and stabilization of silver nanoplates. By harnessing the oxidative power of H2O2, various silver sources including silver salts and metallic silver can be directly converted to nanoplates with the assistance of an appropriate capping ligand, thus significantly enhancing the reproducibility of the synthesis. Contrary to the previous conclusion that citrate is the key component, we have determined that the group of ligands with selective adhesion to Ag (111) facets can be expanded to many di- and tri-carboxylate compounds whose two nearest carboxylate groups are separated by two or three carbon atoms. The improved insight into the specific roles of the reaction components and significantly enhanced reproducibility are expected to help elucidate the formation mechanism of this interesting nanostructure.

COLL 289

Surface structure and depth profile study of pyrite thin films grown by MOCVD

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Iron pyrite (FeS_2) is a promising earthabundant semiconductor for thin film solar cells because of its exceptional optical absorption coefficient and suitable band gap. However, recent studies suggest surface defects, impurities, and mixed phases of FeS_2 may cause a photovoltage reduction. Utilizing tunable-energy synchrotron x-ray photoemission, absorption, and valence photoemission spectroscopies, we explore the surface and electronic structures of pyrite thin films grown by metal organic chemical vapor deposition (MOCVD). We also resolve different types of sulfur chemical states and elemental composition depth profiles on the surface of substrate-dependent pyrite thin films. Additionally, we study the in situ oxidation process under different oxidizing environments by Ambient Pressure Photoemission Spectroscopy. Our results suggest that the surface monosulfide species is oxidized first, and the reduction in the total density of states near the Fermi surface is caused by oxide layers.

COLL 290

pH influence of reactive poly(ethyleneimine) (BPEI) for decontamination of chemical warfare agent (CWA)

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The aim of this research is to develop a self-decontaminating polymeric system capable of providing comprehensive protection against chemical attack. Our approach consists of imbibing reactive poly(ethyleneimine) (PEI) into the desired fabric that decontaminates all classes of chemical agents (G, V, and H). Branched poly(ethylenimine) (BPEI), containing primary, secondary and tertiary amine groups, is a very reactive chemical species in decontaminating chemical warfare agents (CWAs) and provides an efficient platform for destroying chemical threat agents.

BPEI is responsible for the nucleophilic degradation of the organophosphate group of nerve agent simulant, Methyl Paraoxon (MPO). However, depending on the micro-local environment of the BPEI, it can generate more or less reactive sites for decontamination. Formation of ammonium salt, using hydrochloric acid (HCl) causes unavailability of some amines and thereby varies the availability of the reactive amine groups. The correlation of structures vs. reactivity against MPO will be discussed in more detail.

COLL 291

Immobilization of bovine serum albumin in spherical poly(acrylic acid) brushes as observed by small angle X-ray scattering

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Nano-sized spherical poly(acrylic acid) brushes (SPB) with polystyrene core were synthesized by photo-emulstion polymerization. Bovine serum albumins (BSA) were immobilized into SPB due to electrostatic interactions in buffer solution, which can be determined by UV spectrum and observed by small angle X-ray scattering (SAXS). Upon increasing the ionic strength or pH value, the adsorbed amount of BSA in SPB reduced accompanying with the shrink of SPB.

COLL 292

Synthesis of praseodymium-doped zircon pigment by a two-step method and its application in ceramic inks

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A two-step method to prepare novel yellow praseodymium-doped zircon pigments was reported. In the first step, nano-sized intermediate powders were synthesized by hydrothermal process. In the second step, nano-scaled yellow praseodymium-doped zircon pigments were prepared by treating the intermediate at high temperature. The obtained pigments were characterized by XRD, TEM, SEM, reflectance and the CIE L*a*b* parameters. The hydration temperature, precursor's pH value and the calcination temperature have a significant impact on the composition, crystalline, morphology and CIE L*a*b* parameters of the products. Ceramic inks with high performance were prepared based on the obtained pigments with organic solvents and surfactants by ball-mill method.

COLL 293

Synthesis of nanocomposites with percolated microporous networks using organic sol-gel methods

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Nanocomposites with percolated microporous networks were synthesized that are potentially applicable in molecular transport membrane. Nanoparticles were synthesized from tetrakis(4-aminophenyl)methane and hexamethylene diisocyanate by organic sol-gel polymerization to produce the 3D microporous organic molecular network. The nanoparticles dispersions were mixed with poly(amic acid) using various dianhydrides and diamines. Casting onto the glass plate followed by thermal curing gave nanocomposite film. We investigated on the morphological structures subjected to different reaction time and composition of nanoparticles. Continuous interconnected nanostructures in polymer matrix were prepared by controlling spinodal decomposition and reaction between numerous reactive amino and isocyanato functional groups of nanoparticles and polyimide chains. The microporosity of synthesized nanocomposite was characterized by carbon dioxide isotherm at 273K and their permeability of the membranes to small molecules such as water, carbon dioxide, and nitrogen was also measured.

COLL 294

Molecular sieving by ultrathin membranes of organic molecular nets

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A new solution-based molecular layer deposition (MLD) method was studied. Alternating deposition of tetra-functional, tetrahedral molecules gave nanometer thick films of three-dimensionally cross-linked organic molecular networks. Varying the number of deposition cycles enabled to control the film thickness precisely on the molecular level. MLD was conducted on a nanoporous alumina support to fabricate molecular nets as an ultrathin skin layer of thin film composite (TFC) membrane. The morphology of the films was studied using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The flux and rejection of the TFC membrane was investigated by filtration of the aqueous solutions containing organic solutes. Ultimately, a molecular sieving membrane was demonstrated using the molecular nets. This work was supported by a Korea Science and Engineering Foundation (KOSEF) grant [2010-0026421] funded by the Korean government (MEST) and the Program for Integrated Molecular Systems (PIMS) at GIST.

COLL 295

Impact of the alkyl chain carbon atom number of uronic acid-derivative surfactants on interfacial and colloidal systems

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Uronic acid-derivative surfactants represent today an attractive group of Carbohydrate-based amphiphilic compounds for both fundamental and practical reasons [1,2]. In the continuity of our screening of their basic properties, and the approach in establishing relationships between their structure and properties [3,4], the impact of the alkyl chain carbon atom number on interfacial and colloidal systems has been systematically investigated. In this communication, the effect of odd-even number of carbon atom from C11 to C18, and the particular behavior of long chain derivatives on interfacial properties, as well as their impact on the formation and stability of colloidal systems, are presented. Experimental approaches have been conducted by investigating their

properties and behaviors at gas-liquid and liquid-liquid under dynamic, equilibrium, and oscillatory interfacial conditions. Results are completed by and discussed with single molecule models established by theoretical approaches.

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COLL 296

Thermodynamic, kinetic, and structural study of the adsorption of bovine serum albumin to the surface of gold nanoparticles

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Gold nanoparticles have attractive optical properties, and can be used in various biomedical applications, such as biomedical imaging and cancer treatment. Due to the high surface to volume ratio of the nanoparticles, protein adsorption in biological media is expected, forming a new interface known as the “protein corona”. Furthermore, protein adsorption to the nanoparticles could result in protein structural/functional changes due to possible unfolding or misfolding on the nanoscale surface. In this study, we investigate the interaction of a model protein, bovine serum albumin to gold nanoparticle surfaces as a function of particle size, shape, and surface charge using different analytical techniques such as UV-absorption, fluorescence quenching, and calorimetry. Our results show strong association constants between proteins and nanoparticles, which are dependent on charge and particle curvature. The

thermodynamic and kinetic results from these studies will provide a better understanding of the interaction of nanoparticles with proteins in biological media.

COLL 297

Role of Raman reporter molecular surface coverage and distance dependent plasmonic effects on SERS in polyelectrolyte coated gold nanorods

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Substrates and probes for use in SERS, (surface enhanced Raman spectroscopy), can benefit from optimum design based on both physical models and controlled systematic experimentation. Many factors play into the objective of obtaining maximum enhancement. Excitation within the visible spectrum induces electromagnetic fields in noble metal nanoparticles making them ideal candidates for such studies. We compare the SERS signal intensity of Raman reporter molecules attached to polyelectrolyte coated gold nanorods. Experimental results coincide with theoretical predictions of dramatic decrease in signal intensity with increasing nanometer distances from the nanorods surface.

COLL 298

Hydrodeoxygenation of furan and guaiacol over noble metal phosphide catalysts

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Silica-supported noble metal phosphide catalysts (e.g. Ru_2P, RuP, Rh_2P) were prepared, characterized by XRD, TEM and chemisorption, and their properties for furan and guaiacol hydrodeoxygenation (HDO) were investigated. The HDO properties were compared with those of reduced noble metal catalysts having the same loading. The furan HDO activity was observed to depend strongly on the P/Ru molar ratio of the catalyst precursors, with the maximum furan HDO activity observed for a Ru_2P/SiO_2 catalyst prepared from a precursor having P/Ru = 0.86. The furan HDO product selectivities of the metal phosphide (e.g. Ru_2P/SiO_2) and reduced metal catalysts (e.g. Ru/SiO_2) differed significantly. Preliminary guaiacol HDO activity and product selectivity

data will also be presented. The observed trends in HDO activity, selectivity and resistance to poisoning of the noble metal phosphide catalysts will be discussed.

COLL 299

SERS-based detection of glucose using a boronic-acid containing Raman probe

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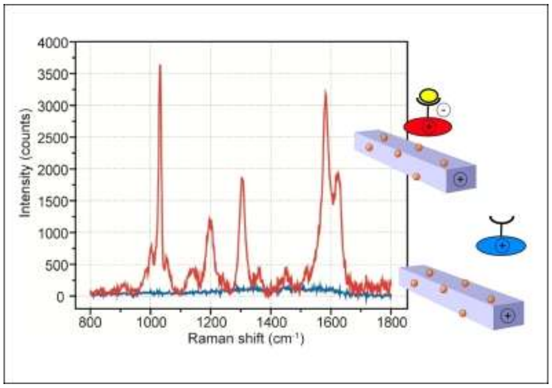
Surface-enhanced Raman spectroscopy (SERS) offers a way to capitalize on new nanomaterials for sensing applications. Here we present a glucose-binding Raman probe in conjunction with two SERS substrates: silver nanoparticles, and zinc-oxide nanowires decorated with gold nanoparticles. In each case, a glucose-dependent enhancement of the Raman signal is seen at physiological pH. The results are consistent with an electrostatically controlled interaction between probe and substrate.



COLL 300

Effect of shape and surface chemistry on gold nanorod transport in residential and agricultural soil columns

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The increasing prevalence of functionalized nanomaterials in a variety of applications will inevitably lead to an increase in nanomaterial soil and groundwater contamination. It has been shown that the size, shape, and surface chemistry of functionalized NPs strongly influence their interactions with biological and environmental systems, however, the influence of these properties on NP fate and transport in soil is not well-understood. Gold nanoparticles are excellent model probes to assess the behavior of NPs in soils, because their size, shape, and surface chemistry can be exquisitely controlled, and their progress through soils can be closely monitored. We prepared gold nanorods with different aspect ratios and surface chemistries using a poly-electrolyte layer-by-layer coating strategy, and investigated how their properties influences their rate of transport through soil. We found that AuNRs with positive surface charge were strongly retained by soil, while negatively-charged AuNRs were quickly eluted from the soil columns.

COLL 301

Examination of strategies for silica-coated gold nanorods and the effect of silica shell quality and thickness on SERS response

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Silica-coated gold nanoparticles have become an increasingly important research interest due to their tunable surface chemistry, size, and morphology, as well as their high biocompatibility, optical transparency, and controlled porosity. These silica-coated metal nanoparticles are ideal candidates for many applications, especially surface enhanced Raman scattering (SERS) spectroscopy. Coating gold nanorods with a thin, homogenous, and optically transparent silica shell should ensure a large surface enhancement while permitting no direct contact with the gold core and the analyte. A variety of established silica coating strategies are examined, and the quality of the silica shell on the nanorods is determined with respect to uniformity, thickness, and SERS response.

COLL 302

YSA-conjugated gold nanorods as anticancer therapeutics: Rate of cellular uptake and photothermal treatment

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Gold nanorods (AuNRs) have been shown to be strong candidates for non-invasive photothermal cancer therapies by virtue of their tunable optical properties and size. Absorption of near-IR light by AuNRs induces heat emission that can be harnessed to destroy developing tumor cells, if the cancerous cells can be selectively targeted. Studies have found that EphA2 receptors are over-expressed in various tumorigenic cells. In addition, a variety of EphA2-specific antibodies and derivatives can be prepared, one of which, YSA, has been shown to successfully target cancer cells. We

have prepared YSA-functionalized gold nanorods that can successfully be deployed *in vitro* as anti-cancer therapeutics against prostate cancer cells (PC-3). We show that incubation of the functionalized AuNRs in PC-3 cell cultures can induce cellular retraction, and that the functionalized AuNRs are effective photothermal agents against PC-3 cells. The rate and mechanism of the cellular uptake of YSA-functionalized AuNRs are also investigated.

COLL 303

Molecular photovoltaic system based on fullerenes and carotenoids co-assembled in lipid/alkanethiol hybrid bilayers

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A new molecular photovoltaic system based on fullerene and lutein (a natural carotenoid species) co-assembled in self-assembled hybrid bilayers of alkanethiols and phospholipids on gold electrode is reported. First, a self-assembled monolayers (SAM) of alkanethiol is formed on gold, and then, liposomes containing photoactive fullerenes and lutein are incubated on top of SAM to form hybrid bilayer membranes (HBMs). Either anodic or cathodic photocurrent generation can be obtained with this system, when ascorbate (anodic) or methyl violgen/oxygen (cathodic) is used as a sacrificial electron donor/acceptor respectively. More importantly, at loadings of 1-3 mol %, the photoinduced electron transfer between lutein and fullerene can effectively compete with the fast relaxation of excited lutein, resulting in a significant modulation of the photocurrents generated by the co-assembled fullerenes; whereas, the system containing lutein alone is found to be inefficient in generating photocurrent.

COLL 304

Preparation of degradable silsesquioxane nanoparticles

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Since silica nanoparticles have low toxicity and are easily modified with other active ligands, they are widely studied in the fields of drug delivery and imaging. In vivo studies show that the solid silica nanoparticles accumulate in many organs due to the lack of degradability, which potentially threatens health. Our work will address this shortcoming by producing degradable silica nanoparticles via the incorporation of organic groups. A bridged silsesquioxane is used as the precursor of the particles and upon cleavage of the carbamate groups in the acid condition, the spherical structure collapses and releases non-toxic sugar. The fundamental study of the structure and properties of the bridge silsesquioxane nanoparticles also helps us to learn more about the mechanism of the formation of hybrid silica nanoparticles.

COLL 305

Effect of nanofiber seeding in classical polymerization systems

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The nanofiber seeding method is typically used to synthesize bulk quantities of conducting polyemr nanofibers. When extended to classical polymerization systems, e.g., free radical polymerization of styrene, methymethacrylate, and anionic polymerication of cyanoacrylates, nanofiber seeding yields unexpected results. There is a dramatic change in bulk nanostructure morphology (size, shape, polydispersity, etc.) in these systems that is fundamentally different form what is observed with conducting polymer systems. A new seeding mechanism based on a pearl and necklace model is presented to account for the experimental results.

COLL 306

Encapsulation of staurosporine using a novel intraliposomal stabilization strategy: Therapeutic efficacy in glioma

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The objective of the present study was to address this limitation with a highly potent antitumor agent whose clinical use is presently not possible, but which could be made feasible if the compound were to be successfully delivered by liposomes. Liposome-based delivery systems have been used to enhance drug efficacy and reduce toxicity. The most successful systems have been engineered for long circulation times and stable liposomal encapsulation of the active drug. We successfully encapsulated staurosporine into PEG liposomes using a novel gradient method. Our confirmatory tests showed high encapsulation efficiency and a favorable drug release profile and serum stability. We also showed the favorable clinical potential of liposomal staurosporine in terms of anti-tumor potency with different glioblastoma cell lines in culture, radiation sensitization of glioblastoma lines, and anti-glioblastoma effects using an *in vivo* subcutaneous mouse model. This method can be used for encapsulation of different classes of drugs.

COLL 307

Lifting the covers on the subsurface

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The role of subsurface atomic species in the observed activity of catalytic systems remains unclear. Transition metal surfaces are the heart of many important heterogeneously catalyzed reactions. In addition to reactions between species adsorbed to the metal surface, subsurface atoms emerging from the bulk can react with adsorbates. These emerging species are often non-equilibrium reagents, and exhibit unique chemistry inaccessible to thermalized surface adsorbed reagents. To study subsurface reagents, prototypical systems of subsurface species and surface adsorbed molecules will be imaged with scanning tunneling microscopy (STM) to unequivocally determine reaction mechanisms. The study presented here seeks to elucidate the dynamics of how an atom moves from surface to subsurface sites, and to understand how these species may be harnesses to guide new synthetic approaches. Once a thorough understanding of the behavior of these transient, energetic reagents is achieved, selective synthetic strategies utilizing their chemistry will be possible.

COLL 308

Coverage dependent configurational transformation of phenol on the Ge(100)-2×1 surface

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Organic functionalization of semiconductor surfaces has gained increasing interest due to development of nanoscale devices, especially with bifunctional molecules because of their potential to create versatile multilayers. In this study, the reaction of phenol on the Ge(100)-2×1 surface at room temperature is investigated using multiple internal reflection infrared spectroscopy and density functional theory calculations. Results show that the phenol molecule undergoes OH dissociation on Ge(100) to form a surface phenoxide group. In the IR spectra, each peak is shifted 10-20 cm^{-1} when the surface is exposed to large doses of phenol. These shifts are explained by a transformation from a lying-down configuration where the phenyl ring interacts with a neighboring Ge dimer, to a non-interacting standing-up configuration. DFT results support this interpretation in terms of adsorption energy and IR peak positions. This study provides a fundamental understanding of the reactivity and configurations of organic molecules on the semiconductor surfaces.

COLL 309

Preparation of nanofiltration membranes with nanoparticles of rigid organic network and polysulfone

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Nanoparticles of 3D rigid organic network were synthesized from tetrakis(4-aminophenyl)methane and hexamethylene diisocyanate by organic sol-gel method. The nanoparticle dispersions were blended with aromatic polysulfone in DMF and then the mixture solutions coated onto the glass plate or other substrate surfaces. Upon evaporation of mixture solutions, thin film membranes with various microstructure resulted via interplay between phase separation and sol-gel transition behavior. The morphology of the membranes was studied using scanning electron microscopy(SEM) and atomic force microscopy(AFM). The flux and rejection of porous membrane was investigated by filtration of the aqueous solutions contacting organic solutes. This work was supported by a Korea Science and Engineering Foundation (KOSEF) grant [2010-0026421] funded by the Korean government (MEST) and the Program for Integrated Molecular Systems (PIMS) at GIST.

COLL 310

Heterogeneous and two-phase catalysis by water-soluble palladium nanoparticles generated from Bunte Salts

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In our previous work, the catalysis of the isomerization of allyl alcohols to their analog carbonyl compounds was achieved by using palladium nanoparticle catalysts generated from sodium S-dodecylthiosulfate. In these reactions, allyl alcohols were introduced to the homogeneous palladium nanoparticle solution in chloroform upon the completion of hydrogen conditioning. Although the reactions were very selective and successful, the separation between the palladium nanoparticle catalysts and the volatile products was quite problematic. In this study, palladium nanoparticles were synthesized with Bunte Salts which contained polar functional groups (Bunte Salts of w-hexylcarboxylate, w-undecylcarboxylate, and oligoethylene glycol) in order to increase the solubility of the palladium nanoparticles in aqueous solution. Palladium nanoparticles were characterized by transmission electron microscopy (TEM), thermogravimetric analysis (TGA), ^{1}H NMR, FT-IR and UV-Vis spectroscopy. By changing the solubility of palladium nanoparticles and working the catalytic reactions under the heterogeneous condition, the separation of the products and the palladium nanoparticle catalysts became fairly efficient. In addition, two-phase catalytic reactions were also studied for the effective separation of the palladium nanoparticle catalysts dissolved in aqueous solution from the organic phase containing the products. Catalytic reactions were performed by conditioning 5 mol% palladium nanoparticle catalysts with hydrogen gas in both heterogeneous and two-phase systems.

COLL 311

Interaction of petroleum-based organosulfur compounds with a TiO_2(110) surface

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We have investigated the interaction of several organosulfur compounds with a TiO_2(110) surface using temperature programmed reaction spectroscopy and X-ray photoelectron spectroscopy. Molecules selected for this study include thiols, thiophenes, and their derivatives, many of which are found in natural petroleum sources and prove problematic in current desulfurization processes. By comparing desorption activation energies, we have established trends in relative binding energies which correlate binding strength with Lewis basicity, suggesting that several of the compounds bind to the surface via the lone pair electrons on sulfur. We have also explored the reactivity of these molecules with a highly reduced, ion-bombarded TiO_2 surface. Of the species explored, benzenethiol is found to decompose over the surface, giving rise to the desorption of benzene. These findings provide an important first step towards designing substrates capable of removing sulfur from the larger refractory species found in petroleum.

COLL 312

Detection of organophosphorous pesticides by using heparin-reduced gold nanoparticles

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Heparin-reduced gold nanoparticles were utilized for the detection of organophosphorous pesticides. Heparin is one of glycosaminoglycans with carboxyl and sulfo groups. It plays an important role as a reducing and stabilizing agent for the synthesis of gold nanoparticles. The reaction conditions were optimized, and high resolution-transmission electron microscopic images revealed gold nanoparticles of various shapes. Malathion, fenthion and methidathion in water were detected by simply mixing with heparin-reduced gold nanoparticles. NaCl induced a color change in the mixed solution from wine-red to purple-blue that was solely dependent on the pesticide concentration in the range of 10–1,000 ppb. In order to prepare solid supports for removing pesticides from the contaminated water, heparin-reduced gold nanoparticles were immobilized on a silica gel matrix The incorporation of atomic gold and heparin bound to 2 g of silica gel was determined 4,058 ppm and 33 µg as measured by

inductively coupled plasma–atomic emission spectrometry and carbazole assay, respectively. Fenthion in water was successfully removed by using an AuNPs-immobilized silica gel column.

COLL 313

Green-synthesis of silver nanoparticles by using Leonuri herba extracts and the evaluation of antibacterial activities

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In this report, Leonuri herba extract was used as a reducing agent to synthesize gold and silver nanoparticles. Plant sources, especially leaves and herbs, are valuable for the generation of gold and silver nanoparticles. Various kinds of polyphenols and hydroxyl groups are capable of processing a reduction reaction to generate metals from its corresponding salts. Both 70% ethanol and water extracts were used to synthesize gold and silver nanoparticles without the addition of any other toxic chemicals. The extracts played dual roles as reducing and stabilizing agents. Both oven incubation and autoclaving methods were applied for synthesizing gold and silver nanoparticles and the reaction conditions were optimized. Surface plasmon resonance indicated that the formation of nanoparticles was successful. Images of high resolution-transmission electron microscopy revealed mostly spherical nanoparticles ranging from 9.9 to 13.0 nm in size. A water extract containing silver nanoparticles exhibited significant (approximately 127-fold) enhancement in antibacterial activities against *Pseudomonas aeruginosa*, *Escherichia coli* and *Enterobacter cloacae* when compared with the water extract alone. In addition, antibacterial activity towards gram-negative bacteria was greater than that against gram-positive bacteria. The approach reported here has the possibility to be a new technique to enhance the antibacterial activities of plant extracts.

COLL 314

Non-fouling surface modification via thiol-ene click reaction based on reactive polymers

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How to construct surfaces that can resist non-specific protein adsorption, cell adhesion, and bacterial growth, is an important issue for biotechnology, as well as for the fabrication of cell-based screening devices, diagnostic bioassays, BioMEMS devices, and implant devices. Poly(ethylene glycol) (PEG) or PEG-like molecules have long been reported as promising substances to supress non-specific protein adsorption, or to resist cell adhesion. Thiol-ene click reaction offers numerous advantages, such as chemical robustness, feature of click chemistry, short period of reaction, simplicility to execute, and the high yield without side reactions. In addition, the photoinitiated characteristic of the thiol-ene reaction allows tunable properties for reaction and results in specificity. We herein introduce a surface-initiated thiol-ene click reaction based on reactive polymers that are prepared via chemical vapor deposition (CVD) polymerization. The vinyl-functionalized CVD polymers are used in the study and are coated on a variety of substrates including metal (silver, copper, titamium etc.), silicon, poly(methyl methacrylate), poly(dimenthylsiloxane), poly(tetrafluoroethylene), polystyrene, and stainless steel. Subsequently, thiol terminated PEG molecules are immobilized onto the surfaces through photochemically induced thiol-ene click reaction, and a photomask is used to spatially confine the reaction. The resulting anti-fouling activities are tested against fibronogen adsorption, and finally, the adhesion of murine fibroblasts as well as the growth of Escherichia coli and Staphylococcus aureus on the modified surface are also examined. Surface-initiated thiol-ene reaction based on reactive polymer indeed provide a general, simple route of surface modification for biointerface engineering and may find applications in cell culture studies, tissue engineering, lab-on-a-chip devices, and medical devices.

COLL 315

Investigation of adsorption of lignosulfonates at a solid-liquid interface

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The self-assembly multilayers were fabricated from 0.1 wt% LS and 0.1 mM poly(diallyldimethylammonium chloride) (PDAC), and then were used to be the substrates for the adsorption of LS. Results show that the adsorption of LS is driven by the electrostatic attraction and hydrophobic interaction, which depend on solution pH. With the pH below 3.5, lignosulfonates exist as colloidal particles in the dipping solutions because of strong hydrophobic interaction, and the LS colloids with anionic groups as the outmost layer are adsorbed on the PDAC layer because of electrostatic attraction. With pH further increases, the adsorption rate increases steadily owing to an enhancing of electrostatic attraction, while the amount of adsorption decreases gradually due to a weakening of hydrophobic interaction. Thus, this study has recognized, for the first time, the inflection point of pH, at which the lignosulfonate colloidal particles start to disassociate. This work is helpful for understanding the adsorption characteristics of LS on solid surface at molecular level, and further expanding functionalities of LS through manipulation of the adsorption capacity by changing solution pH value.

COLL 316

Synthesis and characterization of water-soluble gold nanoparticle-cored dendrimers with average core size ranging from 1 to 20 nm

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The development of simple and safe way to detect and cure diseases has been considered as a high priority area in the field of biotechnology and medical research. Our research specifically targets the preparation of stable and biocompatible nanoparticle platform for multifunctional diagnostics and therapeutic agents. This poster describes our attempt to synthesize new nanocarrier platform that is water-soluble gold nanoparticle-cored dendrimers (NCDs) with various average core sizes. It has been known that the utilization of metallic-cored nanoparticles in areas such as bio-labeling and receptor-mediated drug transport are strictly predicated upon the control of size and size distribution. Nanoparticle-cored dendrimers (NCDs) represent the dendrimer materials with a nanoparticle core and well-defined dendron wedges. Our synthetic method is based on a strategy in which the synthesis of monolayer-protected nanoparticles is followed by adding dendrons on functionalized nanoparticles by single coupling reaction. This allows us to couple the dendron wedges onto the surface of the gold nanoparticles while preventing disruption to the gold core. Water-soluble gold nanoparticles with average sizes ranging from 1 to 20 nm, which contain thiolate ligands with reactive COOH functional groups, are synthesized and used as templates for the dendron attachment. The produced gold NCDs are characterized using various instruments including transmission electron microscopy (TEM), FT-IR, ^{1}H NMR, and UV-vis spectroscopy.

COLL 317

Investigation of the dissociation of sulfuric acid aqueous solutions using photoelectron spectroscopy

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The microscopic structure of the surface of aqueous sulfuric acid solutions has great industrial relevance, playing also an important role in atmospheric chemistry. As a

strong acid, the bulk of an aqueous solution of sulfuric acid will have H_3O^+, HSO_4^- and SO_4^{2-} present, and at high concentrations, un-dissociated H_2SO_4 may be present. However, the ion composition at the surface is still not well understood. Using a liquid micro-jet, the surface chemistry of aqueous solutions is explored by x-ray photoelectron spectroscopy (XPS). Experiments were performed at Beamline U41-PGM at the BESSY II synchrotron facility. By suitable choice of the photon energy the energy of the photoelectrons is tuned to either surface or bulk sensitive detection. A series of sulfuric acid aqueous solutions is measured and using the peak areas in the XP spectra, the acid dissociation at the surface relative to the bulk can be determined for different solutions.

COLL 318

Preparation of functionalized immunolabels that permit simultaneous imaging of specific proteins and lipids in membranes with high-resolution secondary ion mass spectrometry

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Local variations in specific membrane lipids are thought to influence the activity of membrane proteins. Recent application of imaging mass spectrometers and isotopic labeling techniques to cells has allowed lipid species to be detected at a resolution in parity with their organization in the cell membrane. The development of membrane protein probes that can be simultaneously imaged with the isotopic labels for lipids would allow definitive measurements of the extent of lipid-protein colocalization. For this purpose, we have synthesized fluorine-functionalized colloidal gold immunolables that enable imaging specific proteins in parallel with lipids in the plasma membrane with high resolution SIMS performed on a NanoSIMS. The fluorine in the monolayer enables NanoSIMS detection, whereas the antibody allows for the selective labeling of specific proteins. With the combination of these immunolabels and the metabolic labeling of lipids, specific membrane proteins and cellular lipids can be imaged parallel using NanoSIMS. This method can be extended to other proteins and lipids and provide high sensitivity and lateral resolution, to investigate other reports of colocalization.

COLL 319

Surface mediated photochemistry: Stability of benzoic acid on TiO_2

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We have investigated the thermal and photo stability of benzoic acid on rutile TiO_2 (110) single crystals. Benzoic acid binds to the TiO_2 surface through the carboxylic acid group, an analog to the binding group in dye-sensitized solar cells. We show that electrospray ionization is an effective technique for introducing benzoic acid to our sufrace in vacuum. Using this deposition technique, we find that benzoic acid is thermally stable on the surface below 650 K and decomposes to release benzene and CO at higher temperatures. We use scanning tunneling microscopy and x-ray photoelectron spectroscopy to show that benzoic acid molecules are photochemically stable under UV irradiation. The comparison between the stability of benzoic acid and the instability of other carboxylic acids on TiO_2 demonstrates the importance of molecular structure in surface mediated photochemical reactions.

COLL 320

Self-assembly of gold nanoparticles in solution and their plasmonic application

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Gold nanoparticles (AuNPs) provide Surface Enhanced Raman Scattering (SERS) effect due to their strong plasmon coupling. When nanoparticles are assembled with narrow interparticle nanogap, the intensity of SERS is drastically enhanced. Though many approaches have been proposed to create gold nanoparticle assembly for high-sensitive Raman sensing on substrate, application for Raman detection in solution is rare. In this study, we present the approach to assembly of AuNPs in solution.

Fluorinated organic compounds were newly synthesized. Fluorinated AuNPs were prepared by surface exchange reaction from citric acid to fluorinated thiol compound in THF.

STEM image and DLS measurement indicated that AuNPs were assembled to form hollow structure in THF solution. Raman measurement revealed that nanoparticle assembly is effective to give Raman signals of analytes.

COLL 321

Ag nano ink for c-silicon solar cell

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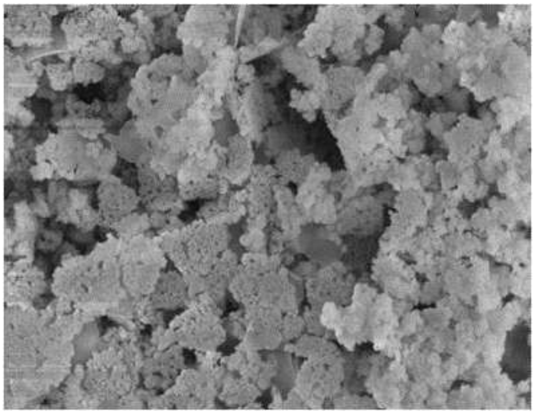
As c-Silicon solar cell becomes thinner, there is an increasing demand of non-contact printing process to avoid any damages during printing process. In addition, thinner front

electrode lines are desirable for higher efficiency solar cells. Due to the above-mentioned reasons, inkjet printing process has become one of the candidates for next generation high efficiency c-silicon solar cells.

Ag nanoparticle-based conductive ink was developed for the formation of electrode in c-Si solar cells and their sintering properties were studied. The ink, unlike the conventional Ag nano inks, includes Ag nanoparticles and nano-sized glass frits and show very unique electrode formation behaviors. In this report, we present the size-dependent behaviors of Ag nano inks for c-silicon solar cells.



COLL 322

Novel amphiphiles for pH-sensitive liposomes with *trans*-2-aminocyclohexanol-based conformational switch and the simplified models thereof

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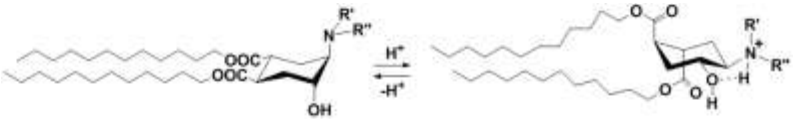
We suggested recently a novel type of pH-sensitive delivery system, "fliposomes", which contain *trans*-2-aminocyclohexanol-based amphiphiles that perform a conformational flip and trigger an instant cargo release in acidic media. A series of new “flipids” has been synthesized, and a good correlation between their conformational switch and the leakage of flipsomes has been observed. The diethyl esters of similar structure were shown to be good models for prediction of the flipids' conformational behavior.



COLL 323

Imaging and single-molecule vibrational spectroscopy of cubanethiolate on Au{111}

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We have measured scanning tunneling microscope (STM) images and inelastic tunneling spectra (IETS) of isolated cubanethiolates immobilized on Au{111} at 4K in extreme high vacuum (XHV). Cubane is the most compact, stable carbon cage molecule, and its tunneling spectra give vibrational information, and structural detail of thiolate binding at the Au surface. Images of isolated cubanethiolate species reveal modest mobility at 4K. Point spectra of adsorbed cubanethiolate were obtained and correlated with calculated spectra at the B3LYP/6-31G level of theory. Spectroscopic modes were assigned and fit. Molecular motion at substrate step edges was also observed.

COLL 324

Design of peptides for catalytic templates of bio-inspired silica mineralization

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Bio-inspired silicification, which is based on the mechanisms of naturally-occuring siliceous bodies, has recently attracted considerable attention, but the realization of topologically complex silica structures has not been achieved yet under physiologically favorable conditions. We designed catalytic peptides for in vitro silicification, based on the functional groups of silicatein-α that is the enzyme for the silica exterior of glass sponge, and used the self-assembled structures of the peptides as a catalytic template for the silicificaiton. The results would give us a better insight into the formation mechanism of biogenic silica and also could contribute to the development of anthropogenic strategies for non-biological inorganic materials.

COLL 325

Generation of water-collecting surfaces inspired by desert beetle

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The water-collecting surfaces were generated by the spatio-selective coating of dopamine on the self-cleaning superhydrophobic anodic aluminum oxide surfaces. The selective coating led to the formation of hydrophilic bumps with the superhydrophobic background, which moderately matched with the wettability patterns of namib desert beetle's wing. The water droplets on the surface rapidly moved toward the hydrophilic bumps, indicating its water-collecting capability.

COLL 326

Ultrasound continuous treatment for interface of quartz fiber/epoxy composites

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Ultrasonic treating system is used to improve, continuously and on-line, the wettability between quartz fiber and epoxy during the process of impregnation. According to the technique feature of preparing quartz fiber/epoxy composites, we establish the ultrasonic treating system. It includes vibrating system, which consists of piezoelectricity transducer and amplitude-transformer, and ultrasonic generator with functions of tracking, velocity stabilizing and current overload protecting. Effects of ultrasound on surface morphology of quartz fiber/epoxy composites are studied. The difference of composite surface between not treated and after treated by ultrasound is watched by SEM and Metallurgical Microscope. The results show that the ultrasound does improve the wettability between quartz fiber and epoxy resin.

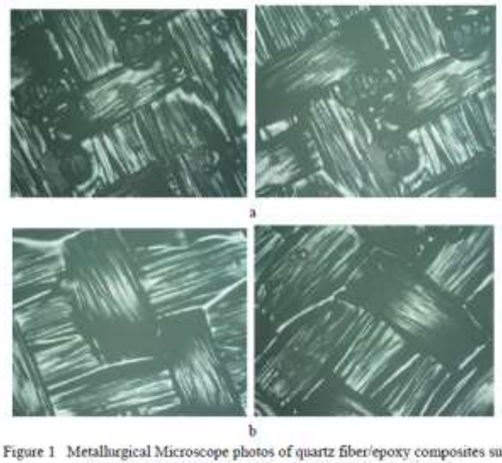

Figure 1 Metallurgical Microscope photos of quartz fiber/epoxy composites surface (a, not treated by ultrasound; b, after treated by ultrasound)

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COLL 327

Surface characterization of lamellar-structured diblock copolymer films by TOF-SIMS and AFM

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Lower disorder-to-order transition(LDOT) block copolymers can offer new types of sensor materials with high-temperature or pressure sensitivity. We report on the characterization of the morphology from LDOT diblock copolymers such as polystyrene-b-poly(n-propyl methacrylate)(PS-PPrMA) and polystyrene-b-poly(2-ethyl hexyl acrylate)(PS-PEHA), where PS blocks were perdeuterated, using TOF-SIMS and AFM. TOF-SIMS depth profiling was obtained for the lamellar morphology of deuterated copolymer which is found to orient parallel to the surface of the substrate. This preferential orientation resulted in a periodic variation in the composition of each block that continued through the entire copolymer film. Their depth profiles showed consistently regular alternative pattern with the same period because the size of the lamellar structure is determined by the total number of monomers in the copolymer chain. Temperature-dependent annealing studies on copolymer thin film were performed to investigate the LDOT properties of diblock copolymers. AFM is also used to visualize the surface topography.

COLL 328

Synthesis of novel periodic mesoporous MCM-41 silica with enhanced mesoporosity, morphology, and hydrothermal stability via mixed double surfactant templating route

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For the past decades, the M41S family of ordered mesoporous silica has attracted interest from both academic and industrial sectors. However, lack of thermal-

hydrothermal stability and presence of electrically neutral framework for ordered mesoporous silicas are considerable drawbacks, inhibiting their practical applications in catalysis and adsorption. We have successfully synthesized stable periodic mesoporous MCM-41 silica using the mixed (double) surfactant templating route at high crystallization time and temperature (125-150 ºC and 1-7 days). Such approach was previously shown to result in mesoporous silica of interesting properties. Four different surfactants together with cationic CTAB was used in the synthesis. These surfactants belong to the family of anionic and nonionic surfactants. Various hydrothermal crystallization factors such as surfactant concentration, nature of surfactant, ratio of cationic to co-surfactant, and crystallization time and temperature were observed to greatly affect the silica mesophase properties. It was observed that the mesostructured, textural properties, and hydrothermal stability were significantly improved for mesoporous silica obtained by mixed templating approach, as compared to single surfactant system. These improvements were attributed to the preferential binding between the cosurfactant head groups and the hydrolyzed product of silica precursors. The enhanced hydrothermal stability can be attributed to the presence of smaller particles of thicker walls.

COLL 329

Graphene and ZnO nanostructures directed by block copolymer thin films

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Cylindrical and lamellar nanostructures of block copolymers in thin films can be perpendicularly oriented to the plane of the films by neutralizing surfaces of the substrates. These perpendicularly oriented nanostructures can be utilized as etching masks and guiding templates to generate directed patterns of functional materials. In this study, perpendicularly oriented cylindrical and lamellar nanostructures of diblock copolymers were fabricated on silicon oxide substrates which were neutralized by the self-assembled monolayer. By dissolving the silicon oxide with hydrofluoric acid, the fabricated films were transferred onto functional materials such as graphenes and ZnO layers. After one of the blocks of copolymers was selectively removed from the transferred films, the remaining copolymers were used as etching masks and guiding templates. Graphene nanostructures were fabricated by etching process with the copolymer etching mask. ZnO nanostructures were also synthesized by hydrothermal process guided by the copolymer template.

COLL 330

Shape dependent immunogenicity of antigen-coated gold nanomaterials

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Various vaccines have several problems about toxicity, vaccine activity and cost for preparation. Virus-Like Particles (VLPs) is one of the best candidates for vaccines because of its balance of toxicity and vaccine activity. VLP requires great care to preparation because VLP is formed only *in vivo* and unable to control of its size and shape. In this report, we prepared and evaluated shape dependence of antigen protein-coated gold nanoparticles (AuNPs) with various shape as vaccine.

AuNPs (Sphere, Cube, and Rod shape) were synthesized and used as templates of vaccines using electrostatic interaction. The ELISA results of sera from mice immunized by antigen coated AuNPs showed that Sphere is the most effective shape as vaccine. It is considered because the size and shape of Sphere AuNP is the closest to wild-type virus (40~50 nm sphere shape).

COLL 331

DNA-mediated photoconversion of AgCl to functional nanocrystals

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Photoconversion of silver halide to functional silver nanoparticles (AgNPs) is of both scientific curiosity and technological importance. The conventional wisdom that colloidal nanoparticles are best prepared in homogeneous solutions has, however, prevented researchers from exploring silver halide as a precursor to silver nanoparticles (AgNPs) due to its poor solubility in common solvents. Here we show that AgCl can be rapidly photoconverted to functional AgNPs with the aid of DNA. The resultant AgNPs are biofunctionalized, and exhibit photostable luminescence and DNA-specific surface-enhance Raman scattering (SERS) signature, allowing for DNA-directed recognition and bioimaging (Chem. Commun. 2011, 47, 9426-9428). The simultaneous targeting and light scattering-fluorescence-SERS multimodal imaging of cancer cells were achieved using AgNPs prepared with a DNA aptamer. Furthermore, the intermediates of AgNP, referred to as Ag@AgCl nanostructure, were found to exhibit DNA-specific photocatalytic performance. The use of these photocatalysts for degradation of organic dyes as model pollutants has also been demonstrated.

COLL 332

Aqueous interfacial chemistry of silver on metal oxyhydroxide surfaces

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In recent years, concerns of silver toxicity have been raised due to popular applications of silver nanoparticles to many consumer products as an antimicrobial agent. As silver nanoparticles enter the environment, there is a great risk for silver to adversely affect human and ecological health. Understanding the fate and transport of silver/silver nanoparticles in aquatic-terrestrial environments becomes critical in regulating its use and assessing the risk. While recent studies showed the ligand complexation and ligand/proton promoted dissolution of silver nanoparticle to predict the bioavailability/solubility of silver in aqueous systems, aqueous interfacial chemistry of ionic silver on sediment mineral surfaces has not been extensively investigated. Therefore, the mobility of silver in terrestrial environment is not well understood. In this study, we investigated partitioning mechanisms of ionic silver in common sediment/soil minerals, metal oxyhydroxides, using experimental geochemistry and in-situ X-ray absorption spectroscopy.

COLL 333

Glutathione-triggered drug release from virus capsules in cells

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Virus capsules consisting of viral proteins are good candidates as drug carrier due to their hollow structure derived from symmetrical arrangement of component proteins, and the inherent targeting potential and efficient cellular uptake by receptor-mediated endocytosis. We represent JC virus capsules enable controlled-release of drugs in response to reducing environment in the cell via cleavage of disulfide bond. Fluorescent dye molecules were encapsulated within the virus capsules by modification of cysteine residues specifically located at the interior surface of the capsules. Fluorescence correlation spectroscopy (FCS) indicated the dye molecules were released from the capsules within 5 min by adding glutathione molecules (10 mM). Confocal Laser Scanning Microscopy (CLSM) observation revealed that the encapsulated dye molecules were released from virus capsules in NIH3Y3 cells, suggesting that this virus capsules may have potential for improving drug delivery efficacy.

COLL 334

Towards single pot grafting of mixed polymer brushes by “grafting to” utilizing reactive/responsive block copolymers

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This work aims at attaching films of responsive polymer brushes using the grafting to method, utilizing block copolymers consisting of poly(N-isopropyl acrylamide)-b-poly(glycidyl methacrylate) (PNIPAM-b-PGMA), and/or poly(ethylene glycol)-b-poly(glycidyl methacrylate) (PEG-b-PGMA). It was found that layers of sub 20nm films or increasing thicknesses of 200nm could be fabricated utilizing the “grafting to” procedure. Single step mixed polymer brushes were also fabricated in a one step grafting to fashion. Surfaces were made that contained both the temperature responsive portion of PNIPAM, with the addition of a hydrophilic aspect from PEG. In-situ multi-angle ellipsometry was used at varying temperatures to probe layer thickness and refractive index changes with varying PNIPAM block size, to investigate the ability of these films to retain their thermo responsive behavior commonly seen with PNIPAM. Wettability changes above and below the LCST of PNIPAM were probed by dynamic contact angle measurements. Single block copolymers of PGMA-b-PNIPAM and mixed brushes containing PGMA-b-PEG were investigated for their ability to absorb and or not absorb fibrinogen at temperatures above and below the LCST of PNIPAM.

COLL 335

Monolithic cellular graphitic carbon from ROMP-derived polydicyclopentadiene aerogels

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Porous carbons and carbon aerogels are useful as electrodes for batteries and fuel cells, catalyst supports and separation/filtration media. Monolithic carbon aerogels are usually obtained by pyrolysis at up to 1100 ^{o}C of organic (polymeric) aerogels, mainly based on resorcinol-formaldehyde resin. Other organic aerogels that have been converted to porous carbons include polyacrylonitrile, polyimide, polyurea and polybenzoxazine. Here, we demonstrate the preparation of carbonizable aerogels based on polydicyclopentadiene (pDCPD) synthesized via ring opening metathesis polymerization (ROMP) of the monomer using a second-generation Grubbs' catalyst. Since pDCPD is not substantially crosslinked, the resulting aerogel monoliths are deformed severely relative to the shape of their molds. That issue was resolved by post-gelation grafting of the pDCPD wet-gels with polymethylmethacrylate (PMMA) using AIBN-induced free-radical chemistry. The resulting aerogel monoliths are uniform and robust. Pyrolysis of those aerogels at 800 ^{o}C under Ar yields electrically conducting

amorphous carbons (yield: 30% w/w), which in turn were graphitized at 2300 ^{o}C to yield (93% w/w) highly conducting monolithic cellular (~3 micron diameter) graphitic carbon.

COLL 336

Conducting polymer coatings for metal oxide nanoparticles

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A method was developed for coating metal oxide nanoparticles with electrically conductive polymers for the purpose of static dissipation. A variety of sonication conditions were evaluated to disperse CuO nanoparticles; a Brownian motion microscope was used to determine efficacy of sonication parameters. Monomers including pyrrole, 2,2'-bithiophene, 3,4-ethylenedioxythiophene (EDOT), and 3-hexylthiophene were oxidatively polymerized in the presence of suspensions of copper oxide(CuO) nanoparticles using ferric chloride as the oxidant. Early attempts to coat bare CuO nanoparticles revealed that the polymers did not adhere to the CuO, necessitating the need for a surface modification prior to polymerization. After surface modification, polymerization yielded uniform coatings as verified using scanning electron microscopy. These samples were pressed into pellets for four point probe conductivity measurements; 10wt% PEDOT samples exhibited much greater conductivity than other polymer-coated nanoparticles.

COLL 337

Inhomogeneity of acetonitrile solutions at the aqueous surface interface

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Aqueous acetonitrile solutions are used often as a miscible solvent in organic synthesis and can impact environmental reactions. They are thought of as heterogeneous but also cluster at higher concentrations. Surface experimental studies and molecular dynamics simulations suggest that acetonitrile has different surface orientations that transition at 0.07 mole fraction from hydrogen bonding with water, and a phase separation at 0.3 mole fraction, from clustering at the aqueous surface interface.

We present ambient pressure-X-ray photoelectron spectroscopy results of aqueous acetonitrile solutions. By varying the kinetic energy, we are able to probe the aqueous

surface interface and the bulk solutions of acetonitrile at various concentrations. The C1s and N1s regions reveal multiple species in both the surface and the bulk of solution. Different regions at the aqueous interface are concentration dependent. These results suggest that solutions of acetonitrile could have different effects as a solvent due to its microheterogeneity in solution.

COLL 338

Nanoparticle cell mimics: Investigating the curvature dependent membrane binding of C-reactive protein

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C-reactive protein (CRP) is a serum protein that is known to bind to lipid membranes. Previous studies have shown that CRP binds preferentially to apoptotic cells, but not to healthy cells. Binding of CRP to membranes occurs through phosphocholine (PC) headgroups; however, since PC lipids are the major constituents of all membranes, it is unlikely that CRP would only interact with PC on apoptotic cells. We hypothesize that membrane curvature may influence CRP binding as apoptotic cells tend to have areas of high local curvature. To this end, lipid coated nanoparticles (PC-NP) were used to create cell mimics in order to evaluate the role of membrane curvature in CRP binding. Current studies involve determining the optimal ratio of surface tethering to ensure system stability and biological equivalency of PC-NPs. Preliminary data suggests that CRP preferentially binds to smaller particles.

COLL 339

Investigating molecular entanglement of alkane oligomers on PDMS modified substrates

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Silver substrates modified with thin films (ca. 10 nm) of PDMS are dewet from dilute solutions of n-alkane chains of lengths from C8 to C18. The properties of the dewetted films are probed by optical and vibrational spectroscopies and contact angle measurements. Results provide evidence that is strikingly supportive of entanglement processes that are though to be responsible for the creation of exponentially increasing film thickness as a function of increasing alkane-oligomer length. Data from the fluid films are interpreted with consideration of fluid viscosity, contact angles, surface roughness, and other possible physical interactions with the polymer substrate. Results are compared to theoretical behavior predicted by van der Waals and hydrodynamic forces. Conclusions differentiate the behaviors associated with these two model

regimes and allude to an additional structural component to be included for future consideration of interfacial film behavior.

COLL 340

Inorganic Janus nanoparticles based on electrohydrodynamic co-Jetting

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We describe anisotropic nanoparticles compartmentalized using electrohydrodynamic co-jetting of Titanium tetrabutoxide solutions mixed with poly(lactide-co-glycolide) in organic solvents. The resulting composite nanoparticles were relatively monodisperse and had uniform spherical shapes. Titania nsnoparticles can be produced through subsequent calcination. The compartmentalized inorganic nanoparticles are successfully applied as anisotropic catalytic supporter for spatially controlled catalysis. Catalytic growth of CNTs induced by localized Fe catalyst resulted in Janus particles displaying hairy CNTs on one face of nanoparticles only.

COLL 341

Biocompatible coating procedures for diamond nanoparticles

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Nanodiamonds have recently been recognized as a versatile material for biological applications, such as drug and gene delivery, labeling/imaging, and magnetic field sensing. After irradiation by high-energy particles, nanodiamonds show strong fluorescence due to the creation of vacancies and the subsequent formation of nitrogen-vacancy centers from naturally present nitrogen impurities. Still, the nanodiamond surface after the fluorescence activation is chemically inhomogeneous. This makes the formation of stable colloidal nanodiamond solutions to be a real challenge.

We have developed a method enabling the coating of nanodiamonds using a crosslinked silica layer. Stabilization of these particles in aqueous solutions was achieved using biocompatible polyethylene glycol spacers (PEGs). By functionalizing the terminal parts of PEGs, we were able to introduce onto the nanodiamonds additional moieties, e.g., fluorescent probes and targeting peptides. The cellular uptake and toxicity of these functionalized nanodiamonds were evaluated on various cancer cell lines.

COLL 342

Rigid macroporous polynorbornene monoliths by ring opening metathesis polymerization

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Rigid macroporous polymer monoliths are widely used as efficient stationary phases for chromatographic separations, flow-through reactors, catalyst supports etc. An efficient sol-gel bottom-up synthetic approach involves polymerization of soluble monomers into an insoluble polymer that phase-separates into colloidal particles that under the right conditions of molecular structure, concentration, solvent and temperature form gels. Early phase-separation, hence smaller colloidal particles, can be induced by molecular-level cross-linking in the growing polymer akin to that in thermoset resins. Alternatively, for highly soluble linear (thermoplastic) polymers, phase-separation can be controlled with non-solvents. This is demonstrated here with open-cell macroporous polynorbornene monoliths synthesized by ring opening metathesis polymerization (ROMP) of norbornene in toluene using isopropanol (*i*PrOH) as non-solvent. Wet-gels were solvent-exchanged with liquid CO_2 taken out at the end as a supercritical fluid (SCF). Changes in the microstructure as a function of the *i*PrOH:toluene ratio was probed by SEM, N_2 sorption porosimetry. Bulk densities range from 0.40 to 0.68 g cm^{-3}. Porosity ranges from 30 to 60% v/v with average pore diameters in the 1.4-2.3 μm range, but the BET surface area is low (1-3 m^2 g^{-1}). The skeletal framework consists of agglomerated particles forming macroglobular structures (1.8 to 4.5 μm in diameter). The monoliths are robust with e.g., ultimate compressive strength under high strain rates (1224 s^{-1}) of samples made with *i*PrOH:toluene = 7:3 v/v (0.51 g cm^{-3}) equal to 50 MPa at 75% ultimate strain.

COLL 343

Development and surface analysis of novel environmentally benign marine coatings

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The accumulation of microorganisms, plants, and animals on underwater surfaces, has been a hindrance to seafaring vessels for centuries. In addition to high costs from increased fuel consumption, removal of these fouling agents is also a severe economic burden. Increasing regulations of traditional marine coatings have put emphasis on alternative coating systems that are environmentally benign. In this work, quaternary ammonium salts have been incorporated into low surface energy polymer backbones to

provide an active antimicrobial defense mechanism. Furthermore, hydrolysable moieties have been incorporated into these polymers in order to provide “renewable” antimicrobial activity to the coating system as the coating slowly erodes in a controlled manner. Because of the extended lifetime and slow hydrolysis rate of these systems, a unique method of monitoring hydrolysis was developed. Synthesis, characterization, and hydrolysis kinetics of these systems will be discussed.

COLL 344

Effect of unsaturated polyester resin impregnation capability under ultrasound treatment

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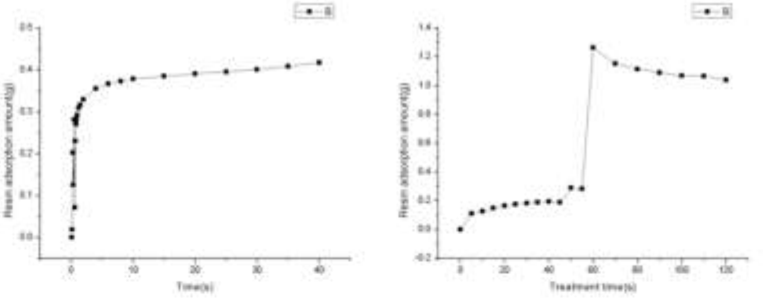
The cavitation and the agitation action in the liquid aroused by ultrasound improve the adsorption, diffusion and wetting of unsaturated polyester resin on the surface of fiber, enhance the mechanical properties and finally utilize fully the outstanding property of fiber reinforced composites. Effects of ultrasonic treating parameters such as amplitude and treating time on the viscosity and surface tension are studied. The experiment proves the main factor that the viscosity and surface tension of the unsaturated polyester resin decrease with the increase of the amplitude of ultrasound and the decreasing tendency can be maintained is the high pressure and high temperature in the local region of the unsaturated polyester resin due to cavitation

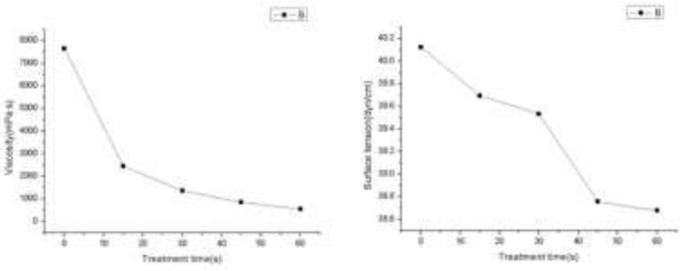


a

b

Figure 1 a, not treated by ultrasound; b, after ultrasonic treatment

. Then the experiment of wetting shows that the wetting speed and adsorption amount at the wetting system are raised after ultrasonic treatment.



a b

Figure 2 a, the relationship between resin viscosity and ultrasound treatment time;
b, the relationship between resin surface tension and ultrasound treatment time

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COLL 345

Effect of heparin on protein aggregation: Inhibition vs. promotion

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Heparin appears to both inhibit and suppress or even reverse protein aggregation. It is not understood whether this diverse behavior is a consequence of the particular protein or of the conditions chosen, and this reflects limited understanding of the mechanism from which these effects arise. Since protein aggregation can be induced in multiple ways, involving different molecular processes, the influence of heparin may occur at many points. In seeking an explanation of these apparent contradictions, we consider the likelihood that the unfavorable effects may arise when heparin interacts not with the native state monomer or dimer, but with a denatured or already aggregated species. It is therefore of interest to study the anti- or pro-aggregative effects of heparin on proteins under conditions favorable to folded (native state multimer) or denatured states. Three proteins are chosen for the current study: bovine serum albumin (BSA), b-lactoglobulin (BLG), and insulin. The ability of heparin to inhibit, suppress or reverse aggregation is examined using turbidimetry and dynamic light scattering.

COLL 346

Quantification of active surface sites on platinum nanocatalysts dispersed in aqueous solution by attenuated total reflectance infrared spectroscopy

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Dispersion factors, used in calculating catalytic turnover frequencies, may be estimated from particle sizes determined by electron microscopy analysis. Furthermore, these values may be more accurately determined from experimental chemisorption methods. Still, there are difficulties in extending these methods to colloidal nanocatalysts operating in aqueous solution. In our work, we are monitoring the chemisorption of probe molecules, such as carbon monoxide, as well as selected aldehydes and ketones, on various 1.7 to 7.1 nm platinum nanocatalysts capped with poly(vinylpyrrolidone) (PVP). We are using absorbance data to calculate molar absorption coefficients, thereby quantifying the number of adsorbates, and hence the number of active surface sites, present on each catalyst surface. We are comparing these results with dispersion factors calculated from particle sizes determined with transmission electron microscopy (TEM), and will use these findings to develop a more complete molecular level picture of the catalytic behavior of these nanocatalysts in aqueous solution.

COLL 347

Surface interfacial properties of carbon-Nafion composites

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Real (ideal) contact angle (smooth surface) and surface energy are important factors in determining the surface interaction and dynamic surface properties of composites. The focus of this work is to investigate the surface properties, such as real contact angle, surface energy, and resistance of carbon-Nafion composites. Carbon-Nafion composites were fabricated by controlling the Nafion fraction from 5% to 70%. Apparent contact angle of carbon-Nafion composites with different compositions were measured by Kruss DSA 100 surface analyzer. Roughness of surface and average thickness of samples were measured by profilometer. According to Wenzel model, the real contact angle of carbon-Nafion systems was calculated from apparent contact angle and roughness. Surface energy was calculated by using four different theories, which are Acid base, Equation of state, Wu, and Fowkes. Then resistance of carbon-Nafion systems was investigated by electrochemical impedance spectroscopy (Auto Lab). Other analytical characteristics will be investigated in further research.

COLL 348

Aligned photoresponsive nanofibers by magnetic field assisted electrospinning

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This research is designed to develop photoresponsive polymeric materials, as well as incorporate new production methodologies and functionalization techniques. Current research on stimuli-responsive polymeric materials relies mainly on highly cross-linked liquid crystals, which suffer from large area production difficulties, long response time, and inefficient alignment of mesogens. To overcome these issues, our research aims to functionalize polymerized azobenzene moieties with Fe_3O_4 nanoparticles and electrospin the polymer in a magnetic field creating highly ordered polymers that allow for much deeper stimuli penetration. These polymers should generate a quicker response and a much larger stimuli/reponse ratio. The mats formed from the magnetic field assisted spinning will also be post-photopolymerized using a UV curable optical adhesive in order to increase the anisotropy of the system. Once optimized, the methods developed can easily be scaled up for various applications, such as artificial muscles, sensors, and photonic motors.

COLL 349

Graphite oxide/chitosan aerogels as sorbents for CO_2 capture

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Chitosan (CTS) aerogels containing various amounts of graphite oxide (GO) were prepared using freeze-drying. The aerogels were characterized using Raman, FTIR and X-ray diffraction techniques. The N_2 adsorption/desorption isotherms at -196 ^oC indicating that the BET surface area increased from 153 to 374 m^2/g by introducing 10 wt% GO into the CTS sorbent. Adsorption measurements were conducted from low pressure to 1 bar at temperatures of 25, 50, and 75 ^oC. The effects of GO content and carbonization on the specific surface area of the aerogels and CO_2 capture were investigated. Breakthrough curves showed that the CO_2 adsorption capacities increased linearly with GO content. The amount of CO_2 adsorbed at 25 ^oC increased from 1.92 to 3.48 mol/kg with addition of 10 wt% GO. The Freundlich isotherm model showed a good fit of the adsorption data at 25 ^oC.

Keywords : GO; chitosan; CO_2; thermal and mechanical properties, adsorption.

COLL 350

Factors affecting catalytic activity for nitrophenol hydrogenation on colloidal platinum nanocatalysts

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Hydrogenation reactions are typically considered to be structure insensitive, but in certain instances changing particle size may influence catalytic activity. One such

reaction has been proposed to be the hydrogenation of p-nitrophenol to p-aminophenol using sodium borohydride. Still, no direct evidence has been published regarding this hypothesis. In our work, we are utilizing polyvinylpyroolidone (PVP) capped Pt nanocatalysts synthesized in the 1-10 nm size range to catalyze this reaction under pseudo-first-order conditions. UV/Vis absorbance spectroscopy is being employed to monitor product disappearance and calculate apparent rate constants for the selected particle sizes. Data from reactions carried out at selected temperatures over the 293 to 333 K temperature range are being used to calculate apparent activation energies for the reaction catalyzed by platinum nanocatalysts of selected particle sizes. These results will be used in further clarifying the molecular level steps involved in the mechanism of this reaction.

COLL 351

Multilayered polymer brush system

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The present study is focused on synthesis and characterization of multilayered brush system consisting of polyglycidyl methacrylate (PGMA) and polyacrylic acid (PAA) layers. The polymer brush assembly was fabricated by grafting the polymer chains to the surface of silicon wafer in a sequential fashion. Swelling of the system in an aqueous environment at different levels of pH and electrolyte concentration was investigated using atomic force microscopy. It was found that one-layer PAA brush grafted to the PGMA anchoring layer had higher extension in the aqueous environment than PAA brush sandwiched between layers of PGMA. The extension of the PAA brush was restricted due to hydrophobic nature of the topmost PGMA layer. In addition, the three layered PGMA/PAA/PGMA system demonstrated increased surface roughness when it was exposed to water.

COLL 352

Surface affects of halides on silver nanoparticles

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Determining the reaction kinetics of halide salts with silver nanoparticles is important for understanding the fate of the nanoparticles in various environments. We have found that addition of chloride ion in the form of NaCl causes a layer to form which inhibits further reaction on the nanoparticle surface. Neither bromide nor iodide ions form such a passivating layer and, in fact, both strongly enhance the oxidation of the surface. Studies involving halide-induced aggregation of the nanoparticles show that the surface

charge is significantly reduced when chloride ion is added. We propose that the charge reduction is due to replacement of adsorbed citrate (used as a capping agent in the silver nanoparticle synthesis) by adsorbed $AgCl_2^-$, but an alternate explanation is partial desorption of the citrate ions when a layer of AgCl is formed. We are investigating these possibilities through mixed-halide and variable-temperature studies.

COLL 353

Dispersion strategies for nanoparticles in polymeric media using oligomers and short polymers

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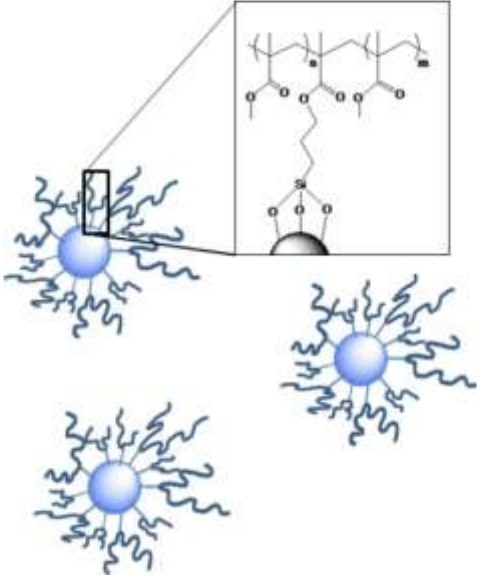
Brush–matrix polymer interactions are important in determining the ability of polymer-grafted nanoparticles to disperse in a polymer melt. Graft density (σ), brush (*N*) and matrix (*P*) polymer lengths are the critical parameters that influence the wetting-dewetting transition. It is generally assumed that long polymer brushes (*P)* and an optimum graft density are necessary to achieve a good dispersion. Here we demonstrate that nanoparticles tethered with short, dense polymer brushes can exhibit a highly stable, fine dispersion in the polymer melt, contradicting conventional theories. The quality of the dispersion of the nanoparticles was characterized by measuring physical properties that are sensitive to the state of the dispersion. The factors that result in such stability will be discussed and dispersion strategies for a variety of nanoparticles in different polymeric media will also be presented.



COLL 354

Lipid-based hybrid nanostructures mimicking biological membranes

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We have developed two types of hybrid, biomimetic, lipid-based nanostructures that have potential applications in biosensing, drug targeting, and drug delivery.

One of these consists of multi-walled carbon nanotubes (MWCNTs) in which lipid bilayers are covalently anchored to the surface of nanotubes to support the insertion of membrane proteins. First, MWCNTs with sufficient radius of curvature for formation of lipid bilayers were covalently modified with primary amine-bearing phospholipids. Then, a second monolayer of lipids was self-assembled on the MWCNT surface in a sonication process. Multiple analytical techniques confirmed the formation of biomimetic lipid bilayers on MWCNT surfaces capable of supporting membrane protein insertion. The bilayer-coated MWCNTs were dispersible in aqueous buffer and the resulting suspensions were highly stable.

To improve liposome stability, we have constructed poly(ethylene glycol) (PEG) hydrogel-anchored liposomes. A PEG hydrogel was fabricated in the core of liposomes made from lipids that covalently integrate into the gel network.

COLL 355

Excited-state interaction between chromophores and CdSe quantum dots

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In photo catalysis, energy and electron transfer between photo-excited semiconductor and fluorophores are important phenomena. Direct binding of a fluorophore to a semiconductor surface often results in quenching of the excited states. Electron and energy transfer are considered to be the major deactivation pathways for excited fluorophores on semiconductor surfaces. Dyes in contact with semiconductor nanoparticles have been employed to enhance the overall photo catalytic activity. However, the interfacial electron and energy transfer processes have to be understood fully, inorder for potential applications in solar energy conversion and catalysis. We present excited-state quenching studies of the CdSe quantum dot (QD) luminescence of different sizes by structurally and energetically well-defined 4–methyl–7–[(4–methyl–2–oxo–chromen–7–yl)sulfanylmethylsulfanyl]chromen-2-one (dMC), a dimer of the fluorophore coumarin. The crystal structure of dMC has been determined. By probing the system with UV-visible absorbance and fluorescence spectroscopy, we have been able to see enhanced two-photon cross-sections for dMC. dMC binding to QDs exhibit a size dependence, which is monitored via fluorescence quenching and lifetime changes.

COLL 356

Preparation of an alkane thiol-photoacid to make photoswitchable self-assembled monolayers on gold surfaces

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Self-assembled monolayers (SAM's) have been developed as an effective method to change the surface property of a metal or metal oxide. Alkanethiols have been used for the formation of SAM's on gold surfaces, and the properties of the surface depend on the functional groups of alkanethiols. For example, alkanethiols with photoreactive functional groups can produce a photoreactive surface. There are two strategies for preparing a functionalized SAM on a surface. The first one is attaching functional groups after forming SAM of precursors, and the second one is forming a SAM with pre-functionalized precursors. Using the second approach, we have synthesized an alkanethiol with a terminal 1-naphthol group by linking 11-mercaptoundecanoic acid and 5-amino-1-naphtho using 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide as an activating agent. 1-Napthol is a strong photoacid, and the goal is to use this SAM to make a photoswitchable surface whose ionic properties can be continuously adjusted by varying the light exposure. The synthesis of this molecule, its photophysical properties, and its properties as a SAM surface coating on a gold surface will all be reported.

COLL 357

Early stages of calcium carbonate formation in the presence of polyionic additives

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The precipitation behavior of $CaCO_3$ has been studied intensively over the last century and subsequently $CaCO_3$ has developed into a model system to study nucleation and growth. However, very little is still known about the very early stages of a precipitation process (nucleation and early growth). The goal of our current work is to gather more information about the structure of key intermediates and to get a deeper understanding of the precipitation mechanism involved and how they can be specifically manipulated in the presence of organic additives. We use TEM and DLS in order to monitor nucleation and growth of the particles. Various polyelectrolytes (PMA, PSS, (AA)x(AMPS)y copolymers) have been investigated regarding their Ca^{2+}-complexation behavior in the prenucleation stage by means of potentiometric, calorimetric and scattering techniques

as well as regarding their impact on nucleation time, growth rate and surface stabilization of the resulting $CaCO_3$ nanoparticles via DLS and TEM.

COLL 358

Halide specific effects on the acid-base equilibria of the silica/water interface studied by second harmonic generation spectroscopy

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Characterizing the silica/water interface is critical to understand numerous geochemical, environmental and industrial processes. Many of these processes depend on the surface charge density and thus on the acid-base equilibria of the silica/water interface. Using the Eisenthal group's $X^{(3)}$ technique of second harmonic generation spectroscopy, we recently observed that these acid-base equilibria are largely specific to the ions present in the aqueous phase. Consistent with previous observations that anions exhibit more pronounced ion specific effects, herein we present how the acid-base behavior of the silica/water interface varies quantitatively depending on what halide ions are present. Chloride, bromide, and iodide, with both sodium and potassium co-ions, demonstrated very different acid-base behavior that eventually led to different effective pK_a values for the silica/water interface. The fraction of deprotonation of the surface silanol groups at a certain pH and its specificity to the halide ions will also be discussed.

COLL 359

Influence of amino acids with silver nanoparticles and their antimicrobial properties against Escherichia coli

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Due to their optical and antimicrobial properties, silver nanoparticles are being used in an increasing number of commercial and medical applications. Since their effect on the environment and living organisms is only partially known, probing their behavior in various solution conditions is important. The goal of our work is to study the interaction of amino acids with the nanoparticles and examine their antimicrobial effects on Escherichia coli. We have found that if an amino acid adsorbs to the nanoparticle's surface, they tend to aggregate due to hydrogen bonding of the carboxylate and α-amino groups. We are undertaking pH studies of these species and probing the effect of amino acid derivatives to determine if we can manipulate the surface charge present on the nanoparticles and prohibit this aggregation. Once this is accomplished, we intend to investigate their antimicrobial properties by measuring the optical density as a function of time.

COLL 360

Measurement of reactivity of Pd, Pt, and Ru nanocatalysts in hydrogenation reactions

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Nanoparticles (NPs) of palladium (Pd), platinum (Pt), and ruthenium (Ru) 2-5 nm in diameter were synthesized with n-dodecyl sulfide (NDS) as the stabilizing ligand. The experiments were performed in poly(dimethylsiloxane) (PDMS)-glass microfluidic reactors using either 1-bromohexene or pyruvic acid as the substrate in methanol. To enable catalyst reuse and recycling, the NPs were immobilized *in situ* in two steps: a) a solution of 3-aminopropyltrimethoxysilane (APTMS) was infused into the microfluidic reactors and bonded to the PDMS and glass reactor walls; b) a solution of NPs was infused into the microfluidic reactors, and adhered to substrate-bound APTMS, thus resulting in effective particle immobilization through chemical bonding. The annular-flow, three-phase reaction product was collected and analyzed via gas chromatography (GC) or GC-mass spectrometry (GC-MS). The reactions achieved 30-100% conversion for the Pd, Pt, and Ru nanoparticles, confirming successful catalyst immobilization and demonstrating their catalytic viability.

COLL 361

Microcapillary microfluidic fabrication of asymmetric giant lipid vesicles with minimal organic solvent

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We introduce a microcapillary microfluidic technology for the fabrication of compositionally asymmetric giant unilamellar vesicles (GUVs). Monodispersed water in oil in water (w/o/w) double emulsion droplets were formed in a single step in a glass microcapillary system. Lipid vesicles were formed after removal of the oil phase by evaporation. By incorporating different small unilamellar vesicles (SUVs) into each of the water phases, an asymmetric membrane can be fabricated, with compositionally distinct lipid monolayers formed at each water-oil interface. Lipid bilayer membrane asymmetry is confirmed by binding of labeled annexin V to membranes formed with an asymmetric composition of phosphatidylserine.

COLL 362

Antimicrobial effects of enhanced antibiotics mixed with silver, gold and ZnO nanoparticles

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Inappropriate use of antibiotics is the main reason for the microorganisms to develop methods to increase their resistance to these antimicrobial agents. Scientists are developing new antibiotics to fight bacterial infections, but bacteria reproduce fast and the number of resistant bacteria increases exponentially. Nowadays, Nanotechnology is helping areas such as medicine by using nanoparticles to develop new treatments for different health conditions. Because of their size, 1-100 nanometers, these nanoparticles are a useful tool in medicine and engineering. Some studies have been published about the antimicrobial properties of silver nanoparticles. This study presents the antimicrobial effects of enhanced antibiotics mixed with silver, gold, and zinc oxide nanoparticles. Our goal is to develop more effective treatments against resistant bacteria infections, by increasing the potential of antibiotics mixed with nanoparticles, or developing new antimicrobial agents using nanoparticles. Three antibiotics, Gentamicin, Ciprofloxaxin, and Cephalexin, of three different concentrations were chosen to perform this study against Escherichia coli (ATCC # 10536) and Staphylococcus aureus (ATCC # BAA-1026). Nanoparticles of Gold, Silver and ZnO were chosen to mix with antibiotics. Our results revealed that some nanoparticles increased the potential of a specific concentration of antibiotics while in other concentrations of antibiotics mixed with nanoparticles, nanoparticles decreased the potential of the antibiotics.

Keywords: Nano/Materials, nanoparticles, antibiotics, antimicrobial effects

COLL 363

Hollow polymeric nanocapsules with tunable rigidity by thiol-ene photopolymerization

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The poster describes a direct, template-free method for the fabrication of hollow polymeric nanocapsules by thiol-ene photopolymerization of a resorcinarene thiol with various alkenes. Our investigations reveal that the rigidity of the nanocapsule can be systematically varied by altering the valency of the alkene building blocks. The rigidity of the nanocapsules can be further modulated by varying the photopolymerization duration. Notably, we show that residual oxygen also plays a major role in determining the morphology of the polymers.

COLL 364

Synthesis of gold nanoparticles and their application to biomolecules sensing

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Our work is based in the synthesis of gold nanoparticles, and their interaction with amino acids. Four series of Gold nanoparticles were synthesized by reducing the Chloroauric Acid with Ascorbic Acid, Sodium Borohydride, Glucose, Sodium Citrate, and stabilized with Polyethylene Glycol (PEG). A successful synthesis was achieved obtaining a variety of colors from amber, orange, pink, purple, and blue. We described the study of the effect of the addition of selected amounts of Methionine, and Cysteine aminoacids in gold nanoparticles absorption. Two sizes of gold nanoparticles were chosen for this study 12nm and 20 nm. Gold nanoparticles samples were monitored varying the amounts of aminoacids added. Optical properties of gold nanoparticles were measured using a Lambda 25 UV Spectroscopy. Gold Nanoparticles Localized Surface Plasmon Resonance (LSPR) range was between 515nm and 580 nm. Stabilization studies were performed studying variations in the LSPR with time. The AuNP series reduced by ascorbic acid never stabilized with PEG, but were stabilized with styrene. The addition of amino acids to the nanoparticles brought interesting results showing a new band in a wavelength of ~670 nm that was assigned to the interaction with the nanoparticles. This new band increased in intensity according to the concentration of the amino acid added to the nanoparticles.

COLL 365

Synthesis of nanostructured materials and their application to fingermarks

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Powder materials have been used routinely for the detection of fingerprints in the Forensic Science Field. Previous studies in the application of nanostructure Zinc Oxide (ZnO) powder to fingermarks impressions are reported in the literature. However more studies in the application of nanoparticles to the improvement of fingermarks detection are needed. Our work consisted in the evaluation of the effectiveness of nanostructures materials for the enhancement of fingermarks impression resolution. We successfully achieved the synthesis of nanostructure ZnO powder[1]. A preliminary study was performed using Aluminum and ZnO powders. Fresh fingermarks and aged fingermarks on dry nonporous surfaces were studied. Sebaceus fingermarks and natural sweat fingermarks impressions were obtained by volunteer students. The impressions samples were divided in three groups for the study. Group I was treated at the moment, group two and three were treated four and ten days later, respectively. It was found that the samples treated with nanostructure ZnO powder presented higher definitinion and details than the samples treated with Aluminum powder. powde. Fingermarks prepared with the natural fingers sweat shows more definition and details. Also we are working in the coupling of metal nanoparticles and fluorescent semiconductor nanoparticles with the nanostructure ZnO powder for their application in wet and porous surfaces.

Keywords: Nano/Materials, fingermarks, fluorescent nanoparticles, forensic science

COLL 366

Singlet oxygen production for photodynamic therapy using zinc sulfide semiconductor nanocrystals

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The application of semiconductor nanocrystals for the treatment of excess bilirubin in photodynamic therapy is of particular interest. In order for these materials to be utilized, their properties must to be well-understood. Our research concerns the synthesis, characterization, and photocatalytic activity of zinc sulfide nanocrystals capped with polyvinylpyrrolidone, polyphosphate, and L-histidine and doped with selected amounts of manganese(II) ion. The nanocrystals are prepared using colloidal solution methods to create particles in the 2 to 5 nm size range. Photoreactions involving bilirubin are being carried out under pseudo-first-order conditions, with initial results indicating that doping the ZnS nanocrystals enhances the rate of reaction, possibly through singlet oxygen production. Additional experiments are being carried out with the intent of quantifying the amount of singlet oxygen produced using Singlet Oxygen Sensor Green (SOSG) as an indirect probe. These findings provide preliminary evidence that these semiconductor nanocrystals may be tailored for certain phototherapeutic applications.

COLL 367

Mechanical property study of asymmetric membranes

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We present a study of mechanical properties of compositionally asymmetric giant unilamellar vesicles (GUVs), using micropipette aspiration and vesicle fluctuation analysis. Through a micropipette, negative pressure is applied to the vesicle membrane, and the resulting strain is observed in order to evaluate its bending, compressibility, and Young's moduli. In the latter, nonintrusive technique, thermal fluctuation of the membrane is used for determining its mechanical properties. The holistic examination through comparison of both techniques deduces the effects of membrane asymmetry.

COLL 368

Synthesis and characterization of silver nanoparticles for biosensors design

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Silver nanoparticles have been used in several biological, technological and medical applications. It is already known that the size of nanoparticles play an important role in their electrical, optical and magnetic properties. Simple syntheses methods allow us to prepare nanoparticles controlling their size and inhibit growth are object of study. Our research focused in synthesis of silver nanoparticles for their application as biosensors. We described the preparation of silver nanoparticles using different reducing agents. ascorbic acid, glucose, sodium borohydride and sodium citrate were the reducing agents selected for the study. A variety of colors like yellow, amber, gray and translucent were achieved. Ultraviolet-visible spectroscopy was performed for to confirm the formation of silver nanoparticles. The analyzed samples show an absorption band center between 380nm and 430 nm. Yellow nanoparticles were selected to perform the interaction with functional groups and biomolecules. After the addition of selected amounts of biomolecules to colloidal nanoparticle samples, important changes in the absorption band were observed. The study was performed with urea, cysteine, glycogen, dextrose and lecithin.

Keywords: Nano/Materials, nanoparticles, aminoacids, optical properties

COLL 369

Interactions of miltefosine and phospholipids at the air/water interface

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Several Langmuir monolayer studies have suggested that the drug Hexadecylphosphocholine (miltefosine) has a mode of action which is directly related to the cell membrane. With the exact mode of action still unknown, this study was aimed at examining the interaction of miltefosine and phospholipids. More specifically, the phospholipid 1,2-Dioleoyl-*sn*-Glycero-3-Phosphocholine (DOPC) and miltefosine were investigated. Surface pressure-area isotherms of various solutions were recorded and characterized. Solutions analyzed were DOPC, miltefosine and mixed solutions of 0.25, 0.5, and 0.75 X_{DOPC}. The films were spread at room temperature on a subphase of pure water. Compression modulus (C_s^{-1}) values were examined. Interactions of the molecules were analyzed through mean molecular areas and quantified through calculated excess free energy of mixing values. The results indicated DOPC and miltefosine molecules to be miscible forming a homogeneous mixed film.

COLL 370

New approasches to the surface chemistry of sensor system by using systems of new formulation techniques

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The development of surface chemistry for biosensor system by using systems of new formulation techniques

COLL 371

One pot simultaneous synthesis of fluorescent nanoclusters and quantum dots directed by a protein: A Langmuir monolayer study

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Bovine serum albumin (BSA) was used to synthesize two fluorescent probes simultaneously, gold nanocrystals (AuNCs) and cadmium sulfide (CdS) quantum dots in a one pot method. BSA-AuNC-CdS was formed in 12 hours at human body temperature (37 °C.) Surface chemistry and spectroscopic studies of BSA-AuNC, BSA-CdS and BSA-AuNC -CdS were examined in aqueous phase and as a Langmuir monolayer. In situ UV-vis and fluorescence spectroscopy were used to verify the homogeneity of the protein Langmuir monolayer and to identify the chromophore residues in the protein. Domain formation was examined through Epifluorescence and Brewster Angle microscopy. The conformation of protein was examined by Circular Dichrosim (CD) and Fourier transform infrared spectroscopy (FITR) in aqueous phase and at air-water interface by reflection absorption spectroscopy (IRRAS).

COLL 372

Effect of structure and functional groups of a drug delivery system on endosomal escape

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Most drug delivery systems due to their size are taken up into cells by endocytosis. However, once inside endosomes the drugs are either ineffective because their sites of action are at the cytosol or are eventually degraded in lysozomes. Thus in most cases in order to achieve efficacious drug delivery a vehicle should not only internalize into the cell but also be able to escape the endosome effectively. In order to determine the effect of structure and functionalities on endosomal escape, a series of polymers containing pendant amino acid functionality were compared with crosslinked nanogels made of the same functionalities for their endosome disrupting ability.

COLL 373

Reprogramming of the plant virus as extracellular matrix mimetic

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Tobacco Mosaic Virus (TMV) has been well characterized since its initial discovery in the late 19th century. Recent studies with viruses as nanoscale scaffolds have renewed interests in manipulating the surface properties of TMV without disrupting the integrity and morphology for a wide range of applications. In our previous studies, the virus coated substrates have been reported to enhance the differentiation of mesenchymal stem cell towards osteoblasts. Here, we report the insertion of a variety of peptides near the carboxy terminus of TMV capsid to mimic the extracellular matrix. These inserts, based on the sequences from natural extracellular matrix proteins, are displayed on the viral particles at high copies (> 2000 peptides in a 300 nm x 18 nm space) with high regularity.

Among the mutants, six variants showed systemic infection in the tobacco plant host, and the mutants can be continuously produced in a laboratory setting with minimal upkeep with yields reaching up to 1-2 g per kg of wet leaves. The genetic and protein stabilities of these mutants were followed for several generations (or passage to passage), with distinct observance of proteolytic degradation of mutants during prolonged storage without alterations in the genetic code. Lastly, an adhesion screening assay was employed to screen the accessibility and functionality of the mutants against mammalian cell lines. Several ongoing studies regarding the mutants' ability to affect cell differentiation, motility, or proliferation will also be reported.

COLL 374

Growth mechanism of atomic layer deposition of ZnS thin films: A density functional theory study

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Density functional theory B3LYP method is used to investigate the growth mechanism of atomic layer deposition (ALD) of ZnS on the silicon surfaces. The ALD process is designed as two H_2S half-reactions. Both the diethylzinc (DEZn) and the H_2S half-reactions proceed through a C_2H_6 elimination mechanism. By comparison with the reactions on silicon surfaces with single and double –SH sites, we find that the existence of neighboring –SH can facilitate the adsorption of precursors and lower the activation barrier. This indicates the reactions on silicon surfaces with double –SH sites are energetically more favorable. In addition, calculations show that the DEZn half-reaction is more favorable as compared to the H_2S half-reaction.

COLL 375

Density and surface tension of binary mixtures of 1-ethyl-3-methylimdazolium nitrate with alcohols

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New experimental data of densities and surface tensions are presented for the binary mixtures of the ionic liquid 1-ethyl-3-methyl imidazolium nitrate ($[EMIM]NO_3$) with methanol and ethanol. Measurements were performed at 298.15 K and atmospheric pressure, covering the whole composition range. Excess molar volumes V^E and the surface tension deviations $\delta\gamma$ have been determined and fitted to a Redlich-Kister equation to give the fitting parameters. For the excess molar volumes of binary mixture, there is a region of negative V^E at low ionic liquid mole fraction, passing through a minimum and then V^E increases and becomes positive, showing maximum at higher ionic liquid mole fraction. It is shown that the surface tension deviations $\delta\gamma$ of $[EMIM]NO_3$+methanol system are positive but those of $[EMIM]NO_3$+ethanol system are negative over the entire mole fraction range.

COLL 376

Synthesis of photocatalytic metal oxide nanoparticles for degradation of organic dyes

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Treatment of organic pollutant in aquatic systems is in great need because of health and environmental concerns. One promising method to treat wastewater is to use metal oxide semiconductor nanoparticles to generate radicals upon light irradiation, starting a sequence of oxidation reactions to break down pollutants into less harmful molecules. Many semiconductor nanoparticles have been reported as good photocatalysts and the most well known one is titanium dioxide. However, many of these photocatalysts are

only active under ultraviolet irradiation, which makes up only 4% of the solar spectrum. Thus, a new focus is towards development of photocatalysts that can utilize visible light sources. The development of novel visible light driven photocatalysts by doping known metal oxide nanoparticles with noble metals, or combining more than two metal oxides to create composite nanomaterials will be described, and results of their photocatalytic efficiency using organic dyes as a model system will be presented.

COLL 377

Coffee ring patterns of nanostructured amphiphilic silsesquioxanes on carbon films

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Coffee ring patterns of functionalized metallic or metal oxide nanoparticles on specific surfaces are the basis of technological applications such as the manufacture of transparent conductive coatings, sensors, photonic devices and microarrays used in combinatorial chemistry studies in genomics. In this manuscript it is shown that amphiphilic silsesquioxanes could be also self-assembled into *coffee ring* patterns on the surface of carbon films, a fact that can extend the applications of these patterns due to the versatility of the silsesquioxane chemistry. A precursor based on the reaction of (3-isocyanatopropyl) triethoxysilane (IPTES) with dodecylamine (DA) was hydrolyzed and slowly condensed in a tetrahydrofuran solution, in the presence of formic acid. The resulting colloidal dispersion of silsesquioxane nanoparticles was diluted with methanol and dip-coated on thin carbon films used as covers of TEM grids. A *coffee ring* pattern was spontaneously formed on the carbon surface by a combination of dewetting of the liquid film and induced capillary flow towards the pinning line. Silsesquioxane nanoparticles present in the boundary of each ring were composed of an agglomeration of crystalline nanorods (lengths of about 50-100 nm and diameters of 8 nm, as observed by HRTEM), interconnected by amorphous regions. SAED (selected area electron diffraction) showed that the inorganic Si-O-Si skeleton was organized as crystalline sheets exhibiting a 2D-hexagonal array. SAXS showed a tail-to-tail association of organic branches composed of strongly H-bonded urea groups and extended dodecyl chains (FTIR). A scheme describing the structure of the nanorods is proposed.

COLL 378

Electrochemical spot-welding for the reduction of electrical resistance in 2D single-walled carbon nanotube networks

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The effect of the electrochemical deposition of metal nanoparticles on the overall resistance of 2-dimensional networks of single-walled carbon nanotubes (SWNTs) will be presented. These networks show great potential for applications in energy conversion, sensors, catalysis, medicine, and electronics. The preparation of suspensions of unbundled SWNTs is an important step for the formation of SWNT networks for these studies. The Lay research group has developed an effective non-oxidizing purification method using probe sonication, followed by repeated centrifugation cycles at low centrifugal force (~18,000 G) that results in suspensions of unbundled, high-aspect ratio SWNTs. This involved the use of a common surfactant, sodium dodecyl sulfate (SDS), to disperse individual, undamaged SWNTs into an aqueous solution. These SWNTs suspensions were then deposited onto nonconducting substrates via an iterative deposition process that allowed strict density control. The electrodeposition of metal nanoparticles was observed to greatly reduce network resistance.

COLL 379

Versatile platform for investigating environmentally driven nanoparticle transformations

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Characterizing transformations of nanomaterials during release into the environment is difficult due to the aggregation, agglomeration, and particle loss associated with recovery of these materials. Comparisons of the reactivity on surfaces and in solution also need to be better characterized to be understood. These difficulties limit our ability to fully understand the impacts of nanomaterials released into the environment. We utilize functionalized SiO_2 surfaces to self-assemble a sub-monolayer of nanoparticles on the surface. This approach allows us to view transformations *in situ*. Direct visualization and manipulation of silver and gold nanoparticles allow us to determine effects of exposure to various chemical environments. We were able to show that silver is oxidized and reduced environmentally, and both macro- and nano-sources generated nanoparticles in humid environments. We were also able to show the impacts of manipulating the ligand shells of gold nanoparticles. Using this approach we have been able to visualize changes to these dynamic systems before and after environmentally relevant treatments.

COLL 380

WITHDRAWN

COLL 381

SERS study of L-tryptophan adsorbed on Au/Ag nanoparticles surfaces

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This research seeks to establish the most stable conformation and orientation of L-tryptophan (Trp) on gold and silver nanoparticles surfaces and to determine how these parameters are affected by analyte concentration, nanoparticle size and colloidal pH values. The purpose is to determine if the Trp molecules interacts with the surface through the carboxilate, through the amino groups or through both. Surface-enhanced Raman scattering (SERS) spectra of Trp at 200 – 3200 cm^{-1} spectral range and 785 nm laser line excitation were obtained, since using this technique allows that L-tryptophan to be detected at very low concentrations. Gold nanoparticles were synthesized using the citrate reduction method. On the other hand, silver nanoparticles were prepared following the so called "green synthesis" which consists of the silver nitrate reduction by sodium borohydride as a reducing agent and sodium citrate as a capping agent. Trp solutions were prepared in the concentration range of 10^{-3} to 10^{-9} M. The experimental procedure developed, which includes the use of electrolytes (NaCl and Na_2SO_4) for colloid activation resulted in very high enhancement factors of the Raman signal of Trp on small silver nanoparticles at 10^{-4} M with sodium chloride, and for Trp on gold nanoparticles at 10^{-5} M with sodium sulfate. The observed spectra allow us to suggest that for small size nanoparticles high concentrations of Trp must to be used, and for large size nanoparticles the opposite was needed for achieving high sensitivity of detection.

COLL 382

Novel preparation method of Pt/C using colloidal carbon and Pt

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High surface area carbon support is employed to facilitate the dispersion of expensive Pt active sites, both to enhance the activity and reduce the cost in PEMFC. Pristine carbon support exists as aggregates in the range of 10~50 micrometers. The aggregation of carbon support reduces the availability of surface for the effective dispersion of Pt; leading to the ineffective utilization of Pt. Carbon support with aggregate size close to its primary particle size (i.e. 30 nm) is preferred in order to enhance the utilization of Pt. The current study reveals the key parameters for the preparation of nanometer size (as small as 90 nm) colloidal carbon support such that almost all of the carbon surface are available for the deposition of expensive Pt. Furthermore, methods for the preparation of colloidal Pt (particle size as small as 2 nm) and its subsequent deposition onto the colloidal carbon will also be revealed.

COLL 383

Europium (III) chelating coatings with tunable time-resolved fluorescence properties on amino-surfaces

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There has been a growing interest in surface tailoring for the purposes of immunoassays and DNA detection of biosensors, artificial or intelligent membranes, molecular electronic devices and novel materials. This paper describes an approach to developing repeatedly regenerable time-resolved fluorescent chelating surface, which is based on complexation and dissociation interactions. As a Europium (III, Eu^{3+}) chelator, BCPDA (abbreviated from 4, 7-bis (chlorosulfophenyl)-1, 10-phenanthroline-2, 9-dicarboxylic acid) and its amine derivatives were synthesized in facile procedures. The BCPDA and its derivatives could covalently be attached onto the amino-surfaces of silanized glasses, silica and polymer membrane under relatively mild conditions, generating BCPDA-derivatized coatings capable of chelating Eu^{3+}. Subsequent incubation with Eu^{3+} solution initiated complexation to give time-resolved fluorescent surfaces, thus the fluorescence spectra and related lifetimes were determined. Further immersion of complexed surfaces in acidic solution regenerated chelating coatings as a result of Eu^{3+} dissociation. These results implied promising applications in display and anti-falsification materials, surface micropatterned devices and biomolecules labeling and detection based on such principle of complexing interactions.

COLL 384

Bacterial chemotaxis to enhance bioremediation

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Bacterial chemotaxis is a phenomenon that has been explored as a means of enhancing bioremediation. Chemotactic bacteria demonstrate the ability to sense higher concentrations of organic contaminants and migrate towards them. This study used a two-dimensional microcosm filled with sand to model a homogenous aquifer. Sodium benzoate was continuously injected horizontally across the microcosm. Trials were conducted in which either *P. putida F1* (*PpF1)* or a non-chemotactic mutant were injected and pumped transversely through the aquifer. Samples were taken at the outlet to measure the vertical migration of bacteria towards the attractant, and the migration of *PpF1* was compared to that of the non-chemotactic mutant to determine the extent of a chemotactic response. Results indicated that *PpF1* exhibited greater migration towards the benzoate plume than non-chemotactic bacteria. This suggests that chemotaxis may enhance bioremediation in groundwater systems.

COLL 385

Peptide adsorption to hydrophobic surfaces

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Objective: To gain insight into the mechanisms controlling adsorption, two peptides (beta-casein, alpha-synuclein) were studied by isothermal titration calorimetry (ITC) in terms of their adsorption behavior onto modified hydrophobic polystyrene beads.

Method: Peptide solutions were titrated into the beads in the temperature range from 10 to 47°C.

Preliminary results: The interaction between protein and surface is exothermic and occurs in spite of the fact that at pH 7.4 both are negatively charged. The enthalpy of adsorption becomes more favorable with increasing temperature, indicating a negative heat capacity. The association constant, K, is in a 1/µM range, indicating strong binding. The Gibbs free energy and the adsorbed amount of beta-casein seem to be independent of temperature, while for alpha-synuclein both parameters increase in absolute value with increasing temperature.

Preliminary conclusions: The process is driven by non-electrostatic forces that compensate for unfavorable electrostatic repulsion and loss in conformational entropy.

COLL 386

Quantifying nisin adsorption behavior at pendant PEO brush layers

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An understanding of peptide loading and release from polyethylene oxide (PEO) brush layers will provide direction for development of new strategies for drug storage and delivery. In this work, optical waveguide lightmode spectroscopy was used to record changes in adsorbed mass during cyclic adsorption-elution experiments with the antimicrobial peptide nisin, at uncoated and PEO-coated surfaces. Nisin shows potent activity against Gram-positive bacteria including the most prevalent implant-associated pathogens, does not give rise to resistant bacteria and does not appear to be toxic to humans, suggesting good potential for its use in antibacterial coatings for selected medical devices. Kinetic rate constants for nisin adsorption and desorption were determined at PEO-coated surfaces featuring different chain lengths and chain densities. In addition, kinetic patterns were interpreted with reference to a model accounting for history-dependent adsorption, to evaluate the effects of pendant PEO on the lateral clustering behavior of nisin at these interfaces.

COLL 387

Activity retention of nisin against *Staphylococcus epidermidis* after entrapment within pendant PEO brush layers

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The antimicrobial peptide nisin has been shown to integrate into polyethylene oxide (PEO) brush layers without compromising protein repulsive character. But questions remain surrounding the potential for compromised biological activity of the peptide owing to its surface immobilization in this way. When present in solution at physiologic pH and temperature, nisin was shown to retain activity against *Pediococcus pentosaceus* for up to 28 days, even at nanomolar concentrations. In this work, nisin-loaded, covalently stabilized PEO coatings were synthesized on silicon wafers as well as polyurethane catheter segments. Coated materials were challenged with blood plasma for periods up to 28 days, at physiologic pH and temperature. Surfaces were withdrawn at selected times and placed on plates inoculated with *Staphylococcus epidermidis* to measure kill zone radius in order to quantify nisin activity. Multifunctional coatings based on entrapped nisin prospectively will improve endovascular device biocompatibility through reduction of infection as well as thrombosis.

COLL 388

Block copolymer modified surface for biomolecules conjugation

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Polymer brush layers based on block copolymers of poly(oligo(ethylene glycol) methacrylate) (POEGMA) and poly(glycidyl methacrylate) (PGMA) were formed on silicon wafers by surface-initiated atom transfer radical polymerization(SI-ATRP). Various bioactive molecules can be conjugated directly to the brush surfaces by reaction of PGMA epoxide groups with biomolecule amino groups, while POEGMA, which resists non-specific protein adsorption, provides an anti-fouling environment. The lengths of the blocks, and hence the thickness of the POEGMA and PGMA layers, were controlled by varying the polymerization time. Surfaces were characterized by water contact angle, ellipsometry and XPS to confirm the modification reactions. The influence of relative block thickness on protein adsorption was investigated by radiolabeling methods. Phase segregation of the copolymer segments and its effect on biomolecule (eg lysozyme) attachment was studied using AFM. Such surfaces may be useful as biological recognition elements of high specificity for functional biomaterials.

COLL 389

Secondary structure effects on peptide adsorption

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The impact that protein secondary structure may have on protein adsorption has been, hitherto, largely unstudied. To this end, secondary structures (α-helix, β-sheet) were induced in Poly L-Lysine (PLL) *via* modulating solution pH and temperature. Circular dichroism (CD) and quartz crystal microbalance with dissipation (QCM-D) were used to study adsorption of PLL to Au surfaces. CD results confirmed that secondary structures (α-helix, β-sheet) persist upon adsorption onto Au. QCM-D revealed: (1) initial adsorption rates for α-helix was ~2.4 times higher than β-sheet; (2) plateau adsorbed amount was ~4.6 times more for β-sheet than α-helix; and (3) fitted viscosities suggest α-helix forms a more rigidly bonded layer on Au. Surface interactions between PLL and Au were analyzed by DLVO theory, predicting the ratio of interaction energies for β-sheet and α-helix to Au as ~0.36, which is in good agreement with experimentally estimated value ~0.41 based on initial adsorption rates from QCM-D measurements.

COLL 390

Interaction of galactose modified polyvinylamine with lectin from Ricinus communis agglutinin

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Interactions of glycopolymers with cell surface lectins can be exploited in cell-specific biomedical materials, drug delivery systems and biological recognition substances. We have developed novel glycopolymers synthesized through modification of polyvinylamine (PVAm) backbone with galactose pendant groups. The interaction of this sugar modified polymer with a galactose responsive lectin from Ricinus communis agglutinin (RCA) was investigated using a Dissipative Quartz Crystal Microbalance (QCM-D). PVAm-g-galactose spontaneously bound to a variety of surfaces and the QCM-D measurements showed that the immobilized galactose specifically bound lectin.

COLL 391

Study on sequential adsorption of oppositely charged lysozyme and albumin

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Protein adsorption is a crucial event in biomaterial research since it is the initial body response to an implanted biomaterial and can determine the success of the implant. It is widely known that electrostatic interaction/repulsion plays a significant role in protein adsorption. However, exceptions exist in that factors other than electrostatic attraction can dominate. We examined the sequential adsorption of oppositely charged proteins such as albumin and lysozyme. Protein adsorption was performed sequentially three times and monitored using an attenuated total reflectance Fourier infrared spectroscope. Results elucidated that adsorption can take place in the potential presence of electrostatic repulsion. Protein adsorption was quantified by normalization and simulated to produce adsorption coefficients. The presence of preadsorbed protein can significantly affect additional protein adsorption. When lysozyme was pre-adsorbed, additional protein adsorption was appeared to be greatly suppressed. These results suggest that adsorbed lysozyme can exert steric and passivating effects.

COLL 392

Rheological characterisation of lysozyme adsorption to oil-water interface using double wall ring geometry

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Objectives: To characterize lysozyme adsorption to an oil-water interface, in the presence and absence of surfactants, using the double wall ring (DWR) rheological method and surface tension measurements.

Methods: Oscillatory shear measurements were conducted on a TA AR-G2 rheometer with a DWR geometry (0.1 Hz, 25°C and strain = 1%). The pendant drop used a droplet of 70 mL, formed with a needle (diameter 1.83 mm), and lowered into the oil-phase. The aqueous phase was withdrawn after 10 min to study film formation.

Results: The adsorption of lysozyme to the oil-water interface results in the formation of a flexible film. The DWR method seems more efficient in detecting the starting phase of lysozyme adsorption, especially in the presence of more hydrophobic surfactants.

Conclusion: The DWR geometry is a good tool for characterisation of lysozyme multilayer formation at oil-water interfaces and the results are in coherence with the surface tension measurements.

COLL 393

Responsive polymeric IPN of silk protein for drug delivery

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A series of responsive interpenetrating polymer networks (IPNs) composed of silk protein (silk sericin, SS) were prepared. The responsive hydration and protein releasing profile of the polymeric IPNs were investigated.

First, a temperature responsive IPN composed of SS and poly(N-isopropylacrylamide) (PNIPAAm) was prepared. It was found that the intermolecular interactions between SS and PNIPAAm resulted in miscible polymeric IPNs and the swelling ratio of the IPNs depended strongly on the temperature of the environment.

A fast pH-responsive silk sericin (SS)/poly(methacrylic acid) (PMAA) IPN hydrogels were also prepared constructed. The hydrogels displayed definite pH sensitivity under physiological conditions, as well as sharp changes in the mesh size of their network as a function of the composition and pH of the swelling media. Bovine serum albumin (BSA) was chosen to evaluate the permeation profile through the IPNs in both the simulated gastric and intestinal pH conditions.

COLL 394

Adsorption kinetics of total proteose peptone fractions at the air-water and *n*-dodecane-water interface

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Surface properties of whey proteins are essential in applications requiring oil emulsification in an aqueous phase, or foam structure formation [1]. The adsorption at interfaces constitutes then an approach of the physico-chemical mechanisms of foaming and emulsifying properties. Proteose-peptone is the minor fraction of whey's protein, thermoresistant and acid-soluble protein fraction extracted from milk [2], and known for its interesting surface properties [3]. In this study, the TPP fractions were extracted from skimmed milk UHT (milk TPP) and whey protein concentrate (WPC TPP). Their adsorption kinetics at the air-water and *n*-dodecane-water interfaces was investigated by the drop volume tensiometer method. Protein solutions of 1% (w/v) were characterized under dynamic condition at various pH (4.0; native pH 4.67- 4.70 and 7.0). Milk TPP showed the lowest values as well as a faster reduction in surface tension at both considered interfaces. Therefore, TPP were found to be effective as surfactants. These results let us to presage good emulsifying and foaming properties of milk TPP compared to WPC TPP. The considerable influence of pH and extraction source on proteose-peptone's interfacial property have been highlighted.

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COLL 395

Influence of pluronic F127 on the distribution of protein molecules and resulting spot morphology of microarrays in a porous nitrocellulose substrate

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The protein microarray is an emerging application format in diagnostics. High quality microarrays are produced on various substrates. However, the distribution of printed biomolecules on these substrates is often non-homogeneous, commonly known as the “doughnut or coffee-stain effect”. We studied the influence of pluronic F127 in the printing buffer on spot morphology in porous nitrocellulose membranes (11 µm thick); a high signal-to-noise substrate. Antibodies specific for discriminating tags were printed on nitrocellulose membrane pads on slides using phosphate buffered saline (pH 7.4) and various concentrations of pluronic F127 as a printing buffer. Double-tagged amplicons were sandwiched in an one-step incubation between the printed antibodies and streptavidin conjugated flurophore. Results were analyzed by the 'Z-stack' method of the confocal laser scanning microscope. The intensity distribution in each stack was assessed. Printing antibodies with increasing concentrations of pluronic F127 up to 0.2% (w/v) showed an increasing uniformity of spot morphology.

COLL 396

Bioactive peptide conjugated polymer brushes for controlled astrocyte adhesion and proliferation

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The ability to control and manipulate the properties of implant surfaces without altering bulk properties is important in the design of biomedical devices. In the present work we have developed bioactive polymer brushes conjugated with biologically active peptides to provide a synthetic, scalable alternative to complex extracellular matrix proteins, and thereby promote the specific adhesion and growth of astrocytes for neural implant applications. We synthesized polyhydroxylacrylamide (PHAM) brushes on surfaces and conjugated with four different types of short peptides. Our results show that astrocytes adhered significantly more on laminin and long fibronectin-based peptide modified PHAM brushes compared to other samples when the cells were grown for 3 days on these substrates. Astrocyte adhesion and proliferation depended on surface properties, polymer brush chemistry and the types of peptides conjugated. This approach will have the potential for use as a coating for neural electrode in the treatment of spinal cord injury.

COLL 397

Determining the orientation of electrostatically immobilized cytochrome C by time-of-flight secondary ion mass spectrometry and sum frequency generation

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The ability to orient proteins on surfaces, to control exposure of their biologically active sites, will benefit a wide range of applications. In this study, we examined the change in orientation of horse heart Cytochrome c on both NH_3^+ and COO^- self-assembled monolayers by time-of-flight secondary ion mass spectrometry (ToF-SIMS) and sum frequency generation (SFG) spectroscopy. The positively charged region at one end Cytochrome c electrostatically binds to the COO^- substrate while the NH_3^+ surface elicits the opposite binding orientation. Within the SFG spectra, ordering of the alpha helices within the protein was confirmed by the feature at 1645 cm^{-1} and this change in orientation, induced by the two different substrates, is confirmed by intensity differences within ToF-SIMS spectra between ions stemming from asymmetric distributed amino acids (Glutamic acid, Aspartic acid).

COLL 398

WITHDRAWN

COLL 399

Characterization of protein (BSA) adsorption to the water-oil interface

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Objective. To study interfacial (w/o) adsorption of protein using rheology and pendant drop techniques.

Methods. Solutions of bovine serum albumin (BSA) were mixed with 0-10%v/v thermally unfolded BSA (0.15mM) (final concentration of 1mM) and interfacial properties with Miglyol 812 were determined. Interfacial rheology used a double-wall-ring geometry accessory (oscillation 0.1Hz; strain of 0.1%). Pendant drop measurements used an aqueous drop of 50µL (needle diameter 1.83mm).

Results. BSA formed a viscoelastic region at the w/o interface. Addition of thermally unfolded protein delayed the formation giving similar elastic and viscose moduli after 1h. Surface tension was decreased by native protein alone (to 6.51±0.04 after 10min) with a less decrease for solutions containing thermally unfolded BSA (to 6.66±0.04 after 10min). The magnitude and time-course of behavior suggests effects are due to more than native protein concentration alone.

Conclusion. Rheology and pendant drop measurements are useful to study protein physical behavior at liquid interfaces.

COLL 400

Ligand-mediated sequestering of integrins in raft-mimicking lipid mixtures

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Combined confocal fluorescence spectroscopy, photon counting histogram (PCH) analysis, and epifluorescence microscopy is used to quantitatively study the effect of the native ligands vitronectin and fibronectin on domain–specific sequestration and oligomerization state of integrins ($\alpha_v\beta_3$ and $\alpha_5\beta_1$) in polymer-tethered lipid bilayer systems containing raft-mimicking lipid mixtures. Specifically, experiments were conducted on integrins in bilayer-spanning raft-mimicking domains (TYPE I), binary cholesterol-lipid mixtures (TYPE II), and monolayer raft-like domains (TYPE III). Our experiments show that $\alpha_v\beta_3$ and $\alpha_5\beta_1$ sequester preferentially to liquid disordered domains in the absence of ligands. Remarkably, ligand addition causes substantial changes in integrin sequestering without altering their largely monomeric state in the model membrane. Comparing experiments on TYPEs I-III also demonstrate that alterations in lipid heterogeneity may have substantial impact on ligand-mediated integrin sequestering, thus highlighting the importance of lipid composition on the functionality of individual membrane receptors.

COLL 401

Studies of biological membranes on silica particles

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In the present study we investigated lipid-lipid interactions in membranes adsorbed to the surface of silica nanoparticles. We used an approach that exploits the influence of membrane-associated electron spin labels on the triplet state relaxation kinetics of membrane-bound fluorophores. The singlet-triplet state transition within the dye Lissamine Rhodamine B (LRB) is significantly affected when residing in the vicinity of the stable nitroxide radical TEMPO. These interactions are distance dependent and result in a change in the fluorescence signal, which was measured using fluorescence correlation spectroscopy (FCS). This method allows the measurement of a strong fluorescence signal in studies of low-frequency molecular interactions, because the lifetime of the triplet state is considerably longer than the singlet-singlet transition.

Using the above-described approach we studied the influence of a silica surface on the lipid-lipid interactions in model membranes. The effect of functionalized surfaces on the membrane fluidity is addressed as well as the influence of size and morphology of the silica particle.

COLL 402

N-halamine-based rechargeable and long-term antimicrobial polyurethane tubing

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The polyurethane(PU) tubing surfaces were covalently bound with 5, 5-dimethyl hydantoin (DMH), an N-halamine precursor, using MDI as a coupling agent under one step in site surface modification. The reactions were confirmed by attenuated total reflectance infrared. Upon bleach treatment, the DMH moieties on the PU tubing surfaces were transformed into N-halamine, providing powerful, durable, and rechargeable antimicrobial activities against Staphylococcus aureus (S. aureus, Gram-positive), Escherichia coli (E. coli, Gram-negative), methicillin-resistant staphylococcus aureus (MRSA, drug resistant Gram-positive bacteria), vancomycin-resistant enterococcus (VRE, drug resistant Gram-positive bacteria), and Candida albicans (C. ablicans, fungi). SEM studies demonstrated that the N-halamine-based PU tubing could effectively prevent the formation of bacterial and fungal biofilms. These encouraging results point to great potentials of the new N-halamine-based PU tubing for a wide range of related medical, environmental, and industrial applications to controlling the

formation ofbiofilms.

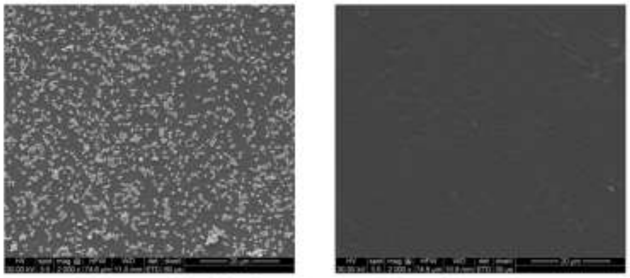

Figure 1. Biofilm-controlling function of (a) the original PU film against *S. aureus*, (b) the chlorinated PU-MDI-DMH film against *S. aureus*

Keywords: Antimicrobial, Biofilm-controlling, N-halamine, Chlorination, Rechargeable, Polyurethane, Tubing.

COLL 403

Long-term drug delivery system to treat Candida-associated denture stomatitis

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Candida-associated denture stomatitis is an inflammatory process caused by *Candida* biofilms, leading to complications including infections and in antifungal resistance. To overcome these clinical concerns, a long-term antifungal denture biomaterial was developed by copolymerizing *N*-vinyl-2-pyrrolidinone (NVP) with diurethane dimethacrylate (DUMA). NVP content varied at 50%, 60%, and 70% in the initial feed. The new resin materials strongly bind antifungal agents, and then slowly release them for weeks to months. The release drugs demonstrated excellent antifungal and biofilm-controlling efficacy against *Candida* species without negatively affecting biocompatibility on mouse 3T3 fibroblast cells. Additionally, the antifungal agents bound onto the denture device can be easily quenched, recharged, and rotated to other antifungal agents. The new antifungal denture biomaterials are attractive candidates for a broad range of biomedical applications.

Keywords: denture stomatitis, biocompatibility, antifungal agents, biomaterials

COLL 404

Chitosan-immobilized polymer surfaces for rechargeable antimicrobial drug binding and releasing

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Microbial contamination on medical device material surfaces causes serious problems such as device-related infections. Here we report a new strategy to produce rechargeable antimicrobial surfaces to address the issue. Methacrylic acid (MAA) was grafted onto the surfaces of polyvinyl chloride (PVC) and polyurethane (PU), two widely used biomaterials with excellent biological and mechanical properties. Chitosan was covalently bonded onto the MAA-grafted surfaces. The new chitosan-containing surfaces strongly bind and then slow release anionic antibiotics (e.g. rifampin) for weeks to months to kill microbes. The released drug can be recharged to further extend antimicrobial duration. Also, the new surfaces demonstrated good biocompatibility against mammal cells, pointing to great potentials for a wide range of biomedical applications.

COLL 405

N-halamine based polymeric antimicrobial additive: preparation, characterization, antimicrobial activity, and biocompatibility

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Abstract: An *N*-halamine-based polymer additive was synthesized by reacting the potassium salt of 5, 5-dimethylhydantoin (DMH) with Poly (2-chloroethyl methacrylate) (PCLMA). The product was characterized by ^{1}H NMR and EA analysis. The new polymer (DMH-PCLMA) was incorporated into cellulose acetate (CA) through solvent casting to serve as an antimicrobial additive. After chlorination treatment with diluted bleach, the resulting CA/Cl-DMH-PCLMA films provide a total kill of 10^6-10^7 CFU/mL of *Escherichia coli* (Gram-negative bacteria), S*taphylococcus aureus* (Gram-positive bacteria), and *Candida albicans* (fungi) within 1 hr. *In vitro* biocompatibility was determined by rat skin cell viability analysis, which demonstrated that the presence of new the polymeric *N*-halamine-based additive did not negatively affect the biocompatibility of the CA films.

COLL 406

Surface active fibrous polymers containing polyoxometalates

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Synthesized Dawson structure polyoxometalates (POMs) with nickel and iron substitutions have been incorporated into polymer matrices in prior studies for surface chemical decomposition. These challenges consist of pesticides and organics residing on painted surfaces. These same materials have also been incorporated into polymer

matrices and electrospun to form thin fibers for applications in nano-functional materials. The current research focuses on the formation of fibrous materials which exhibit high surface areas for the applications of POMs in the decontamination of microbial contaminants. The goal of the fibrous materials is to be incorporated onto surfaces, which could ultimately be utilized in applications such as air filtration as well as other textile materials. These novel fibrous materials of POMs were created by electospinning the polymer/POM mixture to create a surface covered with fibers that were then subjected to microbial challenges or calcinations followed by microbial challenges. The fibrous materials were examined for decontamination challenges against a variety of pathogens and are reported herein. The fibers were also characterized using a variety of surface analysis techniques including SEM to obtain correlation of effectiveness to size distribution and surface area effects on decontamination.

COLL 407

New approaches of a mathematical model to the development of biosensor

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High blood cholesterol is a major risk factor of cardiovascular disease, and coronary disease. A mathematical model has been developed to simulate biosensor kinetic for cholesterol determination

COLL 408

Biodegradable material dynthesis and its application to biological cells

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A biodegradable material made from copolymer PLG can achieve sustained release of the imbedded chemoattractant and microbead to the surrounding tissue.

COLL 409

Tailoring activation of bituminous coal for hampering oligomerization of multicomponent organic contaminants

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Activated carbon has been a reliable technique used increasingly in water and wastewater treatment for the removal of relatively low-molecular-weight organic compounds, such as phenols. Phenol and its derivatives are the basic structural units of a wide variety of synthetic organic pollutants including many pesticides. Studies of the adsorptive properties of activated carbon have shown that presence of molecular oxygen in the aqueous phase promotes chemical transformation, such as oligomerization of the organic compounds on the carbon surface, thus decreasing the regeneration efficiency of activated carbon. Therefore, economic use has been a major concern in activated carbon usage. To solve this problem, this study proposes an approach to produce activated carbon for hampering oligomerization of organic contaminants present as multi-solute and will eventually render the activated carbon more cost effective. Adsorption isotherms of single solute (2,4-dimethylphenol), binary solute (2-methylphenol/2,4-dimethylphenol) and ternary solute (phenol/2-methylphenol/2,4-dimethylphenol) were studied, using developed activated carbon and commercial activated carbon (Calgon F400). All single solute, binary solute and ternary solute adsorption on developed activated carbon showed that no impact of the presence of molecular oxygen on the adsorptive capacity, indicating that the developed activated carbon is very effective in hampering the oligomerization of phenolic compounds for multicomponent adsorption. These results were compared to a commercially produced activated carbon (Calgon F400) where significant oligomerization of these compounds were noticed.

COLL 410

Encapsulation of light-emitting diodes with silver nanoparticle/silicone composite

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Recently, there is an increasing need for high power white light emitting diodes (LEDs) with high efficiency. To be applied for the general lighting applications, even higher efficiency must be achieved. Light conversion efficiency of the phosphors to generate white light using blue-emitting LEDs is one of the crucial factors to determine the overall LED's efficiency. In this study, we fabricated Ag nanoparticle-phosphor hybrid composites to enhance the light conversion efficiency by utilizing the resonant coupling of localized surface plasmon resonance (LSP) in Ag nanoparticles and phosphors. We tuned the absorption and scattering spectra of the Ag nanoparticles in order to achieve the optimal coupling by altering those sizes and shapes. The effects of encapsulation

conditions of LEDs with Ag nanoparticle-phosphor-silicone composites on the light conversion efficiency were also investigated.

COLL 411

Double ammonium salts orientated hollow magnetic ferrites MFe_2O_4 (M=Fe, Mn, Co, Zn) fabrication and comparison

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MFe_2O_4 (M=Fe, Mn, Co, Zn) particles were synthesized via facile solvothermal route by employing ammonium bicarbonate (NH_4HCO_3) and ammonium acetate (NH_4Ac) as structure-guiding reagents. However, the magnetite (MFe_2O_4, M=Fe, i.e. Fe_3O_4) particles obtained under the double ammonium salts are distinguished from MFe_2O_4 (M=Mn, Co, Zn) particles obtained under the same condition. Fe_3O_4 particles with hollow construction were formed by introduction of co-structure-guiding reagents NH_4HCO_3 and NH_4Ac, or by independent introduction of NH_4HCO_3 or NH_4Ac. The architecture, morphology and magnetism of the target Fe_3O_4 particle were controlled by the ammonium concentration. However, the ferrite MFe_2O_4 (M=Mn, Co, Zn) products prepared by employing co-structure-guiding reagents NH_4HCO_3 and NH_4Ac were composed of two different shapes and architectures which distinguished from hollow Fe_3O_4 particles under the same condition. Meanwhile, the MFe_2O_4 (M=Mn, Co, Zn) particles were prepared by single NH_4HCO_3 and NH_4Ac addition respectively, the monodisperse and hollow MFe_2O_4 (M=Mn, Co, Zn) were obtained when and only when by singly introducing NH_4Ac as only structure-guiding reagent, but similar particles couldn't be obtained by NH_4HCO_3 only. The results shown that the NH_4HCO_3 play key role in MFe_2O_4 (M=Mn, Co, Zn) particles formation, and the MCO_3 (M=Mn, Co, Zn) particles-in-process greatly retarded the growth of MFe_2O_4 (M=Mn, Co, Zn) particles formation. Consequently, both the concentration and ratio alteration between NH_4HCO_3 and NH_4Ac highly determined the composition and structure evolution (whether it is hollow or solid) of final particles of magnetic ferrites MFe_2O_4 (M=Fe, Mn, Co, Zn). Also, a possible mechanism of ferrite hollow spheres formation and evolution was proposed and discussed.

COLL 412

Effect of local heating on catalysis by functionalized magnetic nanoparticles under alternating magnetic field

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Magnetic nanoparticles are an important class of materials with a wide variety of applications such as catalytic supports, storage media, agents for targeted drug delivery, MRI contrast, and magnetic hyperthermia. In this study, we synthesized magnetic iron oxide-embedded mesoporous silica nanoparticles (IO-MSN) functionalized with catalytic organic groups. Using the aldol condensation as a model reaction, we studied the catalytic activities of the materials under an alternating magnetic field (AMF). We compared these activities to those obtained by conventional heating in an oil bath. When the two heating methods were adjusted to result in comparable bulk solution temperature, faster kinetics were observed using AMF heating, indicating a local heating effect. The AMF frequency used in the study is not absorbed by the reagents or solvent in the reaction; the enhanced reactivity comes from the iron oxide source. Factors affecting the local heating will also be discussed.

COLL 413

Microreactor for continuous heterogeneous photochemical oxidation via singlet O_2

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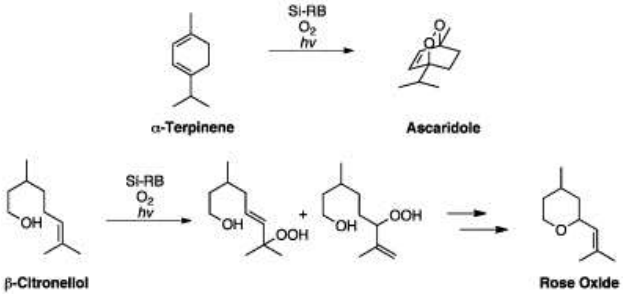
Singlet oxygen was effectively and safely generated in a microscale reactor and used for the synthesis of ascaridole and rose oxide. The technique allows for the continuous generation of singlet oxygen without the inherent dangers of large quantities of oxygenated solvents, through the use of a heterogeneous photocatalyst.



COLL 414

New approaches to the material chemistry application of miniaturization with respect to electronic packaging and component

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This paper represents the material development of new trends and technologies in miniaturization with respect to electronic packaging and component.

COLL 415

Functionalization of gold nanoparticles with metal complexes in presence of cationic surfactant

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Gold Nanoparticles (AuNP) have been a large focus the past years, the stability and versatility of these AuNP allow for multiple variations and functions. Citrate capped gold nanoparticles are functionalized with 6-mercaptohexanoic acid (MHA), where MHA replaced the citrate. The carboxylate end of the MHA was successfully coordinated to a metal complex in presence of cationic surfactant, cetyltrimethylammonium bromide (CTAB) at and above physiological pH. The system was characterized using FTIR, NMR, UV-vis and Raman spectroscopy.

COLL 416

Gold nanoparticles in denture base: Synthesis and influence on polymer's thermal conductivity

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Heat-polymerized acrylic resin with and without gold nanoparticles were prepared and subjected to thermal diffusivity testing. Cylindrical test specimens containing an embedded Pt-wire were used to determine heat conductivity and thermal diffusivity of the investigated system over a physiologic temperature range (0 to70 ^{o}C) based on the in-stationary heat-wire method. The samples temperatures were regulated by performing all the measurements in aqueous media in a thermostat unit LabTemp-30190 in order to exclude any convective influences (See Figure 1).

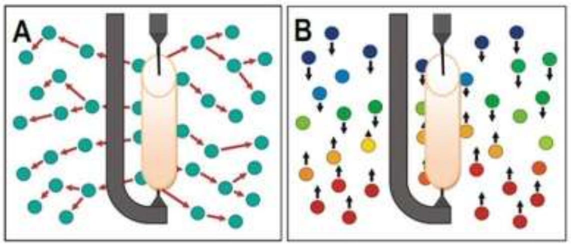

Figure 1: Temperature allocation. In A-homogeneous: The temperature is equal in the whole sample, so almost no convection takes place, while in B-inhomogeneous: The temperature is cool above and warmer on the bottom in which the temperature differences lead to convention

Thermal diffusivities of the composites were found to be significantly higher than the unmodified acrylic resin. It increases in proportion to the content of gold nanoparticles filler, which suggests great dispersion/distribution of gold nanoparticles throughout the insulating polymer matrix that might have formed a pathway for heat conduction. Gold nanoparticles fillers have a potential as added components in denture bases to provide increased thermal diffusivity. These remarkable increases in the heat transfer characteristic of the acrylic resin base material could lead to more patient satisfaction. [The provided support by KACST through project No. AT-100-29 is acknowledged]

COLL 417

pH-dependent synthesis of pepsin-mediated gold nanoclusters with blue-, green-, and red-fluorescent emission

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Here we first demonstrate the pH-dependent synthesis of pepsin-mediated gold nanoclusters (Au NCs) with blue-, green-, and red-fluorescent emission from Au5 (Au8), Au13, and Au25, respectively. Pepsin is a gastric aspartic proteinase (molecular weight 34,550 g/mol) that plays an integral role in the digestive process of vertebrates. We found that the pH of the reaction solution was critical in determining the size of Au NCs (i.e. the number of gold atoms of Au NCs). Interestingly, the enzyme function of pepsin contributes to the formation of these Au NCs. The photo-stability of Au25 (or Au13) NCs is much higher than that of Au5 NCs (i.e. Au25 - Au13 >> Au5). The pepsin-mediated Au25 NCs were also found to be useful as fluorescent sensors for the detection of Pb^{2+} ions by enhanced fluorescence and the detection of Hg^{2+} ions by fluorescence quenching. Although the detailed formation mechanisms of these Au NCs require further analysis, the synthetic route using proteinase demonstrated here is promising for preparing new types fluorescent metal nanoclusters to apply in catalysis, opyics, biological labeling, and sensing.

COLL 418

Identification of a possible source for the nanoparticles found in the classical violin varnish

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The chemistry of the classical violin varnish continues to be debated. Of interest are the nano particles (NP) found in the ground coating. It has been proposed that these NPs were manufactured. The NP size proposes a dilemma, how were they produced? The majority of these NPs are calcium carbonate (CC). At the time of classical violin making, the pigment Bianco di San Giovanni, a partially carbonized CC, was available. The supernatant of this pigment contains NPs of precipitated CC . But why apply this to the violin? By application to maple, pine and violins, we found several interesting results. It can act as a plate stiffener, thus effecting plate acoustics. It can act as a wood dye. It turns the wood a golden brown with grain highlights. These changes are consistent with the nature of the classical ground. If Bianco di San Giovanni was used in violin construction awaits additional confirmation.

COLL 419

New polymeric surfactants made of pseudo–poly(amino acids)

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New amphiphilic polymeric surfactants, possessing a controlled ratio of alternating hydrophilic and hydrophobic blocks in a backbone chain, were designed using pseudo-poly(amino acids). Lipophilic fragments of surfactant macromolecules were synthesized through N-acylation of glutamic acid residues in reaction with saturated fatty acid, and further combining with poly(propylene oxide) sequences of differing length. Hydrophilic fragments of surfactants are based on poly(ethylene oxide) moieties with differing length. Hydrophilic lipophilic balance of the surfactants can be controlled by ratio of lipophilic fragments and length of poly(ethylene oxide) moieties. It is expected that due to presence of two different lipophilic fragments, the segmental mobility of the backbone chain increases. In addition, invertible (responsive) properties will be introduced to the macromolecules of surfactant, due to alternating hydrophilic and hydrophobic fragments in a backbone chain. Surface tension data on pseudo-poly(amino acids)-based macromolecules confirmed the surface activity and micellization of new surfactants.

COLL 420

Studies on high molecular weight cationic polyacrylamide "water-in-water" emulsion by dispersion polymerization

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Cationic polyacrylamide (CPAM) “water-in-water” emulsion refers to one kind of aqueous dispersions that acrylamide and other cationic hydrosoluble monomers carry out in the inorganic salt solution by dispersion polymerization, using a low molecular weight hydrosoluble polymer as stabilizer. Compared with the early CPAM products prepared by aqueous solution polymerization, inverse emulsion polymerization and microemulsion polymerization, CPAM “water-in-water” emulsion overcomes the disadvantages of insolubleness, environmental pollution, high power consumption and high cost, becoming a new direction of research, development and production of polyacrylamide. This emulsion owns its unique advantages of dissolving quickly, energy saving, environmentally friendly, convenient application and lower cost, so it is widely and effectively used in such fields as wastewater treatment, oil exploration, paper industry, ore flotation, etc[1]. It conforms to the tendency of green chemistry.

COLL 421

Surface changes and ion release kinetics of titanium dioxide nanoparticles in aqueous environment

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Previous studies have found the significant role of impurities (i.e., silicon, phosphorus) in the aggregation and sedimentation of TiO_2 nanoparticles in aqueous environment. In this study, we investigated the release kinetics of the impurities from 5 types of TiO_2 nanoparticles (i.e., 5, 10, and 50 nm anatase and 10 × 40, 30 × 40 nm rutile) at various pH and time scale. At both acidic and basic conditions, the 10 × 40 nm rutile showed the most leachable quantities of silicon; whereas, the 50 nm anatase showed the most leachable quantities of phosphorus. Both acidic and basic conditions accelerated the release of silicon, while the basic conditions enhanced the phosphorus release kinetics greatly. In addition, the leachable quantities of silicon and phosphorus increased with the increasing reaction time in aqueous solutions. Raman and FTIR spectroscopies were applied to identify the transformation of the TiO_2 nanoparticles in the aqueous environment.

COLL 422

Clean water with ferrite nanoparticles: Large scale synthesis and structure control

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Ferrite nanoparticles (MFe_2O_4, M = Zn (II), Mg (II) and Fe(II)) with controlled nanostructures were successfully synthesized and characterized with TEM, XRD, TG-DTA and SEM. It was found that the magnetic materials exhibit high ability for removing inorganic contaminants out water with the help of magnetic field. The microstructure and composition effects on the performances of the absorbents were also investigated.

COLL 423

Optical sensing of small ions with colloidal nanoparticles

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Colloidal nanoparticles, in particular gold nanoparticles and quantum dots, can be used in a variety of different assays for optical sensing of small ions in solution. In this review different detection principles are introduced and their potential use for detection in biological samples (such as intracellular sensing) is discussed.

COLL 424

Sulfur dioxide adsorption and photooxidation on titanium dioxide nanoparticle surfaces: Roles of surface hydroxyl groups and adsorbed water on the formation and stability of adsorbed sulfite and sulfate

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Titanium dioxide is a component of mineral dust aerosols which can play an important role in earth's atmosphere. In this work, transmission FTIR spectroscopy is used to probe the details of sulfur dioxide adsorption and photooxidation on TiO_2 nanoparticle surfaces. The role of surface hydroxyl groups and additional insights into the adsorption mechanism were investigated using $^{16}O–H$, $^{16}O–D$ and $^{18}O–H$ labeled surface O–H groups. These data show that surface hydroxyl groups are involved in the adsorption of sulfur dioxide, and in particularly, sulfur dioxide reacts with either one surface O–H group to yield adsorbed bisulfite or two surface O–H groups to yield both adsorbed sulfite and water. The photooxidation of adsorbed sulfite to sulfate occurs with UV irradiation. Furthermore, it is shown here that adsorbed water more easily displaces sulfite from the surface compared to sulfate by forming a stable sulfur dioxide water complex in the presence of adsorbed water. These differences in stability have

implications for adsorbed species that form as a result of surface heterogeneous reactions with sulfur dioxide on TiO_2 particle surfaces in particular and, potentially more generally, on oxide particle surfaces including other components of mineral dust aerosol.

COLL 425

Adsorption mechanisms of copper species on multiwall carbon nanotubes (CNTs): Study of chemical structures and regeneration of hybrids and as-received CNTs

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The copper adsorption on to CNTs is attributed to the formation of an inner-sphere complex between copper and CNT surface functional groups. At pH values exceeding the PZC (point of zero charge), oxygen functional groups give rise to a net negative surface charge promoting metal cation adsorption. CNT hybrids were obtained by recovering CNTs with copper from isotherm adsorption bottles after equilibrium. The solution pH dropped after equilibrium by release of H+ from CNT surface. Zeta potential experiments show that the electronegativity decreased (less negative surface charge) with increasing pH. Kinetic studies demonstrate the copper adsorption rate on OH functionalized CNTs, exceeded that of COOH functionalized CNT surfaces. Network forces within acid and alcohol functionalized CNTs bundles suggest formation of different mesopore structures, leading to the conclusion of different diffusivity driving forces. Kinetic modeling is proposed for the diffusion rate of copper. FTIR spectra compare vibration peaks of hybrids and as-received CNTs. XRD and SEM/EDX experiments confirm the presence of solid copper species at pH 4.7. ICP-AES analysis measures the amount of copper and other metals leaching from hybrids and as-received CNTs after different rinse cycles.

COLL 426

Effect of capping agent on interactions of zinc sulfide nanocrystals with an aquatic plant species

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Semiconductor nanocrystals are utilized in several practical applications, with widespread usage inevitably to result in their release into the environment. The small size of these materials, which is maintained by “capping” with different organic or

inorganic species, may result in harmful interactions with environmental systems. To examine the phytotoxicity of these materials, we have prepared zinc sulfide nanocrystals with three capping agents, sodium polyphosphate (SPP), polyvinylpyrrilodine (PVP), and L-histidine, and carried out growth studies with the aquatic plant *Spirodela polyrhiza*. As concentrations of the nanocrystals were increased in the nutrient solution, the relative growth rate, green frond count, and chlorophyll *a* concentration decreased. At the highest concentration (1000 mg/L), L-histidine was found to have the most detrimental effect on these parameters, followed by PVP and SPP. From the results we will elucidate the role the structure capping agent plays in the environmental fate of these nanocrystals.

COLL 427

Synthesis and immobilization of iron/palladium bimetallic nanoparticles within polymer electrospun nanofibrous mats for environmental applications

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The use of nanoscale Fe/Pd bimetallic nanoparticles (NPs) for environmental remediation is considered to be a promising approach for treatment of contaminated water. However, the conventionally used colloidal Fe/Pd NPs usually aggregate rapidly and result in a reduced reactivity. Herein, we employed electrospun polyacrylic acid (PAA)/polyvinyl alcohol (PVA) polymer nanofibers as a nanoreactor to immobilize Fe/Pd NPs to reduce the particle aggregation. In our study, the electrospun PAA/PVA nanofibrous mats were immersed into the ferric solution to allow Fe(III) ions to complex with the free carboxyl groups of PAA, followed by an in situ reduction reaction with sodium borohydride to form zero-valent iorn (ZVI) NPs. Fe/Pd bimetallic NPs were then formed by the partial reduction of Pd^{2+} with Fe^0 NPs. The functionalized electrospun nanofibrous mats containing Fe/Pd bimetallic NPs with a diameter of 2.8 nm were characterized by scanning electron microscopy, energy dispersive spectroscopy, transmission electron microscopy, thermogravimetric analysis and inductively coupled plasma atomic emission spectroscopy. The Fe/Pd NPs-containing electrospun PAA/PVA nanofibrous mats exhibited higher reactivity than that of the ZVI NPs-containing mats in the dechlorination of trichloroethylene (TCE), which was used as a model contamiant. With the high surface area to volume ratio and high porosity of the fibrous mats immobilized with the bimetallic NPs, the composite nanofibrous mats should be amenable for applications in remediation of various environmental contaminants.

COLL 428

Tip entry mechanisms for carbon nanotube endocytosis and cellular frustration

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The pathogenicity of carbon nanotubes has been linked in some studies to their one-dimensional geometry coupled to long fiber length, which hinders complete cellular internalization. Biophysical models have been proposed for the cell entry of spheres and elliptical nanostructures, but one-dimensional nanomaterials are a more complex case. This work combines in vitro experiments with course-grained molecular dynamics simulations of complete lipid bilayer segments to study the molecular interactions that initiate nanotube internalization. Uptake is shown to occur when the rounded end caps mimic particles and initiate endocytosis through receptor binding, membrane wrapping, and tip-first entry. Asymmetric strain in the membrane causes tube rotation to a near-vertical state, in which the cells cannot sense or respond to the total tube length. The implications of this tip-entry mechanism will be discussed for cell frustration, the activation of toxicity pathways, and the possible safe design of nanotubes through tip reformulation.

COLL 429

WITHDRAWN

COLL 430

Fate and transport of silver nanoparticles and related products in saturated porous media

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Nanosilver is the largest and fastest growing category of nanomaterials. A growing number of studies show that nanosilver may pose significant adverse human and environmental effects. Given the ubiquity of nanosilver and its potential toxicity, it is important to understand its environmental fate and transport. This study examines how nanosilver and related products are transported in saturated porous media. In the study, laboratory synthesized silver nanoparticles (AgNPs) as well as commercial AgNPs were used. Column experiments were then conducted, to study the transport of AgNPs, along with related products (e.g., Ag ions and silver oxide), in saturated porous media. In the study, a conservative tracer, AgNPs, Ag ions, and silver oxide were injected into the inlet of a glass bead packed column, and concentration versus time breakthrough

curves obtained at the column outlet. Breakthrough curves were compared and filtration theory used to analyze the results. Results show that the total mass of AgNPs leaving the column was smaller than the total input mass, indicating the capture of a fraction of the colloidal AgNPs by the porous media.

COLL 431

Disruption of suspended lipid bilayer induced by engineered nanomaterials

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This work explores the mechanisms and conditions of engineered nanomaterial (ENM) induced disruption of simplified model cell membranes, namely lipid bilayers. We hypothesize that under some circumstances ENMs can cause nanoscale defects in bilayers that could result in a path for cellular toxicity. We use an extracellular patch clamp type amplifier as an electrophysiological measurement platform to quantify the ionic current through a bilayer suspended across a 150 micron aperture. Our real-time measurements show that a wide variety of nanomaterials induce disruption and leakage of artificial cell membranes, bilayers. The leakage increases with particle concentration and is consistent with leakage induced by Melittin toxin. These measurements suggest that engineered nanomaterials can increase permeability of cell membranes through non- specific interactions with the bilayer.

COLL 432

QCM-D: A useful technique to study interactions between nanomaterials and model lipid membranes or living cells

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In recent studies, we have investigated how the lipid membrane, one of the most vital structures of a cell, interacts with various types of nanomaterials (polymeric drug carriers, TiO_2 nanoparticles, and graphene oxide) using an interaction screening platform based on the quartz-crystal microbalance with dissipation monitoring (QCM-D) technique. QCM-D measures changes in mass and viscoelastic properties at an interface and has also been used to study, in real time, cellular responses in living cells. Pigment translocation processes are essential features of many amphibians, and we study pigment translocation in frog chromatophores in a combined QCM-D and light microscopy set-up. Nanomaterial interactions were evaluated in systems ranging from

model biological interfaces to specific effects on cellular functions. The results clearly indicate the potential of the platform as a tool for early characterization and screening of novel nanomaterials.

COLL 433

Size-dependent behavior of iron oxyhydroxide minerals: Surface adsorption and iron dissolution in the presence of polyatomic oxyanions

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Iron oxyhydroxide, α-FeOOH, plays a critical role in geochemical and atmospheric processes including as a potential source of iron in the open oceans as well as a reactive component of dust. In this study, we combine dissolution measurements along with spectroscopy and microscopy to focus on nanoscale size effects in surface adsorption of polyatomic oxyanions and iron dissolution in iron oxyhydroxide minerals from gas-phase precursors (like nitric) and as aqueous phase ions. In liquid-phase studies of oxyanions, including phosphate and carbonate, nanorods showed a higher surface adsorption of these anions compared to microrods. These differences are attributed to the presence of more reactive (021) faces with higher surface –OH group density in nanorods compared to microrods. However, in gas phase studies, nitric acid uptake leading to adsorbed nitrate yields a saturation coverage of nitrate on microrods higher than that on nanorods, an interesting size effect which is attributable to surface structural changes that occur as a function of particle size during the reaction.

COLL 434

Sulfidation of ZnO nanoparticles

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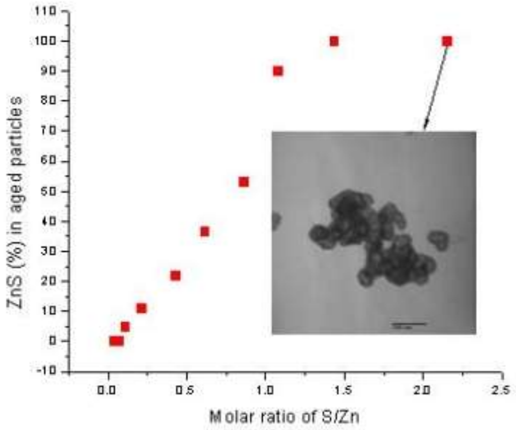
Zinc oxide (ZnO) nanoparticles are used in consumer products, leading to increased interests in the fate of them in the environment. One key process governing fate of ZnO will be sulfidation, which will alter their toxicity, chemical composition, size and morphology, and surface properties. A 30 nm ZnO nanoparticle was sulfidized with different Zn/S ratios to obtain different extents of transformation from ZnO to ZnS. Synchrotron based X-ray Diffraction (XRD) was used to characterize chemical speciation of the sulfidized particles (Fig. 1). Between 5% to 100% sulfidation was obtained and the size of completely transformed ZnS particle was calculated to be 4 nm

using Riteveld fitting of XRD data. This indicated a dissolution re-precipitation mechanism for ZnO sulfidation. Particle size and morphology, surface charge, and dissolution of sulfidized particles was also measured using TEM, DLS, electrophoretic mobility, and atomic absorption spectrometry to characterize the resulting ZnS or ZnO/ZnS particles.



COLL 435

Trophic transfer and long-term accumulation of CeO_2 nanoparticles in Mytilus galloprovincialis

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As the use and production of metal oxide nanoparticles (NPs) continues to rise, the potential for significant environmental contamination becomes more likely. Despite recent investigation into the environmental consequences of NP contamination, the effects of long-term exposure on organisms have largely been overlooked. In this experiment trophic transfer of CeO_2 NPs from phytoplankton to a marine mussel, *Mytilus galloprovincialis*, was simulated by feeding contaminated phytoplankton to *M. galloprovincialis*. Accumulation and effects on clearance rate as a function of NP concentration were measured for five weeks. Additionally, NP sequestration behavior in *M. galloprovincialis* was compared for direct exposure to free CeO_2 NPs and indirect exposure via contaminated phytoplankton.

COLL 436

Biogeochemical assessment of nanosilver particles in reduced soils

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While a large increase in the commercial and home usage of silver nanoparticle (AgNP) products and technologies is expected in the future, few studies contribute to the risk assessment of AgNPs in terrestrial environments. In this study, the effect of AgNPs (total [Ag]: 1-100 mg kg^{-1}, 15-50 nm size with/without polyvinylpyrrolidone capping agent) on soil denitrifying bacteria was investigated via assessment of their physicochemical properties using bench-scale biogeochemical experiments, dissolution studies, X-ray absorption spectroscopy and electron microscopy analysis. Although the effects on denitrification kinetics and pseudo-equilibrium end-points were variable among the AgNPs, the antimicrobial effect resides at the soil-water interface as sorbed-AgNP and -Ag(I) species. There is clear evidence of changes in chemical speciation and spatial distribution of AgNPs that contribute to the toxicity. Changes in physicochemical properties of AgNPs in reduced soils will be discussed to explain antimicrobial effects of AgNPs to the soil denitrification processes.

COLL 437

Fabrication of stable multifunctional composite nanoparticles: Volume labeling SiO2 by radioactive isotope and fluorescence dyes

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We report a new synthesis approach to simultaneously incorporate radioactive isotope C^{14} and organic dyes (fluorescein, Rhodamine and Alexa Fluors) into SiO_2 nanoparticles. The $C\text{-}^{14}$ and fluorescence dye molecules are homogeneously grafted inside the SiO_2 nanoparticles through covalent bonding by polymerization reaction in microemulsion media. The resulting labeled nanoparticles have narrow size distribution and the sizes can be controlled in range of 50-500 nm. In comparison with conventional surface tagged particles modified through post-synthesis surface modification techniques, this process maintains the initial physical and surface chemical properties of the SiO_2 nanoparticles with respect to colloidal stability and allows additional surface functionalization with for different applications. These volume-labeled nanoparticles have proven to be more robust than conventional surface modified particles and exhibit excellent signal intensity and chemical stability when compared with conventional surface tagged SiO_2 nanoparticles as a result of the covalent integration of modifiers into the body of the SiO_2 nanoparticles. The radioactive fluorescent SiO_2 nanoparticles can be use to trace and image the long-term behavior of nanoparticles in biological and environmental systems. To our knowledge, this research is the first report to introduce radioactive isotope to SiO_2 nanoparticles.

COLL 438

Mechanochemical synthesis of polyaniline/Laponite nanoassemblies

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We are currently exploring Laponite nanoscaffolds as templates to catalyze and direct the self-assembly of conductive polymer polyaniline nanoassemblies. Mechanochemical methods were employed using anilinium hydrochloride salts and Laponite nanoparticles to synthesis one-dimensional polyaniline nanorods. Scanning electron microscopy and atomic force microscopy studies including tapping mode topography and phase imaging have indicated that our Laponite/polyaniline nanomaterials have novel heterointerfaces with interpenetrating, bicontinuous structures that support the development of thin film bulk heterojunction solar devices. More specifically, the direct connection between polyaniline nanorods and Laponite nanodiscs offers promise for improving the interfacial area between the active and conductive layers within the heterojunction.

COLL 439

Effects of ferrihydrite nanomineral structure on Fe acquisition by aerobic bacteria: Siderophores and reductive dissolution mechanisms

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The Fe oxyhydroxide nanomineral ferrihydrite may serve as a source of Fe to environmental bacteria, and because it forms the core of the Fe storage protein ferritin, it can potentially provide Fe to pathogens. We compared growth of aerobic *P. mendocina* and *P. aeruginosa* on freshly synthesized 2- and 6-line ferrihydrite. *P. mendocina* is a soil bacterium that releases an Fe chelating siderophore and has a cell-associated reductant. *P. aeruginosa* is a pathogen that releases siderophores and the extracellular reductant pyocyanin, and that also may have cell-associated reducing ability. Growth of *P. mendocina* was considerably greater on 2- than 6-line ferrihydrite, whereas growth of *P. aeruginosa* was identical for the two ferrihydrite samples. Study results suggest that when Fe acquisition proceeds primarily via siderophores, the process is sensitive to ferrihydrite structure. Fe acquisition dominated by a reductive pyocyanin-related mechanism is faster and less dependent on detailed mineral structure.

COLL 440

Properties of NiO, CuO and NiO-CuO bimetallic nanoparticles as surrogates for combustion-generated nanoparticles

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Waste incineration and fuel oil burning produce fly ash, that contains trace amounts of metal oxide nanoparticles, such as nickel oxide (NiO) and copper oxide (CuO). Here NiO and CuO nanoparticles and NiO-CuO bimetallic nanoparticles are prepared on Cab-O-Sil (silica) surfaces as mimics of combustion-generated metal oxide nanoparticles in fly ash. The supported metal oxide nanoparticles are synthesized by impregnating silica with methanolic solutions of metal ion-dendrimer complexes with their subsequent calcination at 500 °C for 5 hours. Nanoparticles less than 5 nm in diameter are observed using transmission electron microscopy. The composition of individual bimetallic nanoparticles is determined using energy-dispersive X-ray spectroscopy using Cliff-Lorimer factors. Bimetallic nanoparticles with different Ni:Cu weight% are observed when the Ni:Cu ratio was varied in the metal-dendrimer complexes. We report on the use of these nanoparticle surrogates as potential catalysts for the pyrolytic formation of dioxins from 1,2-dichlorobenzene.

COLL 441

Effect of surface chemistry on the generation of reactive oxygen species by copper nanoparticles

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Copper nanoparticles have been used in many areas from batteries to facial sprays. They are also found to have antifungal and wound healing potentials, which should increase the exposure of them to humans and environments. Thus it is important to understand the toxicity mechanism in order to reduce copper nanoparticles-induced adverse effects. Surface chemistry is important in controlling physico-chemical and biological properties of nanoparticles. In our study, uniform copper nanoparticles were treated with selected ligands (mercaptocarboxylic acids and PEG ligand) to achieve suitable surface properties to control both dispersity and reactivity. Extracellular reactive oxygen species (ROS) assay was carried out with these copper nanoparticles using 2,7-dichloroflurescein diacetate. We observed strong correlations between surface chemistry and acute reactive oxygen species response. Oxidation kinetics studies showed that different surface chemistry resulted in different surface oxidation rates of

copper nanoparticles and the surface oxidation reactivity of copper nanoparticles related closely to ROS generation.

COLL 442

Integrated nanomaterials for environmental applications

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The application of nanomaterials in water and wastewater treatment often requires separation after their intended functions are accomplished. We propose to eliminate the need of separation by integrating nanomaterials into macroscopic structures such as metal mesh. In this presentation, we will demonstrate the usefulness of this concept with three types of integrated nanomaterials: carbon nanotube arrays grown on mesh for oil-water separation, TiO_2 nanoparticles attached on nanowire-decorated mesh for photodegradation, and gold nanoparticles grown on nanobelt-decorated mesh for catalysis.

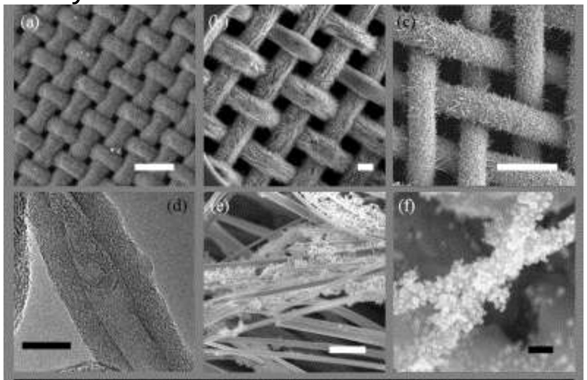

Figure 1. Electron micrographs of integrated nanomaterials for environmental applications. (a,d) Carbon nanotube arrays grown on mesh for oil-water separation. (b,e) TiO_2 nanoparticles attached to nanowire-decorated mesh for photodegradation. (c,f) Gold nanoparticles attached to nanobelt-decorated mesh for catalytic reduction. Scale bars: a – c, 100 μm; e, 1 μm; d and f, 100, nm.

COLL 443

Improving detection of Bacillus thuringiensis suspensions by SERS for important applications

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The time required for identification of pathogens is a determinant factor of infection related sickness; therefore research in this area is very important. Spectroscopic techniques such as normal Raman (NR) scattering and surface enhanced Raman scattering (SERS) are considered fast and *in situ* alternative methods for identification of microorganisms. These techniques provide important information about the spectroscopic signatures of cellular components of in vitro or in vivo organisms for biological warfare agents detection, microbiology, among other fields of application. *Bacillus thuringiensis* (Bt) is a soil-dwelling bacterium, commonly used as a pesticide. It is closely related to *Bacillus anthracis* which is the cause of anthrax. Because of the uses of anthrax as a biological warfare agent we are interested in the detection of Bt for counter biological Weapons of Mass Destruction (WMD). In this research, biochemical components of the vegetative cells and endospores of Bt were identified using SERS effect with silver-citrate capped nanoparticles (NPs) reduced by borohydride. Activation of “hot spots”, aggregation and surface charge modification of the NPs were optimized to obtain good signal enhancements of Bt by SERS. This also allowed the study of the interaction of Ag NPs and the bacteria. Principal component analysis (PCA) of SERS spectra was used to classify and discriminate bacterial samples. These results should help detection of bacterial samples in future experiments using bioaerosols.

COLL 444

Investigation of intra-particle contaminant transformations in nanoscale zero-valent iron with in situ X-ray absorption spectroscopy (XAS)

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While a high efficiency of contaminant removal by nanoscale zero-valent iron (nZVI) has often been reported for several contaminants of great concern, including aqueous arsenic species, the transformations and translocation of contaminants at and within the nanoparticles are not clearly understood. By using *in situ* XAS analysis of the As core level for nZVI-As(III) aqueous reaction systems, we have observed that As(III) undergoes two stages of transformation upon adsorption at the nZVI surface. The first stage corresponds to breaking down As(III) complexes at the particle surface, and the second stage involves gradual migration of arsenic across the thin oxide layer enclosing the nanoparticles. This second stage ends with complete loss of As-O bonds and the formation of a disordered As-Fe intermetallic phase. These results highlight the role of the nZVI microstructure in shaping its chemical reactivity and the relevance of intra-particle diffusion and reduction in contaminant sequestration processes.

COLL 445

Transport of multiwalled carbon nanotubes through porous media

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In this study, transport properties of MWCNTs oxidized by two methods were tested by passing colloidal dispersions of MWCNTs through packed columns of glass beads, using both pulse and step inputs. The surface oxygen containing functional groups were characterized using X-ray Photoelectron Spectroscopy (XPS). Experiments were conducted at IS ranging from 0.5 to 1000 mM (NaCl) and at pH 4, 5.8 and 10. Breakthough curves were collected by UV-Vis using a 5 cm flowthrough cuvette and then analyzed using a simple one dimensional convection-dispersion transport equation that included a first order removal term for colloid deposition. Spatial retention profiles were observed by extracting and analyzing deposited MWCNTs in 10 increments along the column length. The transport studies confirmed that attachment efficiency of MWNTs is increased at higher ionic strength and lower pH and decreased by the introduction of charged functional groups to the MWCNT surface. Modeling of results is underway.

COLL 446

Octanol-water partition coefficient (K_{OW}): Is it a good measure of hydrophobicity of nanoparticles?

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Octanol-water partition coefficient (K_{OW}) is a conventional measure of hydrophobicity of organic compounds, and has been recently applied to nanoparticles (NPs). However, the larger size of NPs may undermine the fundamental assumptions of K_{OW} application. We conducted K_{OW} measurement for different NPs: aqueous C_{60} (aqu-C_{60}), tetrahydrofuran-C_{60}, fullerol, nano-silver, and citrate-coated nano-gold (Au-Ci). Our results showed that larger K_{OW} was obtained from NPs that exhibited greater hydrophobicity. We also showed that as size increased, K_{OW} of aqu-C_{60} increased, but K_{OW} of Au-Ci was not dependent on size. Dark field microscopy revealed that Au-Ci NPs (< 30 nm) mainly remained in bulk water; while majority of Au-Ci (> 100 nm) were accumulated near the water-octanol interface. Overall, our study demonstrated that the partition of NPs is determined by both hydrophobicity and size. The current application of K_{OW} as a measure of hydrophobicity for NPs is inherently flawed and further investigation is needed

COLL 447

New insight into chemical bonding interaction between alumina and nanotube in MWCNT/alumina nanocomposite

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Nanocomposites are being of interest in term of their fabrication and characterization due to the enhancement of their properties. Understanding the interaction between the components allows to control the structure of the material. This paper investigates the possible chemical bond formation between functionalized carbon nanotubes and alumina, in multi-wall carbon nanotubes/alumina composite (MWCNT/Al_2O_3), with the aid of spectroscopic analysis. For this purpose, the composite MWCNT/alumina was synthesized via hydrothermal treatment. Different characterization techniques, scanning electron microscopy (SEM), energy dispersive X-ray spectroscope (EDX), X-ray diffraction (XRD), Fourier transformed infrared spectroscope (FT-IR) and high-resolution transmission electron microscopy (HRTEM), have been used to investigate the interaction of the nanocomposite. The study predicts the possibility of chemical bonding between aluminum atoms and CNT.

COLL 448

Surface modification of poly(dimethylsiloxane) with polycarboxybetaine

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Herein, we report the modification of poly(dimethylsiloxane) (PDMS) surfaces with polycarboxybetaine (PCB) via surface-initiated atom transfer radical polymerization (ATRP). First, the PDMS surface was treated with oxygen plasma, followed by immersion into a THF/acetonitrile solution containing Br-trichlorosilane. Then, the surface-initiated polymerization of carboxybetaine was carried out. Contact angle was measured to characterize the hydrophilicity of the PCB-modified PDMS surface. Atomic force microscopy (AFM) results showed that the surface is very smooth under wet condition. The PCB modified PDMS surface was shown to highly resist non-specific protein adsorption as monitored by Enzyme-Linked Immunosorbent Assay (ELISA). Furthermore, the pCB-modified PDMS surface was also evaluated with various microorganisms.

COLL 449

Kinetics of modularly functionalized anatase nanoparticle attachment to humic acids

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Attachment of engineered nanoparticles to natural organic matter (NOM) is expected to influence their transport and fate in the environment and influence their bioavailability to organisms. Using a novel citric acid derivative, organic ligands were anchored to TiO_2 nanoparticles using azide-terminated polyethylene glycol (PEG) molecules presenting different head groups to solution. The functionalized nanoparticles were characterized by dynamic light scattering, transmission electron microscopy, and infrared and X-ray photoelectron spectroscopy. To examine nanoparticle attachment to humic substances we electrostatically assembled nanoscale films of Elliot soil humic acid on quartz crystal microbalance with dissipation monitoring (QCM-D) and optical waveguide lightmode spectroscopy (OWLS) sensors. We examined nanoparticle attachment over a range of environmentally relevant solution conditions (pH 5-8 and ionic strength = 5-50 mM. Final adsorbed masses, attachment rate constants, attachment efficiencies, and water content (determined through parallel QCM-D and OWLS experiments) were determined.

COLL 450

Transformation of silver nanoparticles in a sulfidic environment

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<h1>Sulfidation of silver nanoparticles with three different surface functionalizations were studied under anoxic conditions at environmentally relevant concentrations of hydrosulfide. Particles were synthesized to have similar size core (10-20 nm) and were coated with either citrate, polyvinylpyrrolidone, or gum arabic. They were characterized before and after exposure to sulfidic conditions by UV-Visible spectroscopy, dynamic light scattering, Raman spectroscopy, inductively-coupled plasma atomic emission spectroscopy, X-ray photoelectron spectroscopy, and transmission electron microscopy. We found that exposure to hydrosulfide caused a rapid loss of the characteristic plasmon of the Ag nanoparticles regardless of surface functionalization, aggregation of the particles thereafter, and formation of silver sulfide. Raman and XPS were used to monitor changes to the nanoparticle surface, specifically focusing on the sulfur speciation. Environmental implications include decreased ionization of the silver cores and increased likelihood of sedimentation.</h1>

COLL 451

Environmental implications of nanoparticle aging in the processing and fate of copper based nanomaterials

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The unique optical, magnetic and electronic properties of copper-based nanomaterials have resulted in their large scale production and a wide variety of applications. Metallic copper nanoparticles which often have a thin surface oxide layer, becomes more oxidized over time under ambient environmental conditions. In this study, we characterized three different types of copper-based nanoparticle (NP) samples designated as Cu(new) NPs, Cu(aged) NPs and CuO NPs that differ in the level of oxidation. The solution phase behavior of these samples was investigated as a function of pH and in the presence and absence of common, complexing organic acids (citric and oxalic acid) which showed interesting differences. In particular, Cu(aged) NPs exhibit unique differences in terms of oxide phases that are present, oxide phases that form and surface adsorption properties. Overall, the current study provides some insights into the impacts of nanoparticle aging and how the physicochemical characteristics and reactivity of nanomaterials can change.

COLL 452

Patterning graphene and gold electrodes by nanoshaving nanolithography

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We report a low-cost alternative to e-beam lithography and photolithography for nanoscale graphene device fabrication. Nanoshaving nanolithography based on an atomic force microscope was used to define patterns on octadecanethiol self-assembled monolayers on gold films evaporated on graphene flakes, followed by metal wet etching and/or oxygen plasma etching to develop the pattern on the gold films or graphene, respectively. A few examples of graphene and gold patterns made by this method were demonstrated with feature sizes down to ~ 100 nm. Finally, a graphene transistor with a silicon back gate was fabricated with a graphene channel width of 130 nm and a length of 480 nm. The resulting graphene device is p-type and its corresponding electron and hole mobilities are 1770 and 1600 cm^2/Vs, respectively.

COLL 453

Zn K-edge EXAFS investigation of Zn(II) sorption at Al- and Si-bearing ferrihydrite surfaces

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The iron oxide nanomineral ferrihydrite (Fh) is recognized for controlling the mobility of pollutants in the environment by means of sorption reactions. However, its properties as an adsorbent are strongly affected by composition. Al and Si are commonly associated with naturally occurring ferrihydrite. Although the structure of impure Fh's is beginning to be understood, little is known about the structure and composition of their surfaces. In this study we investigate the surface chemistry of Al- and Si- bearing Fh by Zn(II) adsorption experiments. Zn(II) adsorption isotherms indicate that pure Fh is the most reactive, followed by Al-Fh, and Si-Fh. Zn K-edge EXAFS data confirm the presence of Zn-Fe complexes similar to pure ferrihydrite for all samples. However, in the case of Si-Fh, these complexes are scarce, indicating that Si may be primarily bound at Fh particle surfaces. The less significant effect of Al on the reactivity of Fh may be due to its incorporation in the Fh structure.

COLL 454

Humic acid adsorption on ceria nanoparticles: Effect of surface chemistry

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Engineered nanoscale ceria, a diesel fuel catalyst, has been subject to numerous toxicological studies. This study reports sorption isotherms of humic acid onto ceria nanoparticles. Ceria nanoparticles were synthesized with different surface coatings: citrate (negatively charged), amino-silane (positively charged), and different coating coverage: monolayer and multilayer. The coating thickness was estimated by thermogravimetric analysis. The adsorption amount was quantitively determined using UV-vis spectroscopy at the wavelength of 288nm. Both surface charge and lateral effects can influence humic acid adsorption and lead to heterogeneous behavior. Toth and Sips models were applied to the isotherm data and the adsorption site energy distributions were estimated using model parameters. The analysis of the peak position and width of site energy distribution provided essential information about the adsorption mechanism.

COLL 455

Characterization of nanoparticles in complex environmental matrices by field flow fractionation inductively coupled plasma mass spectrometry

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The effects of natural matrices on the physiochemical state and properties of nanoparticles must be investigated to accurately determine fate and toxicity. The current work describes the use of Field Flow Fractionation interfaced to Inductively Coupled Plasma Mass Spectrometry for the detection and characterization of nanoparticles at parts per billion levels after exposure to soil, natural waters, and biological systems. These complex systems, when coupled to biological and photochemical reactions can drastically alter the stability of nanoparticles and their biogeochemical properties. Results indicate that photolysis of polymer coated nanosilver will remove the stabilizing coating, resulting in agglomeration, whereas biological exposure can result in particle size increases and decreases, depending on the system and matrix components.

COLL 456

Photoinduced disaggregation of TiO2 enables transdermal penetration

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Although particle coagulation has been studied for over a century, the effect of light on the state of aggregation has not been considered before. Since much of the preliminary work associated with the environmental and toxicological implications of nanoparticles (NPs) has pointed to the importance of NP size and aggregation state, where the degree of aggregation can serve to estimate key environmental and ecologically important processes, photo-induced disaggregation can have significant effects. Using pig skin as a model memrane, we show that ambient light can disaggregate some primary NPs from particle aggregates and increase the dermal transport of nanoparticles, such that small particles can readily diffuse into and through the dermal profile. The results of this work show that photo-induced disaggregation is an important factor in predicting nanoparticle fate, transport, and toxicity.

COLL 457

Role of material properties in controlling nanoparticle aggregation

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Particle size of nanoparticles (NPs) influences not only their environmental transport but also their toxicity. In natural aquatic or subsurface systems, the aggregation of NPs leads to reduced mobility due to sedimentation, deposition, and filtration; while NPs with strong resistance to clustering tend to remain suspended and travel long distance. To date, studies have investigated the effects of solution chemistry on NPs aggregation, while little has been done to reveal the influence of material properties on NPs aggregation. In this study, the aggregation of four titania (TiO_2) NPs with different morphologies (spheres, dots, wires, and rods), size, crystal structure (anatase, rutile, and amorphous) are being investigated. Results to date have shown distinct charging

behavior and aggregation kinetics of TiO_2 with different morphologies. The aggregation of rod shape TiO_2 is more resistant to salt concentration change than the other three TiO_2. The diffusion limited doublet formation rate (k_{11}) of TiO_2 wires was much higher than dots and rods, possibly due to wires' aligned attachment along the long axis. Size's role in controlling TiO_2 aggregation was also pronounced that bigger particles aggregate faster with the same ionic strength. The ongoing work is to identify the diffusion-limited aggregation regime and reaction-limited aggregation regime and to determine the fractal dimension of the aggregates.

COLL 458

Bio-inspired *slippery* anti-frost coating on aluminum for energy efficient refrigerator heat exchangers

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Ice formation on metal surfaces, such as aluminum, is a serious economic and safety issue for aviation and refrigeration industries. To mitigate this problem, we investigated an approach to coat the surface of aluminum with hierarchically-structured material that can alter the wetting properties of the surface and delay ice formation. Conductive polymers offer ample opportunities to precisely tune nanoscale morphology by varying the conditions for synthesis. We have developed a one-step electrodeposition method to create a nanostructured polypyrrole coating on the surface of aluminum, which can significantly delay ice formation compared to uncoated aluminum. We envision further studies on this low-cost and scalable approach combined with newly developed bio-inspired SLIPS (Slippery Liquid Infused Porous Substrates) technique will eventually lead to robust icephobic coatings that can significantly reduce the energy and capital cost currently consumed in refrigeration industry.

COLL 459

Removal of trichloracetic acid by iron based bimetallic nanoparticles

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Trichloroacetic acid (TCAA) is one of the disinfection by-products (DBPs) in chlorination process, which is with great potential risk to human health. This work investigated the removal of TCAA by using laboratory-synthesized Pd−Fe bimetallic nanoparticles.

Pd−Fe nanoparticles were characterized in terms of surface area, morphology, and particle size. The results indicate that Pd-Fe nanoparticles were spherical with the diameter of 47±11.5 nm, and the specific surface area was 36.5 m^2/g. Pd−Fe nanoparticles showed prominent activity in removal of TCAA. Pd content, Pd−Fe addition, initial pH value of reaction system, and initial concentration of target pollutant were found to have effect on the removal efficiency of TCAA. Some of the important parameters, such as Pd content, metal addition, and initial pH value of reaction system were optimized for higher removal efficiency. Dechlorination kinetics of TCAA were also investigated.

COLL 460

Sedimentation of nanomaterials: A study on size and protein adsorption

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Nanomaterials, the building blocks of engineered nanotechnology, can make their way into the environmental ecosystem or into biological organisms either accidentally or purposefully. The sedimentation rate of nanomaterials in the environment can have an impact on the scale of the affected ecosystem as well as the organisms within. In this study, we investigated the parameters that affects the sedimentation of nanomaterials and specifically focused on the effect of size and protein adsorption. Using centrifugation to accelerate the sedimentation rate, we studied the recovery of the gold nanoparticles ranging from 5 to 15nm in diameter. We found that smaller size nanoparticles have a slower sedimentation rate. Interestingly, temperature has an important role in the sedimentation rate, with higher temperature resulting in slow sedimentation. Nanoparticles with protein adsorption further decreases the sedimentation rate, and larger amount of the adsorbed protein and bigger size of the protein seem to further decrease the sedimentation.

COLL 461

Titanate nanotube preparation: Microwave irradiation time and temperature effect on photoactivity

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Nanostructured titanate nanotubes (Ti-NT) were reported to be the most efficient and environmentally benign photocatalyst for the oxidation of organic compounds. Here, Ti-NT was synthesized using alkaline microwave-assisted (MW) hydrothermal treatment method to achieve rapid and selective heating and rates of crystallization of photoactive titanate phase. The adjustment and control of the synthesis time and temperature affect

the structural, chemical and electronic properties of Ti-NT resulting in significant enhancement in the photocatalytic activity of titanate nanotubes.

The nano-size photocatalyst were evaluated for treatment of endocrine disrupting compound, diclofenac in water under UV irradiation (6W fluorescent lamps-F6T5/BLB). MW treatment at 180^{o}C for 30 min shown to be the most active for photodegradation of organic pollutants in water, with activity significantly higher than most reported in literature. Crystallinity, pore size and band gap energy are the three most dominant factors for photocatalytic oxidation performance based on the studies.

COLL 462

Molecular rectification: Synthesis and characterization Of D-sigma-A molecules

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This paper represents suitable organic molecules function as a rectifier when properly organized. The preparation and characterization of D-sigma-A molecules has been accomplished.

COLL 463

Alternative energy: The computer software application in chemistry, a cellular data system of cyberworlds, and hardware system to self-generating equally complex systems

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This paper represents an alternative method of chemistry, cloud computing to provide the necessary combination to achieve an automated self-generating software system.

COLL 464

Preparation and photophysical properties of polypyridylruthenium derivatived polystyrene

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Amide-linked polystyrenes grafted with trisbipyridine ruthenium complexes have been prepared via atom transfer polymerization (ATRP), followed by amide coupling reaction. Although the amide link is short and the Ru complex is bulky, both of which may introduce significant steric hindrance, Ru complexes have been loaded as side groups on polystyrene in large quantity under mild reaction condition, and fully loaded under reflux condition. The grafted polystyrenes disperse stably in solution, fluid and film. Transition state measurement shows energy migrates fast along the adjacent Ru complex in both partially and fully loaded polystyrenes. Meanwhile, theory calculation results are in good agreement with the photophysical measurement.

COLL 465

Laterally fluid surface to explore cell-substratum interactions

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By using interfacial self-assembly techniques, amphiphilic block copolymers are fabricated into dynamic bilayer films with the potential to control cell adhesion and force generation. The dynamic character of the bilayer film is tuned by the addition of a short hydrophobic homopolymer, which is thought to reduce the inter-leaflet friction. By using fluorescent recovery after photobleaching, lateral diffusivities were determined and found to have increased dynamic range over lipid membrane counterparts. To study cell interactions with these films, the block copolymers were labeled with a cell adhesive peptide ligand. By testing various mammalian cell types, we have found that specific cells are able to selectively discriminate between 'dynamic' (i.e., laterally-diffusive) films and 'static' films bearing the same amount of adhesion ligand. Such films therefore present a novel platform to explore dynamic cell-surface interactions between tumor and nontumor cell lines, irrespective of surface biomarkers.

COLL 466

Single cell microfluidics for systems oncobiology

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The singular term “cancer” is never one kind of disease, but deceivingly encompasses a large number of heterogeneous disease states, requiring systems approaches to patient stratification and personalized treatment. We developed a single cell microfluidics chip that can measure a panel of proteins associated with inter-cellular signaling network in tumor microenvironment. Hundreds of single cancer cells were analyzed in parallel. We conducted highly multiplexed profiling of signle cell secreted proteins including tumor-immune signaling molecules from both cancer cells and immune cells, and observed profound cellular heterogeneity with all functional phenotypes quantitatively identified. Correlation analysis further indicated the existence of an intercellular cytokine feedback loop in which TNFα-induced secondary signaling cascades further increased functional cellular diversity. Upon further development, this platform may potentially become a clinical tool for patient stratification based upon the inter-cellular signaling network and aid the design of new anti-cancer therapy by targeting microenvironmental components.

COLL 467

X-ray activated release of molecules from gold nanoparticles

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X-rays are highly penetrating compared with other forms of radiation that can initiate chemical reactions (UV, vis, etc). Therefore, it is advantageous to use X-rays to activate chemical reactions and mechanical motions. Nanochemistry can facilitate this process. Here, we show that it is possible to utilize commonly available medical imaging X-ray radiation to activate the release of molecules attached to the surface of gold nanoparticles by cleaving DNA linkers between the two. Fluorescence quenching is used to probe the cleavage. The role of the gold nanoparticle surface was found to be non-trivial, and it is discovered that the cleavage can be enhanced with the right choice of additives. This study provides the guidance for developing this method for many future applications, including drug delivery, sensing, and molecular machines that can be activated with highly penetrating X-rays.

COLL 468

Bioorthogonal nanoparticle labeling and detection of biomarkers through supramolecular host-guest interaction

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Supramolecular interactions play a pivotal role in assembling smaller molecular components into functional architectures, which can be engineered to function in biological systems. We describe here the use of synthetic supramolecular host-guest interaction for highly efficient bioorthogonal labeling of cellular targets. β-cyclodextrin modified antibodies against targets of interest were used as scaffolds to bind adamantane linked nanoparticles onto live cells via a host-guest interaction. Compared to conventional labeling techniques, the supramolecular interaction-based approach showed much higher efficiency and robustness in cellular labeling. Furthermore, we show that this technique has broad utility for a range of biodiagnostic applications, including magnetic sensing, immunostaining and cell sorting. This supramolecular strategy represents a new class of coupling platform that not only increases targeting capabilities but also extends detection limits by improving labeling efficiency.

COLL 469

High affinity DNA aptamer against $VEGF_{165}$ on colorectal cancer cells for growth inhibition

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Vascular endothelial growth factor (VEGF165) is a potent angiogenic mitogen commonly overexpressed in cancerous cells. It contains two main binding domains, the receptor-binding domain (RBD) and the heparin-binding domain (HBD). This study attempted to identify the specific sequences of DNA aptamer that can bind to $VEGF_{165}$ with high binding affinity using a simple truncation strategy. Using surface plasmon resonance (SPR) spectroscopy for binding affinity analysis (Table 1), truncated aptamer segments showed various binding affinity and one segment (SL_2-B) exhibited a dissociation constant K_d of < 1nM against HBD, which is 100 to 1000 times better than the existing commercial monoclonal antibody (Avastin, with K_d of 2000nM). This SL_2-B segment also exhibited high specificity to HBD with negligible binding affinity for $VEGF_{121}$, an isoform of VEGF lacking HBD. Exposing colorectal cancer cells to the SL_2-B segment further confirmed the binding affinity and specificity of the aptamer to the target $VEGF_{165}$ protein. Hence, our approach of aptamer truncation can potentially be useful in identifying high affinity aptamer sequences for the biological molecules and targeting them as antagonist for cancer cell detection.

Truncation of aptamer segments for HBD binding analysis	**K_d**
VEa5	120 nM
SL_{12}	5.0 nM
SL_1	No binding
SL_2	49.0 nM
SL_2-A	10.0 nM
SL_2-B	0.5 nM
Avastin (monoclonal antibody)	> 2000 nM

Table 1: Different aptamer segments along with their equilibrium dissociation constant (Kd) values determined using surface plasmon resonance (SPR) spectroscopy.

COLL 470

Design of polyvalent ligands

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Polyvalency, which refers to the simultaneous binding of multiple ligands on one entity to multiple receptors are another, represents a promising approach to inhibit undesired biological interactions (e.g., the binding of a toxin or pathogen to a target cell), promote desired cellular responses, and control recognition events at surfaces (e.g., the recognition of target cells). We will describe our group's efforts to design and characterize polyvalent ligands that are several orders of magnitude more potent than the corresponding monovalent counterparts. Specifically, we will discuss studies relating the composition and structure of these polyvalent ligands to their activity.

COLL 471

Stable gold nanorod-poly(aminoether) assemblies for transgene delivery and photothermal ablation of cancer cells

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Gold nanorods (GNRs) have emerged as promising nanomaterials for diagnostics, imaging, photothermal treatment and therapeutic delivery in cancer diseases. Chemically synthesized gold nanorods demonstrate rapid aggregation and poor colloidal stability in biologically relevant media. As a consequence, we generated poly(amino ether)-functionalized gold nanorods, or PAE-GNRs, using a layer-by-layer deposition approach; polymers from a poly(amino ether) library recently synthesized in our laboratory were employed to generate the PAE-GNR assemblies. PAE-GNRs are stable for up to four weeks and demonstrate a robust photothermal response, which was exploited for the hyperthermic ablation of prostate cancer cells. In addition, sub-toxic concentrations of PAE-GNRs generated using polymers from our laboratory demonstrated higher transgene expression and exhibited lower cytotoxicities when compared to similar assemblies generated using 25 kDa poly(ethylene imine) (PEI25k-GNRs), a current standard for polymer-mediated gene delivery. Our results indicate that

surface engineering using judiciously selected biocompatible polymers leads to multifunctional gold nanorod-based assemblies that combine high stability and low cytotoxicity with photothermal ablation, transgene delivery, and optical imaging capabilities on a single theranostic platform.

COLL 472

Thermosensitive liposomal doxorubicin and tumor hyperthermia: Matching the heating protocol with the liposome system

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Liposomal anthracyclines offer considerable improvements in toxicity and preferential tumor accumulation, however, stable drug entrapment limits their therapeutic benefit due to reduced drug bioavailability. A strategy to improve that is to combine temperature-sensitive liposomes (TSL) with hyperthermia (HT) to spatiotemporally trigger selective drug release. To study the pharmacokinetics of various types of clinically relevant TSL, three different liposome systems were dual-labeled with ^{3}H-CHE lipid and loaded with ^{14}C-doxorubicin. Their blood profile, tissue distribution and therapeutic efficacy were studied to determine the localization of liposome and doxorubicin tumor-accumulation on therapeutic efficacy. The TSL system with lowest serum stability, showed rapid drug release kinetics and the highest doxorubicin release (7.6%ID/g) 1h after HT. Alternatively, serum-stable systems showed impressive tumor accumulation from 15 to 30%ID/g 24hr post-HT, however, did not lead to improved therapeutic efficacy. Overall our results emphasize the importance of matching the HT protocol with the thermoresponsive and pharmacokinetic characteristics of the liposomal doxorubicin to maximize therapeutic benefit.

COLL 473

Surface modification of a silica nanoprobe for fluorescence bioimaging of HeLa cells

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Surface modification of silica nanoparticles (SiNPs) containing an aggregation-enhanced fluorescent dye was performed to specifically target folate receptors in HeLa cells for *in vitro* and *in vivo* tumor bioimaging. Surface modification was characterized by zeta potential measurements and NMR spectroscopy, while nanoparticle size was determined by light scattering and TEM measurements. *In vitro* studies using HeLa cancer cells, which are enriched in folate receptors (FRs), indicated specific cellular uptake of the functionalized nanoparticles while the functionalized SiNPs were found to exert low cytotoxicty. The SiNP exhibited folate receptor (FR) targeting *in vivo* in nude

mice bearing HeLa tumors. Two-photon fluorescence bioimaging was then conducted to acquire detailed three-dimensional *ex vivo* images of HeLa tumors.

COLL 474

Protein adsorption and monocyte activation on a degradable polar hydrophobic ionic polyurethane

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A degradable polar hydrophobic ionic polyurethane (D-PHI) has previously been shown to support a less pro-inflammatory monocyte activation relative to tissue culture polystyrene and poly(lactide-co-glycolide). The mechanism by which D-PHI supports this differential response has been evaluated in terms of protein adsorption and surface chemistry in the present study. Surface analysis was performed by X-ray photoelectron spectroscopy (surface chemistry) and water contact angle measurements (surface wettability). The composition of the adsorbed protein layer was probed through 2-D electrophoresis. Protein pre-adsorbed and non-coated D-PHI surfaces were shown to support reduced pro-inflammatory monocyte activation. It was demonstrated that α2-macroglobulin (A2M) supported differential monocyte activation when pre-adsorbed to the above three biomaterials, with the differences showing that the A2M receptor was active on monocytes interacting with A2M pre-adsorbed to D-PHI, but not the two other biomaterials. This study illustrates the importance of protein adsorption in eliciting inflammatory-related biological responses to different biomaterials.

COLL 475

Manipulating competitive protein adsorption using surfaces with immobilized nanoparticles and other tiny contact points

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Manipulation of protein-surface interactions is an important objective in biomedical applications, for instance in the development of implants, and in pharmaceutical applications, where purification is the top priority. In either case, the near-permanent binding of proteins to a surface, along with the associated unfolding, complicates and confounds performance. While it can sometimes be advantageous to employ surfaces which do not adsorb proteins, there is much to be gained by their interfacial manipulation. One route to protein manipulation involves protein adsorption onto surfaces which are non-adhesive, with the exception of small (less than 10 nm) contact points which potentially limit protein unfolding. Our lab has created libraries of surface designs, based on polymers and nanoparticles, which interact with proteins through

contacts smaller than the proteins themselves. We report the ability, based on the size and binding energy of the contact points, to capture single proteins on each adhesive element, to capture multiple proteins, or to adsorb proteins only when they bridge between the adhesive points. This talk demonstrate the tuning of these behaviors and highlights the ability of these surfaces to accomplish sharp targeted adsorption (with order 99 purity) based on the size and charge of target proteins.

COLL 476

Influence of glycopolymer brush structure on complement activation

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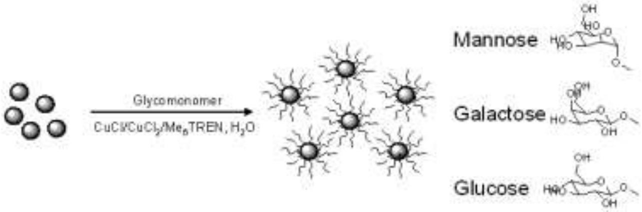
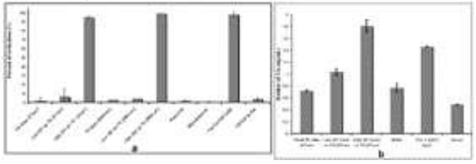
The ability of the artificial materials to activate complement system depends on the chemistry of the surface and presentation of ligands. In the present work, we investigated the influence of glycopolymer brush structure on complement activation particularly the types of carbohydrate residues, graft density and curvature of the surface using well defined glycopolymer brushes carrying mannose, galactose and glucose units in its natural form



. Our results showed that the total complement consumption in serum depended on the graft density of the brushes. High graft density brushes gave highest level of complement activation and there was no complement activation observed from low graft density brushes



. The results were well correlated with the analysis of C3a generated in serum measured by ELISA analysis. Unlike surface grafted glycopolymer brushes, soluble glycopolymers did not activate complement system. Also the curvature of the surface did not have much influence on complement activation.

COLL 477

Protein-specific empirical model of protein adsorption on surfaces

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Predicting protein adsorption from solution to a surface is an important problem in biomedicine and related fields. Despite constant attention in the literature, it is not currently possible to predict quantitatively the amount of adsorbed protein given environment, protein and surface parameters. In this paper, we present a purely empirical approach to predict protein adsorption using a linearly piecewise model with breakpoint. This model is capable of accounting for over 90% of the variance in the data, despite the fact that the adsorption data spans over three orders of magnitude. We fitted and validated this model using the Biomolecular Adsorption Database, an online collection of protein adsorption data collected from the literature freely available at http://bad.molecularsense.com.

COLL 478

Time dependent formation of protein-ceria nanoparticle complex

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The main aim of this work has been to study the surface interaction between most abundant protein bovine serum albumin(BSA) and differently sized (~12nm and ~20nm) and charged(positive and negative) cerium oxide nanoparticles. The experiments were carried out on fixed concentrations of protein and varying the size and surface charge of cerium oxide nanoparticles. The time dependent formation of protein coating on cerium oxide nanoparticle surface was characterized by dynamic light scattering and zeta potential measurements. The conjugation of protein to ceria nanoparticle surface is validated by altered size and surface charge of cerium oxide nanoparticle from their native state. The UV-Vis spectroscopy technique was used to quantify the amount of protein bound to ceria nanoparticle surface. An interesting observation in this study is beyond native size and surface charge of ceria nanoparticles, the dynamic formation of BSA coating on ceria nanoparticle surface is largely time-dependent phenomenon.

COLL 479

Evaluation of protein adsorption at polymer brush surfaces based on the water structure surrounding the surface

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Biological responses are strongly related to the adsorbed protein layer on a materials surface. To understand protein adsorption at a materials surface, it is important to clarify the factors for surface properties dominant to protein adsorption. The perspective of this study is to elucidate the protein adsorption behavior at the biomaterials surface from a viewpoint of a water structure surrounding the material surface. In this study, the properties of water molecules enclosed among the micro-beads with the polymer brush layers were analyzed with ^{1}H-NMR measurement. The nano-newton ordered adsorption forces of protein against the polymer brush layers were analyzed with atomic force microscopy. The zwitterionic polymer brush layers, which had little adsorption force of protein, made a thick hydrated layer with high mobility around them. We will quantitatively discuss the relationship between the water structure and protein adsorption behavior at the biocompatible polymer brush layers.

COLL 480

Orientation of adsorbed antibodies: In situ monitoring by QCM and random sequential adsorption modeling

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Diagnostic assays based on antibodies rest on their adsorption, usually on hydrophobic substrates, in an orientation allowing interactions between variable domains and corresponding antigens. The present work is part of a project which aims at producing chimeric antibodies showing a preferred adsorption in end-on orientation, with the constant domain interacting with the substrate. The ability of different isotypes of rat and mouse immuno-γ-globulins to adsorb and to recognize the corresponding antigen was examined using quartz crystal microbalance. Results show that the highest adsorbed amount is obtained with IgG2a from mouse, while IgG1 and IgG2a from rat achieve the highest level of antigen binding. For most antibodies, the molar ratio of bound antigen *vs* adsorbed antibodies was in the range of 0.6-0.9, indicating a preferred end-on adsorption, in contradiction with the fact that side-on adsorption is energetically more favorable. Random sequential adsorption modeling was then successfully used to understand this paradox.

COLL 481

Using nanodiscs as a plattform to study membrane protein function and structure on surfaces

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The use of 2D oriented membranes has been presented as a method for obtaining structural information from non-crystalline proteins in a biologically friendly environment. However, the functional properties of isolated membrane proteins cannot be probed using continuous lipid bilayers as several membrane proteins are reconstituted into the same lipid matrix. Nanodiscs are self-assembled nanostructures composed of a belt protein (MSP) and ~50 nm^2 patch of lipid bilayer, in which single membrane proteins can be solubilised. We suggest that a 2D matrix of nanodiscs is a more appropriate choice of oriented membrane model. Herein, we present how nanodiscs can be aligned in organized monolayers both at the solid-liquid and just below the air-water interface. As a proof of concept neutron reflectivity and Quartz Crystal Micro-balance studies of the NADPH dependent conformational changes of cytochrome P450 reductase as a function of lipid bilayer charge and phase are presented.

COLL 482

Molecular interactions of mussel protective coating protein mfp-1

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Protective coating of the byssus of mussels has attracted public attention as a new paradigm of medical coating due to its high compliance and hardness co-existence without their mutual detriment. Only known biomacromolecule in the extensible and tough coating on the byssus is mussel foot protein-1 (mfp-1), which is made up with large amount of positively charged residues and lacks of negatively charged residue. The modified amino acid L-3, 4-dihydroxyphenylalanine (DOPA) features prominently in these proteins. Here, adhesion and molecular interaction mechanisms of DOPA-rich *Mytilus californianus* foot protein-1 from California blue mussel (mcfp-1), and DOPA-deficient Asian green mussel foot protein-1 from *Perna viridis* (pvfp-1) were investigated using a surface forces apparatus (SFA). The strong adhesion mechanism induced by cation-pi interactions for both mcfp-1 and pvfp-1 provides new insight into the development of biomimetic underwater adhesives and coatings for biomedical applications. (References: PNAS, 2010; Soft Matter 2011 submitted; Biomaterials, 2011 submitted.)

COLL 483

Soft X-ray spectromicroscopy of protein interactions with phase segregated polymer surfaces

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Characterization of biomaterial surfaces and their interaction with relevant proteins helps understand fundamental issues of protein – polymer interactions and can provide insights into biocompatibility. Synchrotron based X-ray photoemission electron microscopy (X-PEEM) and scanning transmission X-ray microscopy (STXM) are being used to study distributions of proteins adsorbed on chemically heterogeneous polymer surfaces with ~30 nm spatial resolution. X-ray absorption spectroscopy provides speciation and quantitation of both adsorbed proteins or peptides (and in combinations) simultaneously with imaging the underlying polymer substrate (B.O. Leung, J.L. Brash and A.P. Hitchcock, Materials 3 (2010) 3911). Results from two recent investigations will be reported: (1) A study of the relative sensitivity of X-PEEM and STXM for detecting human serum albumin (HSA) adsorption to spun-cast PS/PMMA thin films. (2) A study of HSA adsorption to a PS/PMMA-b-PAA blend which demonstrates control of electrostatic interactions between protein and protonated or deprotonated PAA segments.

COLL 484

Role of growth temperature in the specific and nonspecific force interactions and the mechanical properties of bacterial surface biopolymers as they relate to the adhesion of pathogenic *Listeria monocytogenes* EGDe to silicon nitride

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Role of five temperatures of growth (10, 20, 30, 37 and 40°C) in the specific and nonspecific force interactions, and the mechanical properties of bacterial surface biopolymers as they relate to the adhesion of pathogenic *L. monocytogenes* EGDe to a model surface of silicon nitride in water was investigated using atomic force microscopy (AFM). Our results indicated a higher adhesion force for the bacteria grown at 30°C, followed by 37, 40, 20 and 10°C, respectively. To decouple the measured adhesion forces into the specific and nonspecific force components, Poisson statistical analysis was applied to the AFM adhesion data. The specific and nonspecific interaction forces showed the same temperature dependency; both were superior at 30°C. The higher adhesion observed at 30°C compared to the adhesion at other temperatures was associated with longer and denser bacterial surface biopolymers as predicted from fitting a model of steric repulsion to the approach distance-force data.

COLL 485

Cells mechanics with AFM: Direct comparison of different methods

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AFM is a suitable technique to study mechanics of cells. Cell is far from being a homogeneous medium. To study it, a few major problems should be solved:

1. <u>Cellular surface brush</u> (microvilli, glycocalyx..) surrounds cells. A simple model to separate the brush and cell deformation will be overviewed.

2. <u>Problem of nonlinearity</u> of stress-strain relation. Although unsolved, this may indirectly tested: the rigidity modulus should be reasonably independent of penetration. We will show that it can be achieved when using relatively dull AFM probes (the radii of microns) *only*.

3. <u>Heterogeneity of cell surface</u>. Cells are not homogeneous over the surface. We will discuss the question how many points is enough to characterize the cell.

We will exemplify the above with human cervical epithelial cells. We will demonstrate that without proper consideration of the above problems, the error in defining the modulus of rigidity can easily reach an order of magnitude.

COLL 486

Correlated imaging and nanomechanical force mapping

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Combining scanning probe microscopy, force spectroscopy and fluorescence microscopy on the same microscope platform provide high sensitivity and spatial resolution that facilitate functional, correlated imaging and molecular level characterization of biological processes. The expression of cell surface marker CD38 on chronic lymphocytic leukemia (CLL) B-cells is heterogeneous and carries a prognostic significance. We aim to identify and quantitatively determine the B-CLL cell surface markers CD19, CD20 and CD38 by fluorescence microscopy and image processing methods. The diagnosis based on the cell imaging results was supported by the flow cytometry results. These multimodal imaging tools allow to image individual molecules and to probe molecular assemblies by AFM, with the advantages of fluorescence

microscopy for the selective and specific visualization of labelled molecules in bacteria and mammalian cancer cells.

COLL 487

From ligand-receptor interaction to whole cell manipulation using atomic force microscopy

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Cells in a multicellular tissue interact with neighboring cells and the surrounding extracellular matrix to maintain normal tissue properties. Matrix functionalized atomic force microscope (AFM) tips were used to study integrin-matrix adhesions and to induce mechanical stimulation of live cells. Fluorescence imaging experiments performed in combination with AFM studies allow the investigation of the role and molecular interactions between sub-cellular structures involved in transducing mechanical signaling and inducing cellular remodeling. Our results show that stressing integrin-matrix bonds induces intracellular biochemical pathways activation that eventually triggers downstream cellular remodeling. Conversely, intracellular induced pre-stress alters cytoskeletal tension and integrin-matrix adhesions. Thus, we were able to analyze the correlations between (i) cytoskeletal tension, actin fibers remodeling and cell stiffness; and (ii) focal adhesions remodeling, protein activation and strength of integrin-matrix bonds. This novel integrative approach followed by quantitative data analysis provides better understanding of the complex process of cellular adaptive response to microenvironment.

COLL 488

Stiffness nanotomography of human epithelial cancer cells

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The mechanical stiffness of individual cells is important in both cancer initiation and metastasis. We present atomic force microscopy (AFM) based nanoindentation experiments on various human mammary and esophagus cell lines covering the spectrum from normal immortalized cells to highly metastatic ones [1]. The combination of an AFM with a confocal fluorescence lifetime imaging microscope (FLIM) in conjunction with the ability to move the sample and objective independently allow for precise alignment of AFM probe and laser focus with an accuracy down to a few nanometers [2]. This enables us to correlate the mechanical properties with the point of indentation in the FLIM image. We are using force-volume measurements as well as

force indentation curves on distinct points on the cells to compare the elastic moduli of the nuclei, nucleoli, and the cytoplasm, and how they vary within and between individual cells and cell lines. Further, a detailed analysis of the force-indentation curves allows study of the cells' mechanical properties at different indentation depths and to generate 3D elasticity maps.

[1] A. Fuhrmann, J. R. Staunton, V. Nandakumar, N. Banyai, P. Davies, and R. Ros; AFM stiffness nanotomography of normal, metaplastic and dysplastic human esophageal cells, *Physical Biology* **8** 015007 (2011).

[2] O. Schulz, F. Koberling, D. Walters, M. Koenig, J. Viani, R. Ros; Simultaneous single molecule atomic force and fluorescence lifetime imaging, *Proc. of SPIE* **7571** , 757109 (2010).

COLL 489

Surface functionalization of polymeric lipid bilayers for coupling a model membrane with molecules, cells, and 3D objects

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Methodologies to immobilize biological molecules on the solid surface are important for a wide range of biomedical applications. We previously developed substrate supported model cellular membranes composed of polymeric and fluid phospholipid bilayers. The polymeric bilayer acts as a framework that supports embedded lipid membranes with defined boundaries. The embedded lipid membranes, on the other hand, retain some important characteristics of the biological membrane such as fluidity. Herein we describe a technique to chemically functionalize the surface of polymeric bilayers. Polymeric bilayers having ethanolamine groups at their hydrophilic surface could be functionalized with biological molecules such as biotin and peptides. By using the functionalized surfaces, we could immobilize proteins, cells, and 3D objects (e.g. micro-fabricated elastomer) by molecular recognition. This technique enables to vertically extend the model membrane system, giving possibilities to integrate model membranes and various analytical platforms.

COLL 490

Stabilized surface glycosylated lipid and polymer nanoparticles for systemic delivery

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We have implemented the disaccharide trehalose as an agent to protect particle surfaces from protein opsonization and to preserve assembled structures against destruction upon dehydration. This strategy has been explored with regard to both lipid and polymer nanoparticles for use in delivery. Sugar chemistry developed to provide effective particle conjugation will be discussed.

COLL 491

Probing the mechanism of exciton-based hydrosilylation on silicon

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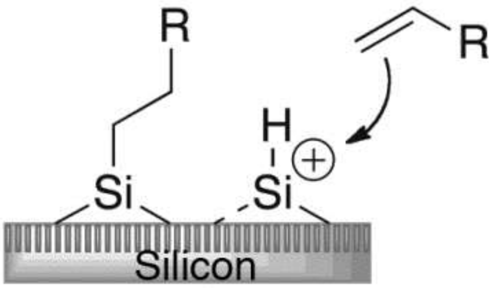
Silicon surface chemistry remains rich with mechanistic questions and intrigue. A pervasive question has been the parallels between molecular silicon chemistry, reactions on flat surfaces, and those on (potentially quantum-confined) nanocrystalline silicon materials. In this talk, dedicated to Professor Hamers, we will discuss recent work on understanding the role of excitons in nanocrystalline silicon - the electron-hole pair can be used to drive surface reactions, particularly those involving silicon-carbon bond formation. Through the use of electron- and hole-trapping agents, kinetics, and surface coverage analyses, we attempt to provide a general reaction scheme for the mechanism of exciton-driven hydrosilylation chemistry



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COLL 492

Semiconductor surface functionalization: Target surfaces in vacuum and in ambient

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Since the 80's, the reactions of organic and organometallic compounds with group IV semiconductor substrates have been of great interest both from fundamental and from practical applications points of view. Two basic approaches focused on either UHV surface functionalization of clean single crystals or on the reactions of H-terminated substrates. Most recently, the focus of our research has been in preparing the surface functionalities normally achievable in UHV but using wet chemistry approaches. The discussion will bring up the use of multiple spectroscopic and microscopic techniques and DFT calculations to investigate the functionalization of semiconductors with the primary emphasis on nitrogen-containing compounds. The differences and similarities of reaction mechanisms in vacuum and in ambient will also be addressed.

COLL 493

Photochemical activities of nitrogen and iron doped rutile and anatase surfaces

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TiO_2 has been widely used in heterogeneous photocatalysis investigations since the discovery of its utility for the photoelectrolysis of water. One of the major limitations of TiO_2 is that it absorbs relatively little of the solar spectrum. Many groups have attempted to achieve visible-light photochemical activity through cation or anion doping of TiO_2. This presentation highlights recent insights into doping of TiO_2 using single crystals as model photocatalysts. Doped films were prepared using molecular beam epitaxy on lattice-matched substrates. The photoactivities of these structurally well-defined N- and Fe-doped TiO_2 rutile and anatase films were examine in the UV and visible using trimethyl acetic acid (TMAA) as a photochemical probe molecule sensitive to valence band holes.

COLL 494

Chemical functionalization of hydrogen-terminated silicon surfaces for sensing and energy applications

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Future silicon-based devices for biomedical and energy applications are likely to use *hybrid* organic/inorganic *oxide-free* junctions, requiring the functionalization of hydrogen-terminated silicon surfaces. Hamers *et al*. have not only developed methods for organic functionalization, but also provided a fundamental understanding of the UV-induced mechanisms. Here, we describe thermal methods to functionalize H-terminated Si. In addition to standard hydrosilylation with alkene molecules, a novel method has been developed to produce hydroxyl-terminated surface on oxide-free Si(111), thus greatly extending the ability to functionalize surfaces with standard organic monolayers

such as phosphonates. We show that, in contrast to hydrophilic oxide surfaces, isolated OH groups on oxide-free Si surfaces are more reactive, leading to facile grafting of high quality phosphonate self-assembled monolayers at room temperature. Applications to sensing and energy are discussed.

COLL 495

Fundamental studies of organic photochemistry on TiO_2

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Photochemical processes on titania play key roles in environmental remediation and in catalytic synthesis. Our work is focused on developing a fundamental understanding of the interplay between surface and molecular electronic structure in determining efficiency and selectivity. We have focused on organic oxygenates because they are prototypical volatile organic compounds (VOCs) and because their thermal chemistry has been investigated. We use imaging (scanning tunneling microsopy), X-ray photoelectron spectroscopy and reactivity studies to probe the fundamental processes leading to photochemical activation of ketones and alcohols.

COLL 496

Molecular sensing on chemically modified silicon surfaces: From gas phase to solution

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On semiconductor surfaces, adsorption and reaction events that lead to charge re-distribution can alter the substrate conductivity through long- range electric field effects. These effects can be exploited to develop methods for electrically based chemical and biological sensing. Electrical transport measurements using hydrogen and alkyl monolayer terminated silicon on insulator (SOI) substrates have been used to observe large reversible field effects upon adsorption of polar molecular species from the gas phase. In particular, alkyl monolayer passivated SOI surfaces show a large reversible response to the prototypical electron acceptor TCNE, suggesting that sensitive detection of high electron affinity compounds is possible. We will also discuss challenges and progress in using alkyl monolayers for biosensing applications, which requires stabilizing the electrical properties of the interface during extended exposures to aqueous buffer. Alkyl monolayers formed on the H-terminated surface are shown to be suitable gate dielectrics for biological field effect transistors (BioFETs).

COLL 497

Heterogeneous electron transfer and homogeneous energy transfer of molecule-like gold nanoparticles

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We present the energy and heterogeneous electron transfer properties of molecule-like gold nanoparticles (NPs), whose diameter is ~1.1 nm. As prepared by the modified Brust's method, the core of a gold NP consists of about 25 gold atoms and its surface is protected by ~18 phenylethanethiol ligands. We modified the NP surface with various alkanethiolates for our studies: n-$C_6H_{13}S$-; n-$C_7H_{15}S$-; n-$C_8H_{17}S$-; n-$C_9H_{19}S$-; n-$C_{10}H_{21}S$-; n-$C_{11}H_{23}S$-; and n-$C_{12}H_{25}S$-. These NPs were prepared by ligand exchange reactions, and ~50 % of the original phenylethanetholates was replaced with alkyltholates. Heterogeneous electron transfer properties were investigated with cyclic voltammetry and digital simulations, measuring heterogeneous electron transfer rate constants which decrease exponentially with increasing the ligand length. Homogeneous energy transfer properties were examined with fluorescence quenching by surface-modified gold NPs. A laser dye, PBBO, was used to determine quenching rate constants which also decrease exponentially with increasing the ligand lengths.

COLL 498

Dialkyldithiophosphinic acid self-assembled monolayers (SAMs) on gold: The dependence of head group binding and SAM structure on alkyl chain length

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We have previously shown that SAMs of dihexadecyldithiophosphinic acid (DTPA) molecules ($[CH_3(CH_2)_{15}]_2PS_2H$) on gold show head group binding that is dictated by the surface roughness of the underlying substrate. Here, we present a study of head group binding and SAM structure of DTPA SAMs with chain lengths n = 5, 9, 11, 13, 15 formed on both template-stripped (TS) and as-deposited (As-Dep) gold substrates. For all chain lengths studied, head group binding is controlled by the surface roughness of the chosen substrate, and the organization and crystallinity of the organic layer is controlled by the length of the alkyl chain. Head group binding was studied by X-ray photoelectron spectroscopy (XPS). Alkyl chain crystallinity was studied by reflection absorption infrared spectroscopy (RAIRS), contact angle goniometry, and lateral force microscopy (LFM). Barrier properties were studied by electrochemical impedance spectroscopy (EIS).

COLL 499

Covalently bonded films on gold nanoparticles

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Tailoring the surface chemistry of metallic nanoparticles is generally a key step for their use in a wide range of applications. There are few examples of organic films covalently bound to metal nanoparticles. In this presentation we will show that aryl films are formed on gold nanoparticles from the spontaneous reduction of diazonium salts. The structure and the bonding of the film is probed with surface enhanced Raman scattering (SERS). Comparison of the SERS spectrum with spectra computed from density functional theory models reveals a band characteristic of a Au-C stretch. The observation of this stretch is direct evidence of a covalent bond. The bonding of these types of films through a covalent interaction on gold is consistent with their enhanced stability observed in other studies. These findings provide motivation for the use of diazonium derived films on gold and other metals in applications where high stability and/or strong adsorbate-substrate coupling are required.

COLL 500

Highly efficient and controllable PEGylation of gold nanoparticles prepared by femtosecond laser ablation in water

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Although it has been extensively studied for over 10 years, conjugation of a defined number of biomolecules onto surface of gold nanoparticles still presents a major challenge. Here, we present a new method for fabrication of stable gold nanoparticle-poly(ethylene glycol) (PEG) conjugates with a defined number of PEG molecules, which are directly bound to gold nanoparticle surface with almost 100% efficiency and the PEG surface coverage is tunable from 0 to 100%. Gold nanoparticles for the nanoparticle PEG conjugates are prepared by femtosecond laser ablation of bulk target in deionized water. This method for fabrication of god nanoparticles creates surface which is negatively charged and chemically clean. This facilitates uniform and controlled binding of thiolated PEG molecules to the surface of the gold nanoparticles. The method could be readily applied in the same way to construct a mixed monolayer composed of other biologically important molecules onto surface of gold nanoparticles.

COLL 501

Use of gold nanoparticle for colorimetric and SERS detection of toxins

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Development of sensitive and on-the-spot detection probes of toxins is an ongoing area of current research. This research is focused on development of gold nanoparticle (AuNP) based probe to detect such molecules quickly and accurately with excellent discrimination of other molecules. In the current research we have developed organic ligand functionalized and polyoxometallate functionalized AuNP for colorimetric and SERS detection of pollutants and toxins without any dye tagging in ppm and/or ppb level. Other techniques including UV-vis, DLS and ^{1}H-^{1}H DOSY are also utilized to characterize the gold nanoparticle based probes.

COLL 502

One-pot synthesis of gold nanoNachos: Molecular nanoheaters

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Most of the methods to produce NIR absorbing Au NPs relies on challenging synthesis with several steps and/or seed-mediated approaches with cetyltrimethylammonium bromide (CTAB) as a surfactant, a well-known toxic cationic surfactant. The development of straightforward and scalable synthesis methods of non-cytotoxic Au anisotropic NPs is of the most importance. Herein, we report a straightforward one-pot synthesis of single-crystalline gold nanoprisms that we have called NanoNachos (NNs) due to the characteristic shape they resemble. In a typical synthesis, NNs were prepared by reduction of chloroauric acid by sodium thiosulfate in water at room temperature. While the thickness of NNs remained constant (8 nm), the edge can be tuned from 80-200 nm by adjusting the final concentration/molar ratio of gold salt and reducing agent (sodium thiosulfate). This allows tuning the surface plasmon band of NNs along the NIR range. NNs are shown as non-cytotoxic and efficient nanoheaters for biomedical applications.

COLL 503

Silver nanostructured surfaces for optimized SERS performance: Application for the detection of organophosphonates

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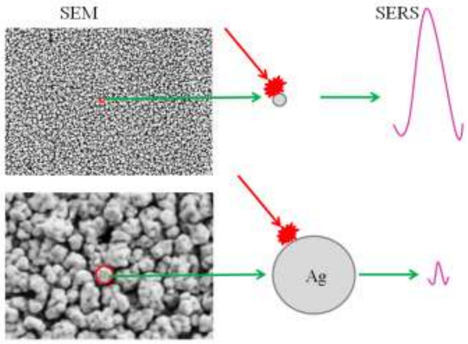
This work focuses on the detection of analytes using metallic nanostructures (NSs). Presently, the preparation of Ag NSs requires valuable chemicals, multiple steps and difficult fabrication methods towards applications in surface enhanced Raman

spectroscopy (SERS) or electrochemical sensing[1]. Here we report the results of a study into the interactions of electrochemically prepared Ag NSs surfaces[2] with organophosphonates by electrochemical methods and by SERS. The effects of nanostructure/particle size on the SERS signal are discussed.



COLL 504

Impact of storage conditions on the physicochemical characteristics of silver nanoparticle suspensions: A best practices study

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The effect of environmental and particle based variables on the stability of citrate capped silver nanoparticle (AgNP) suspensions was investigated. AgNP suspensions were prepared according to specific sets of conditions out of a matrix of variables to model over 80 different storage conditions over a lifetime of up to 104 days. Variables studied included temperature, silver and citrate concentrations, dissolved oxygen content and presence/absence of light. Transformation in optical properties, size, aggregation state and speciation of breakdown products were examined with UV-vis spectroscopy, DLS, AFM, NMR, and XPS. Additional studies will investigate the impact of specific products on toxicity. Results suggest that while all variables effect the lifetime of AgNP stability, the most important variables to control are light, [AgNP] and [citrate]$^{-3}$ in maintaining their initial physico-chemical characteristics.

COLL 505

Seeded growth of silver nanocrystals with controlled sizes and shapes

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Silver nanocrystals have gained grant interests due to their LSPR/SERS properties highly depending on their sizes and shapes. It is this situation that motivates us to develop a seed-mediated growth method to tailor and fine-tune the size/shape of silver nanocrystals, and thus precisely control properties. We first experimentally manipulated the size of seeds, and the number/type of defects formed in the seeds. We also systematically investigated the effects on both thermodynamic and kinetic parameters including capping agent, reducing agent, and adding rate on growth of Ag nanocrystals. The size/dimension of resultant nanocrystals can be controlled by simply varying the ratio of the seeds to the added precursor. With the use of appropriate seeds and a suitable reducing agent, we were also able to manipulate the shape of the resultant nanocrystals.

Figure 1. Growth of silver nanocrystals with concave surfaces.

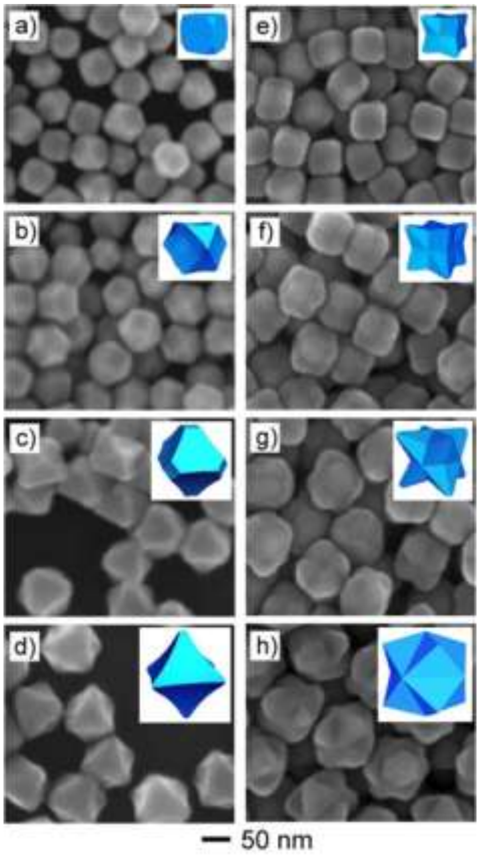
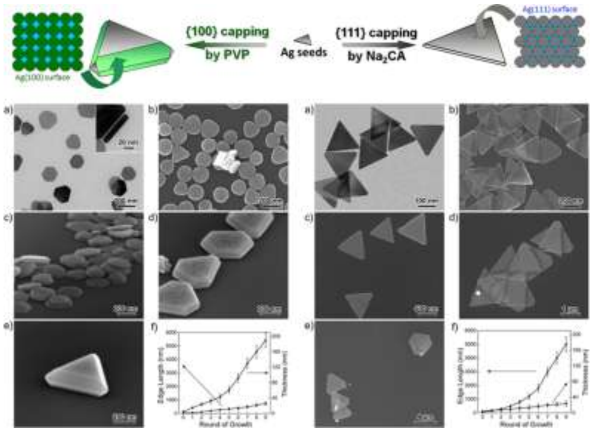


Figure 2. Growth of silver nanoplates.



COLL 506

Tailored plasmonic nanostructures for surface-enhanced spectroscopy using nanosphere template lithography

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Noble metal nanostructures that support localized surface plasmon resonances (LSPRs) are of interest as substrates for surface-enhanced spectroscopies. The LSPR wavelength is dependent on structure size, geometry, and composition and can be tuned from the ultraviolet to mid-infrared region of the spectrum. This tunability can be controlled through physical parameters used in the fabrication process. We present investigations of gold and silver nanocrescents and disks fabricated through nanosphere template lithography to allow control of the size, shape and material of the resulting nanostructure. During fabrication, aggregation of the template produced clusters of disks with junctions of roughly 20 nm. Due to the local enhanced electromagnetic fields, these junctions act as accessible hot-spots for surface-enhanced Raman scattering signals of adsorbed molecules. Signal enhancements of 4-nitrothiophenol molecules have been observed on the surface of gold and silver nanodisks. In addition, methods to prepare tunable aluminum plasmonic structures have been investigated.

COLL 507

Effects of amines on formation of atmospheric sub-3 nm particles and their subsequent growth

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Atmospheric nucleation is an important initial step in the chain reactions that lead to cloud formation, but the nucleation mechanisms are poorly understood. Recent field studies and quantum chemical calculations show that amines can contribute to formation of nanometer size particles. Amines and ammonia often have common atmospheric emission sources and have similar chemical and physical properties. While the effects of ammonia on aerosol nucleation processes have been previously investigated, laboratory studies of homogeneous nucleation involving amines are critically lacking. We have conducted kinetics studies of multicomponent nucleation with sulfuric acid, water, ammonia and amines under conditions relevant to the atmosphere. Concentrations of aerosol precursors are measured with chemical ionization mass spectrometers, to provide constrained precursor conditions needed for nucleation. Particles sizes larger than 2 nm are measured with a nano-differential mobility analyzer and number concentrations of particles larger than 1 nm are measured with a particle size magnifier. These particle instruments allow us to investigate the nucleation and growth processes, independently. In this presentation, we will show how different amine compounds affect nucleation and growth of sulfuric acid particles, in comparison with ammonia. We will also show how ammonia and amines together affect formation of clusters and nanometer size particles. Our results show that these organic and inorganic base compounds should be together taken into account in atmospheric aerosol formation processes.

COLL 508

Amine reactivity with molecular clusters relevant to ambient new particle formation

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Ambient new particle formation (NPF) occurs when gas-phase species come together to form nuclei in the low nanometer size range, which then grow quickly over time. While nucleation is driven in large part by sulfuric acid, many additional chemical species contribute to particle growth. Amines are of particular interest for growth since they have been detected at elevated levels during NPF. An important mechanism of amine uptake is aminium salt formation, either by substituting for ammonium ions that already exist in the particle or by opening new channels for salt formation that are not favorable with ammonia. This presentation will focus on recent experimental and computational work in our group to study amine uptake into charged nanoclusters of sulfuric acid and ammonia. We find that amine reactivity is dependent on the size, composition and charge of the cluster. The implications of these dependencies for NPF will be discussed.

COLL 509

Carbonate mineral nucleation on mineral surfaces: In situ GISAXS and microscopy studies

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The precipitation of carbonate minerals –mineral trapping– is considered the safest CO_2 sequestration mechanisms. However, the physico-chemical factors controlling nucleation and growth of carbonate minerals in geological carbon repositories are not very known known. The goal of the present study is to obtain values for the heterogeneous nucleation rates of carbonate minerals on mineral surfaces representative of carbon reservoirs, such as quartz, olivine or mica. In this talk we will present results obtained using Grazing-Incidence Small Angle X-ray Scattering (GISAXS), and complemented with Atomic Force Microscopy. GISAXS allows detecting nanometer-scale nuclei and follow their growth over time. Performing experiments at different saturation indexes allows obtaining an effective interfacial energy for each surface. These *in situ* and *ex situ* observations yield important quantitative parameters readily usable in reactive transport models of nucleation at the reservoir scale.

COLL 510

Molecular dynamics simulations of early stage of nucleation of iron oxyhydroxide nanoparticles in aqueous solution

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Acid mine drainage can contain high concentrations of dissolved iron. These solutions contaminate aquifers and discharge into lakes, bays and the sea. En route, solutions are neutralized, causing deposition of abundant, and typically nanoparticulate, iron oxyhydroxides. This impacts iron geochemical cycling and the form and distribution of other elements that co-precipitate and adsorb onto particle surfaces. Nucleation and growth of iron oxyhydroxides are important steps in these processes. In this work, we used molecular dynamics simulations to study the ferric iron molecular cluster formation and aggregation upon neutralization of ferric ions by hydroxyl groups, a process that leads to nuclei formation and growth and eventual precipitation. Results suggest that gibbsite-like layered ferric hydroxide clusters form at the very early stage of nucleation, followed by deprotonation that leads to formation of 3-deimenional ferric oxyhydroxide clusters. Aggregated ferric oxyhydroxide clusters display short-range atomic order similar to that found in small ferrihydrite nanoparticles.

COLL 511

Using cryogenic transmission electron microscopy to characterize nanoparticle aggregation in aqueous solutions

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The fate and transport of nanoparticles in aqueous systems is strongly dependent upon their aggregation state. Aggregation state is sensitive to solution variables like ionic strength and pH, as well as the presence and concentration of other chemical species like natural organic matter. Results tracking changes in aggregation state as a function of changing solution conditions, using cryogenic transmission electron microscopy as the primary technique, will be presented. Finally, results from experiments testing the reversibility of aggregation will be presented.

COLL 512

Metal sulfide nanoparticles in the marine environment

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Metal sulfide nanoparticles are ubiquitous in a variety of waters and porewaters including hydrothermal vent waters. Here, we center our attention on iron, zinc and copper sulfides in vent waters. FeS and FeS_2 (pyrite) nanoparticles can be detected by a combination of voltammetry, XRD, TEM and SEM. Zn and Cu can be included in pyrite nanoparticles defined here as that material that passes through 200 nm filters. TEM analysis shows that pyrite nanoparticles (collected from black smokers at Lau Basin in May 2009) are as small as 4 nm, and aggregate into larger nano-framboids of 50-350 nm in size. The stability of pyrite nanoparticles to oxidation and their possible transport in seawater will be discussed as recent data demonstrate that iron emitted from hydrothermal vents has an impact on the iron budget of the world ocean. Other metal sulfide nanoparticles (e.g.; Zn, Cu, Cd) will likely exhibit similar behavior.

COLL 513

Effects of substrate properties on nucleation, growth, and aggregation of metal oxides in aqueous systems

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Nucleation, growth, and aggregation of metal oxide nanoparticles in aquatic systems can significantly alter the fate of organic and inorganic contaminants. In this study, we aimed to provide more accurate quantitative and qualitative information about nucleation, growth, and aggregation of iron oxide nanoparticles. We used a time-resolved simultaneous small angle x-ray scattering (SAXS)/grazing incidence (GISAXS) setup for real-time monitoring of nanoparticle formation at water-mineral interfaces. The size and shape of nanoparticles and the location of iron oxide nanoparticles from the substrates were monitored. The substrates were quartz, mica, aluminum oxide, and organic polymer coated surfaces. To complement the observations, atomic force microscopy, high resolution transmission electron microscopy, dynamic light scattering, and electrophoretic mobility analyzer were utilized. In this talk, we will also present the reactive surface area evolution as a function of time, which is often found in the environment due to thin surface coatings of these nanoparticles.

COLL 514

Study of formation and aggregation of akaganeite nanoparticles using In situ small angle X-ray scattering

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Nucleation, growth and aggregation are important processes in the environment involving nanoparticles. In this work, we studied the formation and aggregation kinetics of akaganeite nanoparticles during thermal hydrolysis of $FeCl_3$ solutions (0.02, 0.2, and 0.8 M) at various temperatures (50 – 80 ^oC) using *in-situ* small angle X-ray scattering (SAXS). Results showed that particle size increased dramatically with time and the growth kinetics strongly depended on the temperature. After a certain reaction time, developing particles in the 0.2 M solutions suddenly assembled to form periodic aggregate structures with inter-particle distances of 20 - 30 nm, as shown by the presence of pronounced diffraction peaks at several small angles. Each inter-particle distance slightly increased with reaction time, implying growth of nanoparticles. The texture indicated by 2-D diffraction images suggests the presence of preferred orientation of assemblies. This phenomenon was observed in neither 0.02 M nor 0.8 M $FeCl_3$ solutions, indicating its concentration dependence.

COLL 515

Applications of the QCM-D method (quartz crystal microbalance with dissipation monitoring) to solid-liquid interface studies

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The QCM-D technique was developed in the first half of the1990ies for operation in liquids (Rodahl et al, RSI 66 (1995) 3924). It has been applied to a variety of solid-liquid interface measurements, like protein and lipid bilayer adsorption, polyelectrolytes, corrosion, electrochemistry, hydrogen storage, solar cells, nanoparticle interactions with bio-membranes, and cell-surface interactions (q-sense.com/publications). QCM-D was turned into a commercial instrument via the university start-up company Q-Sense AB. Nearly 1000 publications have been produced with these instruments. Specific examples covered in this presentation are; lipid bilayers and their use for nano-drug screening and nanoparticle toxicity/safety screening, dye impregnation of DSSC solar cells, cell-surface interactions, electrode corrosion in fuel cells and metal (Al, Cu) corrosion.

COLL 516

Using QCM-D and ellipsometry to determine the orientation and state of hydration of antibodies adsorbed on a hydrophobic surface

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Adsorbed antibodies can take several orientations: end-on/fab-up, end-on/fab-down, side-on and flat-on. Since the accessibility of antigens will depend on the antibody orientation, we have used QCM-D to monitor transient adsorption and have determined the orientation as a function of coverage. In addition, we have used simultaneous QCM-D and ellipsometry to distinguish between the "wet" mass consisting of protein plus coupled water and the "dry" mass consisting only of the protein. Finally, we have developed an alternative protocol for determining the state of hydration using only QCM-D. This involves a D_2O exchange that allows determination of the dry mass. We conclude that the QCM-D signal of proteins in liquids contains a major component from coupled water.

COLL 517

Antiviral mode of action of AH peptide determined by combined surface science techniques

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An amphipathic, α-helical (AH) peptide derived from the N-terminal region of the hepatitis C virus (HCV) NS5A protein represents a breakthrough, broad-spectrum antiviral drug candidate. Uniquely compared to other antiviral medicines in development or in the clinic, the virocidal activity of AH peptide was originally discovered by surface science techniques probing model biological interfaces—namely lipid vesicles serving as surrogates for lipid-enveloped virus particles. Quartz crystal microbalance with dissipation (QCM-D) monitoring identified that addition of AH peptide ruptures a layer of intact lipid vesicles to promote structural transformation to a planar lipid bilayer. Based on this structural transformation, we have used simultaneous QCM-D monitoring and optical reflectometry to determine the antiviral mode of action of the AH peptide. Collectively, these results lay the groundwork for the engineering of AH peptide therapeutics with optimized properties as well as for the broader application of surface science techniques to drug discovery and development.

COLL 518

Mechanism of adsorption of peptides and surfactants on metal surfaces

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We will illustrate how specific adsorption of peptides, amino acids, and surfactants to metal surfaces in aqueous solution is predominantly guided by soft epitaxy and induced charges. Computer simulations using the CHARMM-METAL force field have shown excellent agreement with experimental data with respect to facet specific adsorption, the relative order of amino acid adsorption on gold {111} surfaces, and allow insight into shape control and catalytic properties of metal nanostructures. Examples of peptides in contact with Au, Pd, and Pt surfaces will show details of adsorption and sequence specific design.

COLL 519

Using QCM-D to deduce the mechanism of SMAP-29 action on a model membrane

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Antimicrobial peptides (AMPs) are naturally occurring molecules that can kill bacteria by destabilizing bacterial membranes and causing lysis. However, the active mechanism behind the membrane destabilization is not well understood. Quartz crystal microbalance with dissipation monitoring (QCM-D) was used to investigate the action of sheep myeloid antimicrobial peptide-29 (SMAP-29) on a supported lipid bilayer of phosphatidylcholine. The changes in frequency and dissipation of the film, which can be related to changes in mass and viscoelasticity, were measured as it was exposed to SMAP-29. Concentrations of SMAP-29 above 2 μM resulted in an increase in the membrane's mass, which was non-uniform throughout the bilayer, indicating both

peptide adsorption on the bilayer surface and insertion into the membrane to form pores. By analyzing various AMP and lipid bilayer systems using QCM-D, we will be able to gain a more detailed understanding of how AMPs interact with bacterial cell membranes in future work.

COLL 520

Zn^{2+} adsorption at glucosamine- and undecanol-functionalized fused silica/water interfaces

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Adsorption of Zn^{2+} to glucosamine-functionalized and undecanol-functionalized fused silica/water interfaces is studied using second harmonic generation (SHG). We characterize the surface using vibrational sum frequency generation (SFG) and X-ray photoelectron spectroscopy (XPS), and employ the SHG $\chi^{(3)}$ technique to track Zn^{2+} adsorption directly at the fused silica/aqueous interface, at pH 7 and 10 mM NaCl. We determine the thermodynamic binding parameters using standard electrical double layer models to quantify the change in interfacial potential upon zinc adsorption. The results presented here allow for the possibility of 2:1 to 3:1 carbohydrate:metal coordination complexes and suggest the possibility for multivalent interactions which have not been observed with glucose in bulk aqueous phase, where 1:1 complexes dominate. We compare these results to undecanol-functionalized fused silica—our simplified carbohydrate system—and show that interactions between metal ions and carbohydrate arrays may be stronger at interfaces, with direct implications for controlling and predicting coordination chemistry.

COLL 521

Influence of tilt angle and droplet size on the sliding rate of water droplets on superhydrophobic surfaces

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A novel method for evaluation of dynamic wetting properties on different superhydrophobic surfaces has been used in order to characterize the sliding rate of water droplets. The motion of droplets has been recorded with high-speed video and the relevant data have been extracted by custom made image analysis software. The influence of tilt angle and droplet size on sliding acceleration has been investigated for tilt angles ranging from 2,5 degrees to 30 degrees and droplet volumes ranging from 1 µl to 10 µl. Special interest has been devoted to the case of zero acceleration, since it determines whether non-stationary droplets will roll off or remain pinned to the surface. The data has been compared with more commonly used methods such as contact

angle hysteresis and roll-off angle. Furthermore, two new surface properties called equilibrium sliding angle and sliding angle hysteresis have been introduced.

COLL 522

Award Address (ACS Award in Colloid and Surface Chemistry sponsored by The Procter & Gamble Co.). "Holey" chemistry at semiconductor surfaces

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Semiconductors such as metal oxides, silicon, and diamond lie at the heart of many emerging applications in renewable energy and biotechnology. Through more than 10 years of effort our studies have shown that UV-induced photoemission is a nearly universal way to initiate grafting of molecular monolayers to semiconductor surfaces via "holey chemistry," in which UV-induced photoemission leaves behind surface-trapped holes that induce nucleophilic addition reactions to form new, self-terminating surface-to-molecule bonds. When combined with modular chemistry such as "click" chemistry, this approach can yield highly stable, redox-active and photo-active surfaces with excellent charge-transfer rates. The unique surface bonding structures at metal oxide surfaces also lead to new types of reactions similar to well-known organic reactions, but with distinct differences arising from the unique chemical properties of surface atoms. Finally, a twist on holey chemistry will be presented, leading to a highly unusual type of surface photocatalytic reaction.

COLL 523

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 Publication Journal Langmuir). Dynamical processes at surfaces examined with molecular beam scattering, scanning probe imaging, and numerical simulations

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This talk will examine current forefront topics in interfacial dynamics, surveying exciting developments in elastic, inelastic, reactive, and photochemical processes at surfaces. Notable advances are occurring in our atomic-level view of such interactions, driven by synergies between scattering measurements, local scanning probe imaging, numerical simulations and theory. Emphasis is increasingly aimed at examining how local structures kinetically form on the atomic level, and how their relative reactivity and physical properties depend on local ensemble configuration. Another trend is the examination of more complex interfaces including structural evolution on multiple length-scales. Examples of this include self-assembling systems, polymers, and hierarchical functional materials. Due to the aforementioned developments, we are

gaining rigorous atomic-level insight into the dynamical processes which govern a wide-range of heterogeneous phenomena, such as catalysis, reaction dynamics, collisional energy transfer, materials growth and erosion, self-organization, and interfacial metallurgy. This presentation will illustrate the above using research from our laboratory.

COLL 524

Award Address (ACS Award for Creative Invention sponsored by the ACS Corporation Associates). Spherical nucleic acid (SNA) nanostructures: Establishing a new paradigm in materials synthesis, molecular diagnostics, and intracellular gene regulation

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The natural defenses of biological systems for exogenous oligonucleotides, such as synthetic antisense DNA and siRNA, present many challenges for the delivery of nucleic acids in an efficient, non-toxic, and non-immunogenic fashion. Indeed, because nucleic acids are negatively charged and prone to enzymatic degradation, researchers have historically relied on transfection agents such as cationic polymers, liposomes, and modified viruses to facilitate cellular entry and protect delivered biomolecules from degradation. However, each of these platforms is subject to several drawbacks, which include toxicity at high concentrations, the requirement of specialty nucleic acids to enhance stability, and severe immunogenicity.

Spherical nucleic acid (SNA) gold nanoparticle conjugates (inorganic nanoparticle cores functionalized with a spherical shell of densely organized, highly oriented nucleic acids) pose one possible solution for circumventing these problems in the context of both antisense and RNAi pathways. Remarkably, these highly negatively charged SNA structures do not require cationic transfection agents or additional particle surface modifications and naturally enter all cell lines tested to date (over 50, including primary cells). Further work has shown the cellular uptake of these particles to be dependent upon DNA surface density: higher densities lead to higher levels of particle uptake. The high-density polyvalent nucleic acid surface layer is believed to recruit scavenger receptors from the cells that facilitate endocytosis. Moreover, the ion cloud associated with the high-density oligonucleotide shell, combined with steric inhibition at the surface of the particles, inhibits enzymatic nucleic acid degradation and activation of the enzymes that trigger the innate immune response of certain cells. In this talk, methods to synthesize such structures and novel applications that take advantage of the interesting properties unique to spherical and other forms of three-dimensional nucleic acids will be described.

COLL 525

Multifunctional fiber technology for chemical biological defense applications

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Current chemical biological (CB) protective garments are layered fabric systems ultimately designed to maximize CB protection (via threat agent shedding and sequestration) while reducing thermal burden. Unfortunately, in order to achieve high CB protection, thermal burden is sacrificed; therefore protective garments exhibit high thermal burden (high thermal resistance and low breathability). The desire is to develop an integrated fabric technology that combines protective capabilities into a single fabric layer. A historical perspective on the approaches and challenges associated with developing CB protective garments will be presented. Efforts to develop multifunctional fibers, to include reactive fiber technology, will be discussed.

COLL 526

Electrospun nanofibers and nanomaterials in textiles and protective clothing applications

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Research on the remediation of environment and pollution has been the subject of interest for many decades. Recently, nanotechnology field is booming and hence both fundamental and applied aspects are focused by various researchers. Nanomaterials such as MgO, Al_2O_3, Fe_2O_3, ZnO, and $TiO_2$are widely explored in the fields of textiles, tissue engineering, and water and air purification. Nanoparticles were extensively studied due to their enhanced catalytic, disinfection and sensing capability, photoprotection capability, and stain resistance and self-cleaning properties. Existing state-of-the-art activated charcoal based materials used in protection and textiles against chemical and biological contaminants have few drawbacks. In this presentation, we investigate an alternative material for charcoal and their possibility of replacement. The nanomaterials and cerami nanofibers are being currently incorporated into nonwoven fabrics to achieve multifunctional capability. The recent trend of exploiting nanoparticles is best possible substitutes to activated carbon in nonwoven fabrics. Some of the issues concerning integration of these materials to use in protective clothing, textiles, and sensors applications studied in our laboratory will be presented. The studies show that the latest buzz of nanotechnology will replace the existing conventional materials.

COLL 527

Adsorption of core-shell nanoparticles on fibers for hydrophobic modification

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The core-shell latexes based on butyl acrylate (BA) and three other co-monomers using cetyl trimethyl ammonium bromide as a cationic surfactant were prepared via seed emulsion copolymerization. The latex particles were applied to cellulose fibre networks either as wet-end additive or coated layer to improve the hydrophobicity of paper. It was found that both approaches increased the hydrophobicity of paper (demonstrated by the increasing of contact angles); and both approaches applied simultaneously indeed created the synergy. The hydrophobic enhancement is proportional to the latex amount added. The cationic surfactant on the latex surface mainly ensured the high retention of latex with cellulose fibres; SEM images confirmed that upon heating the hydrophobic film formed within fibre networks due to the low T_g of latex. However, the improvement in lowering water vapor transfer rate (WVTR) induced by latex was limited, implying that the hydrophobic modification does not necessarily lead to low WVTR.

COLL 528

Effect of fiber morphology on self-decontaminating properties of titanium dioxide containing fibers

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Dermal absorption of toxins is a concern in chemical defense for military purposes. To create a breathable material, self-decontaminating materials can be used to make continuous protection against toxic materials possible. When engineering the self-contaminating protective systems, it is important to investigate the influence fiber morphology has on the catalytic performance of the nanoparticle/fiber composite.

Fibers with self-decontamination functionality were developed by incorporating titanium dioxide nanoparticles into polymers and were found to have the ability to degrade organophosphate toxins. While the fiber structure provides a stable immobilized protective system, the reaction between a toxic compound and active particles is influenced by location near the surface or diffusion to active sites. Thus, different fiber morphologies will change the surface exposure of the titanium dioxide, which leads to enhanced self-decontamination and protection. Fiber morphologies include uniaxial, coaxial, and porous channeled electrospun nanofibers, which are made with a co-continuous polymer electrospinning dope.

COLL 529

Antimicrobial activity of electrospun cationic polyelectrolytes and oligomers

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Nano- to micro-fibrous mats have been produced via a general electrospinning technique. A carrier polymer has been used to incorporate conjugated polyelectrolytes (CPEs) of varying chain length and with different terminal moieties into the mats at loadings ranging from 1 to 10 wt%. Leaching studies were carried out to determine the stability and retention of the active compounds in water, buffer and organic solvents. Mats were exposed to bacterial suspensions both in solution and aerosolized and these were analyzed using confocal and fluorescence microscopy and flow cytometry to determine biocidal efficacy. Several of the CPEs show significant killing of both Gram positive (*S. aureus*) and Gram negative (*E. coli*) bacteria in this format.

COLL 530

Modification of cotton fibers with silica nanoparticles and silica species via microwave synthetic techniques for adsorption of chemical agents

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Monodisperse silica nanoparticles were synthesized by controlled microwave-assisted reactions using tetramethylorthosilicate in acetone. These silica nanoparticles and fluorosilane moieties were incorporated via microwave synthetic techniques into and onto the silica matrix that encases the individual fibers of textile fabrics. The high-surface-area silica nanoparticle-laden matrix provides protection from toxic vapors via adsorption while the fluorosilane provides protection from liquids. The chemical adsorption of vapors is increased due to increased surface area of the silica nanoparticles as well as the porosity of the nanoparticles. The chemical simulants, dimethyl methylphosphonate (DMMP) and 3-hepten-2-one, were tested to measure surface interactions and break-through on treated cotton fabrics. Isotherms and vapor break-through were measured by inverse gas chromatography and by vapor permeation where the cotton treated with silica nanoparticles show a dramatic reduction of DMMP and 3-hepten-2-one.

COLL 531

Polyoxometalate-treated fabrics: Materials that facilitate catalytic air-based decontamination

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Polyoxometalates (POMs) substituted with appropriate 3d metals are highly effective for the catalytic decontamination of several chemical warfare agents (CWAs) and toxic industrial chemicals (TICs) using only ambient air as the reactive. We have successfully incorporated some POM systems into a range of fabrics using several different catalyst immobilization strategies ranging from simple physisorption (deposition from solution) to electrostatic attachment (cationic fabric surfaces strongly bind POMs which bear high negative charges). The fabrics treated with POMs frequently retain the high aerobic decontamination activity of the POMs themselves. We will review the latest POM catalysts and the current challenges for immobilizing these on a range of fabrics without loss of catalytic activity. Recent work on the toxicological properties of the POM catalysts (promising) will also be presented.

COLL 532

WITHDRAWN

COLL 533

Well-oriented antibodies on phospholipid polymer platform recorded high binding affinity

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To investigate the effect of antibody orientation on its immunological activities, we developed a novel and versatile platform consisting of a well-defined phospholipid polymer surface on which staphylococcal protein A (SpA) was site-selectively immobilized. The phospholipid polymer platform was prepared on silicon substrates using the surface-initiated atom transfer radical polymerization technique. An enzymatic reaction was performed for orientation-selective coupling of SpA molecules to the polymer brush surface. Orientation-controlled antibodies were achieved using enzymatic reactions, and these antibodies captured 1.8 antigens on average. Theoretical multivalent binding analysis further revealed that orientation-controlled antibodies had antigen-antibody reaction equilibrium dissociation constants (Kd) as low as 8.6×10^{-10} mol/L, whereas randomly oriented and partially oriented antibodies showed Kd values of 2.0×10^{-7} and 1.2×10^{-7} mol/L, respectively. These findings support the significance of antibody orientation because controlling the orientation resulted in high reactivity and theoretical binding capacity.

COLL 534

Friction force spectroscopy as a tool to study the strength, lateral diffusion, and structure of proteinaceous layers

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Protein layers may act as protective/lubricant barriers where their resistance to wear is of relevance. Despite this, little research has been performed on wear of protein layers due to the lack of experimental techniques. Recently, we showed how the Atomic Force Microscope (AFM) operated in the Friction Force Spectroscopy (FFS) mode can be used to follow the dynamics of the scratching of protein layers. Specifically, this method allows monitoring of the evolution of topography (in the nm range) and of the friction between tip and sample (in the nN range) while varying the applied load. We show how parameters of the layers such as the yield strength, and even information on the lateral diffusion of the proteins within the layers, can be provided. Results are presented for layers formed by globular proteins (BSA), and for layers formed by amphiphilic unordered proteins (β-casein). FFS measurements on salivary films are also presented.

COLL 535

Adsorption of fibronectin on alkylsilane monolayers and its effect on cell adhesion and growth as compared to thiols on gold

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A whispering gallery mode (WGM) biosensor with an integrated flow cell was used to measure the adsorption kinetics of fibronectin (FN) on three different alkysilane self-assembled monolayers (SAMs) down to the lowest solution concentrations yet reported. On hydrophilic polyethylene glycol silane (SiPEG) surfaces and at high solution concentrations on hydrophilic aminated (DETA) and hydrophobic perfluorinated (13F) silanes, experimental results generally agreed with published results. At solution concentrations of 1 µg/ml and below, significantly higher adsorption densities were measured on DETA and 13F compared to alkanethiol SAMs with similar properties. The surface density of adsorbed FN was similar for DETA and 13F surfaces. Mathematical models fitted to the experimental results indicated that FN denatured after adsorption on 13F, but not on DETA. The surface structure and subsequent biological function of adsorbed FN were confirmed by culturing embryonic hippocampal neurons and skeletal myoblasts on FN-coated silane surfaces.

COLL 536

Superlow fouling polyacrylamide grafted on gold surfaces via atom transfer radical polymerization

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The development of nonfouling materials and surfaces is critical to many applications, such as biomaterials and biosensors. Polyacrylamide gel has been widely used in SDS-PAGE for protein separation. Nevertheless, the potential of polyacrylamide to be used as surface coatings has barely been explored. In this study, acrylamide was polymerized via atom transfer radical polymerization (ATRP) to form uniform polymer brush on gold surfaces. The superlow fouling properties of the surface-grafted polyacrylamide to resist protein adsorption and cell adhesion were studied. We demonstrate in this work that polyacrylamide grafted surfaces via ATRP highly resist protein adsorption, not only from single protein solutions, but also from 10% and even undiluted serum and plasma. Moreover, polyacrylamide brush highly resists cell adhesion. It is concluded that superlowfouling surfaces with well-controlled polyacrylamide brushes were achieved on gold surfaces.

COLL 537

What determines protein desorption behavior?

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Detailed insights into the mechanisms governing the behavior of proteins at solid/liquid interfaces are particularly relevant in prefilled drug-delivery systems, where adsorption-induced conformational changes may dramatically affect biocompatibility when high-value biologics contact device surfaces. Although we have the reasonably sound understanding that adsorption generally leads to the perturbation of secondary structure, relatively little is known about how history-dependence of surface-related events affect subsequent desorption. With the goal of elucidating desorption predictability for specific systems, we evaluate structural transitions and kinetic parameters along the adsorption-desorption lifecycle of several proteins on nanoparticle surfaces of varying hydrophobicity, as a function of surface coverage. Screening proteins based on stability and charge difference with the surface enables us to rank the role of electrostatics and intrinsic stability in reversibility of adsorption and pathways of desorption. We find that charge difference plays a determining role in whether Langmuiran parameters can be used to predict desorption behavior.

COLL 538

Adhesive substrate directed modulation of dendritic cell response

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Dendritic cells (DCs) are central regulators of the immune system that operate in both innate and adaptive branches of immunity. Activation of DCs by factors such as danger signals is well established. Furthermore, it is established that adsorbed adhesive proteins on implanted biomaterials modulate inflammatory responses. However, modulation of DC responses upon interaction with adhesive proteins has only begun to be characterized. We have investigated DC functions (activation marker expression, cytokine production, T-cell stimulation) in response to culture on a number of adhesive proteins. Furthermore, we have utilized a "universal gradient substrate for click bio-functionalization" as a high-throughput method to investigate the relationship between DC integrin binding and RGD density-dependent responses. This work has impact on the rational design of biomaterials for diverse applications such as tissue-engineered constructs, synthetic particle-based vaccines and the ex vivo culture of DCs for immunotherapies.

COLL 539

Organic-inorganic hybrids formed by $CaCO_3$ mineralization under β-sheet forming peptide monolayers

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In biominerals, proteins are a key element in the controlled nucleation and growth of the mineral phase. We report here on the coupled evolution of the organic and inorganic structures during the nucleation and growth of $CaCO_3$ under a monolayer of acidic β-sheet forming peptides that mimic the natural proteins found in nacre. The investigation is carried out using *in situ* analytical techniques (X-ray diffraction and IR spectroscopy) in order to provide molecular scale structural information over the whole course of the mineralization process. Mineralization is shown to coexist with β-sheet order while inducing other conformational changes to the peptide assembly. Peptides are observed to promote the growth of unoriented vaterite crystals; no templating effect of the β-sheet order is observed.

COLL 540

Molecular mechanisms mediating protein-surface interactions: Adsorption-induced unfolding of proteins on material surfaces with minimal protein-protein interactions

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In order to study the influence of surface chemistry on the unfolding behavior of adsorbed proteins with minimal protein-protein interactions, circular dichroism spectropolarimetry (CD) was used to quantify the degree of adsorption-induced protein unfolding as a function of protein solution concentration. Studies were conducted using ribonuclease A, hen egg-white lysozyme, and human serum albumin adsorbed on high density polyethylene, poly(methyl-methacrylate), and fused-silica glass. CD results showed that adsorption-induced changes in protein structure steadily increased and then reached a plateau with a maximum degree of unfolding as solution concentration was decreased, thus establishing solution concentration conditions that minimized protein-protein interactions on the surface. The degree of adsorption-induced protein unfolding was found to be protein-surface combination dependent. These results show that adsorption-induced protein unfolding is not solely driven by surface hydrophobicity and suggest a strong influence by adsorption mechanisms that can compete with hydrogen bonds that serve to stabilize protein secondary structure.

COLL 541

GOLD nano particle gradients on flat surfaces for the investigation of protein and cellular adhesion phenomena

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Negatively charged gold nano particles, sized 10 – 50 nm was adsorbed to dithiol functionalized flat gold surfaces. The average distance between the adsorbed particles was tuned from 5– 80 nm by using buffer with different ionic strength. The unoccupied area between the particles was modified by using maleimide conjugated reagents and the surface of the adsorbed gold particles was modified by using different thiol containing reagents. The nano compartment functionalized method was very flexible with regard to the different maleimide (e.g. PEG) and thiol containing reagents (e.g. hydrophobic groups) used. We have also developed an ion diffusion method of making mm-sized gradient with dense coverage of nano particles adsorbed at one end of the gradient and sparsely covered nano particles at the opposite end. This nano gradient method was used in studies of protein adsorption, microbial adhesion and eukaryotic cell adhesion. Many surprising findings related to nano-particles distance were made

COLL 542

BSA and lysozyme delivery from xanthan gum hydrogels

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Polysaccharides hydrogels are of great interest on biomedical applications. Furthermore, proteins diffusion and delivery from hydrogels become an important matter in biomedical field, and the use of models as BSA – bovine serum albumin (protein present in blood and widely used in diagnostic analysis) and LYZ – lisozyme (antimicrobial protein, abundant in a number of secretions, such as tears and human milk), can help us to understand such processes.

Xanthan, a branched anionic polysaccharide, was crosslinked by esterification reaction either in the presence or absence of citric acid at 165^{o}C yielding chemical hydrogels. Obtained xanthan hydrogels presented high pore density, evidenced by scanning electron microscopy. Gel content and equilibrium swelling of these hydrogels can be controlled by citric acid contents. Swelling rate is initially controlled by wicking properties of hydrogel, which depends on the medium pH, once it influences the charge density of xanthan chains.

The obtained hydrogels were tested as systems for BSA and LYZ delivery, at pH 1.3, 7.4, and 10. Diffusional coefficients (n) for proteins delivery were calculated and quasi-Fickian diffusion was predominant (calculated n values between 0.07 and 0.20). However, BSA delivered at pH 7.4 (n = 0.47) and LYZ delivered at pH 10.0 (n = 0.35), presented n values closer to 0.5, suggesting a Fickian diffusion, which should be probably due specific interactions between proteins and polymeric chains.

COLL 543

Regulation of dynamin-mediated fission by endocytic accessory proteins

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Dynamin mediates fission of clathrin-coated vesicles. Here, we studied the effect of dynamin binding partners on dynamin-mediated fission. We tested the major dynamin binding partners: SNX9, Endophilin and Amphiphysin, all of which contain membrane remodeling BAR (Bin/Amphiphysin/Rvs) domains and SH3 domains that mediate the interaction with dynamin's Pro/Arg domain. Using an *in vitro* fission assay, we found that these effectors regulate dynamin-mediated fission at multiple levels. 1) The interaction between the PRD and the SH3 domain negatively regulates fission. 2) In the absence of this interaction fission is facilitated. 3) Our results imply that the SH3 domain negatively regulates the BAR domain. We speculate that BAR domains contribute to membrane curvature in order to facilitate fission. Further assessment of the effect of dynamin binding partners on dynamin's multiple biochemical activities will be necessary.

COLL 544

Surface-functionalized cationic liposome-DNA complexes: Strategies for optimal targetting and endosomal escape for gene delivery

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Cationic liposome (CL) carriers of nucleic acids are primarily studied because of their applications in gene delivery and gene silencing with CL-DNA and CL-siRNA (short-interfering RNA) complexes, respectively, and their implications to ongoing clinical gene therapy trials worldwide [1-3]. A series of synchrotron-based small-angle-x-ray scattering studies has revealed that CL-nucleic acid complexes spontaneously assemble into distinct novel liquid crystalline phases of matter. We will describe recent fluorescence optical imaging experiments and transfection assays using surface-functionalized CL-DNA nanoparticles interacting with cells. The functionalization, which is achieved through custom synthesis of peptide-PEG-lipids and hydrolysable-PEG-lipids, is intended to address and overcome surface targeting and endosomal escape barriers to gene delivery with PEGylated complexes. Funding provided by NIH.

COLL 545

Programmed vesicle transformations and composition

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DNA-lipid conjugates are used to tether lipid bilayer patches and GUVs to anti-sense DNA sequences covalently attached to a support. Stable tethered bilayer patches can be formed with a wide range of compositions, including fusogenic compositions, and these patches can be used as targets for membrane fusion. Because of their planar geometry, individual content transfer events during fusion can be observed by bursts of fluorescence as a concentration quenched dye on the incoming vesicle is dequenched. Quantitative analysis of the time evolution of the fluorescence demonstrates that genuine content transfer has occurred [*Biophysical Journal,* **101** , L37-L-39 (2011)]. Further analysis of the correlation of docking, hemifusion and full fusion demonstrate a rich array of behavior. Individual vesicle lipid compositions can be measured directly by imaging mass spectrometry. Some of the diverse behavior may be a reflection of inhomogeneity in composition.

COLL 546

Regulation of invadopodia by adhesion signaling

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Degradation of extracellular matrix (ECM) is important for migration of cells through tissues. Specialized cell structures called invadopodia are critical for ECM degradation and are formed by invasive, but not non-invasive cancer cells. Using modified ECM substrates, our recent data indicate that ECM is not only a passive substrate for invadopodia but also regulates the formation and function of these structures. Thus we find that physical ECM characteristics such as rigidity and crosslinking are critical modulators of invadopodia activity, with mechanotransduction signaling promoting invasiveness of cells. Our recent data on the role of adhesion signaling in invadopodia regulation will be discussed.

COLL 547

Understanding the role of lipid structure and protein interaction on membrane budding and tubulation

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Membrane budding and tubulation provides the pathway for numerous cellular processes, such as nutrient uptake, biomolecule transport, and pathogen entry. Transformation of the planar membrane into three-dimensional architectures is thought to be influenced primarily by the interfacial assembly and intrinsic curvature of interacting proteins. Using a model membrane system we show an alternative scenario where bud and tube formation are dictated by lipid structure and the effects of protein crowding. We prepared a series of Cu(II)-chelating lipids with tail structures that determine their phase state and direct their assembly into domains in the lipid membrane. Selective binding of his-tagged proteins produced regions of high surface concentration in which localized spontaneous curvature is induced. Formation and physical structure of buds or tubes from these domains were dependent upon mechanical properties of the domain as well as strength of protein affinity, not on any specific shape or interfacial assembly of proteins.

COLL 548

Efficient membrane fusion using lipidated peptides: Factors determining the rate of fusion

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Biological self-assembly is very complex and results in highly functional materials. In effect, it takes a bottom-up approach using biomolecular building blocks of precisely defined shape, size, hydrophobicity, and spatial distribution of functionality. Inspired by, and drawing lessons from self-assembly processes of the natural occurring SNARE protein complex, which is involved in membrane fusion, we used a small heterodimeric coiled-coil motif to control the supramolecular assembly of block copolymers and lipids.

We show that the fusion of large and giant unilamellar vesicles can be controlled by these amphiphilic peptides. This model system imparts all of the key characteristics to membrane fusion that are observed in SNARE mediated fusion. The mechanism of the fusion process will be discussed as well as the factors determining the rate of fusion by varying the molecular structure of our lipidated peptides.

COLL 549

Broad spectrum antimicrobial coatings employing surface segregating amphiphilic moieties

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With the increase in antibiotic-resistant microbes, the production of self-decontaminating surfaces has become an area of research that has seen a surge of interest in recent years. Such surfaces, when incorporated into commercial products such as children's toys, medical devices and hospital surfaces could reduce the number of infections caused by pathogenic microorganisms. A number of active components for self-decontaminating surfaces have been investigated, including common antibiotics, metal ions, quaternary ammonium salts, and antimicrobial peptides. Research in our laboratory has recently focused on the development of a wide range of amphiphilic antimicrobial additives that when combined with low volatile organic content coatings afford surface concentration of the active compounds as the coating cures. We report the development of antimicrobial coatings containing a variety of additives, that are active against a broad-spectrum of potentially pathogenic bacteria (1–7 log kill), as well as enveloped viruses (2–7 log kill) and fungi (1–2 log kill). Additionally, these additives were compatible with water-dispersed urethane and acrylate coatings which have a broad range of real world applicability, and remained active for multiple challenges and when exposed to various cleaning scenarios in which they might encounter in real world situations.

COLL 550

Decontamination of chemical stimulants via photocatalytic coated substrates

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Substrate surfaces which are capable of self-decontamination and self-cleaning can be prepared using photocatalytic titanium dioxide (TiO_2) nanoparticles. Over the past decade, scientific studies on the photocatalytic activity of colloidal titanium dioxide photocatalysis have increased tremendously. However, reports on the photocatalytic activity of these aqueous colloidal dispersions when they are applied as coatings or coating constituents are nominal, specifically in leading to the decomposition of chemical warfare agent simulants. Photocatalytic activity of TiO_2 is initiated by the absorption of a photon of ≥ ~3.2 eV to generate electron-hole (e-/h+) pairs, which promote the formation of free radicals and super oxides at the surface. These surface reactive species can facilitate the degradation of surface-bound organic substances. In our lab, the decontamination of select chemical agent simulants was monitored under a variety of experimental conditions, changing relative humidity, spectral intensity and wavelength distribution, and coating composition, application method and pretreatment process.

COLL 551

Biocidal coatings through self-segregating additives

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Current materials used in military vehicle and soldier protection applications are designed to act as barriers or sorbents to chemical threats. There is no current requirement for antimicrobial activity in military coatings, but materials exhibiting persistent antimicrobial activity would provide many benefits, especially for interior applications. A series of hyperbranched polymer based additives have been developed for incorporation into thermoplastics polyurethane films as well as military primers and topcoates to improve performance against Gram positive, Gram negative, and fungal challenges. A wide variety of antimicrobial activity, assayed using the ASTM E2180 method, has been observed. Up to 6-log reduction has been shown in the best case, whlie a 2-log enhancement in microbial growth has also been observed, depending on the additives employed in the coating. Surfaces were characterized using contact angle measurements and surface compositional analysis using X-ray photoelectron spectroscopy.

COLL 552

Preparation of novel self-decontaminating interpenetrating networks

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A series of polymerizable diallyl quaternary ammonium salts (QAS) having increasing alkyl chain length were prepared and investigated for relative biocidal activity in solution and on the surface of coatings. These QAS homopolymerize in the presence of the thiol-ene, radical step growth process to form phase-separated interpenetrating networks. Thiol (S-H) and ene (C=C) monomers used in the formation of polymer networks included trimethylolpropane tris(3-mercaptopropionate) (tri-thiol) and pentaerythritol allyl ether (tri-ene) and both thermal and UV curing processes were explored. QAS were able to maintain a high biocidal activity of ≥ 99% kill in coatings challenged with common bacteria strains at 10wt% addition of QAS to the overall coating composition. Physical and mechanical coating properties were investigated using AFM, DSC, and TGA as well as surface hardness and tack. Morphology characteristics were probed using AFM analysis. All coating formulations exhibited low glass transition temperatures ranging from -9 to -22°C and high thermal stability.

COLL 553

Copolyoxetane soft blocks with 4FOx (2,2,3,3-tetrafluoropropoxymethyl) side chains: An amphiphilic chaperone for quaternary antimicrobial surface modification

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Contact antimicrobial kill, rather than biocide release, is desired for soft materials such as catheters or coatings in nosocomial environments. In such applications long term durability of biocidal function is desired. Previously, we described modification of linear and network HMDI/BD-PTMO polyurethanes with 2 wt% or less copolyoxetane-based soft block polyurethanes. The soft block contained a semifluorinated side chain “chaperone” and quaternary ammonium side chain. High antimicrobial activity was found, but slow surface phase separation occurred that sequestered quaternary function. A new approach using 4FOx (2,2,3,3-tetrafluoropropoxy-methyl) side chain "chaperones" has resulted in temporal stability of quaternary antimicrobial function. XPS, dynamic contact angle measurements and TM-AFM have been used to characterize the modified surfaces. Antimicrobial activity has been correlated with zeta

potential measurements. The results are important to the development of contact antimicrobial coatings with long term effectiveness.

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COLL 554

Diverse antimicrobial materials containing polyquaternary amines

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Antimicrobial surfaces can be roughly divided into two broad categories, those that do not release antimicrobial agents into the environment and those that do. We have formulated polyquaternary amines into both categories of antimicrobial material. Polyquaternary amines have been shown to be antimicrobial when covalently attached to a surface. The mechanism of action and potency of surface bound polymer is due to the density of positive charges the polymer provides to the surface. While some polyquaternary amines have activity in solution, we have exploited another feature of the polymers to produce polyfunctional materials which release the antimicrobial halogens iodine and bromine. Polyquaternary amines with iodide or bromide counter ions are electrospun into insoluble fiber mats which also contain the enzymes glucose oxidase and horseradish peroxidase. In the presence of glucose these enzymes convert the halide ions into halogens producing a potent antimicrobial. The response is enhanced by the addition of halide salts.

COLL 555

Integrated antimicrobial and nonfouling materials and interfaces

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There are two major strategies to prevent microbial surface colonization and biofilm formation**.** The active route is to attack and kill bacteria such as cationic polymer-based antimicrobial coatings. The passive route is to resist bacteria surface attachment such as zwittionic-based polymer nonfouling coatings. Zwittterionic surfaces have been previously shown to inhibit bacteria biofilm formation for up to 10 days. In this work, we have integrated both strategies into one single coating and have taken advantages of both. Two approaches have been adopted to realize this concept. In the first approach, a switchable smart surface between its initial cationic and final zwitterionic states was devloped. This feature enables the surface to kill and release bacteria and then stay nonfouling. The second approach is to incorporate antibiotic drugs into a zwitterionic nonfouling coating, thus inhibiting bacteria growth through the controlled release of

antibiotic drugs while preventing bacteria surface attachment. Antimicribial wound dressings based on this strategy will be discussed.

COLL 556

Synthetic mimics of antimicrobial peptides

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We are interested in elucidating the rules required to create biomimetics with structure and function rivaling proteins. While scientists have been interesting in polymers for almost 100 years, compared to their biology cousins including proteins and DNA, these molecules remain relatively unsophisticated. Our laboratory has focused on creating novel polymeric molecules with increased functionality in order to enable new properties and applications. In this lecture we will discuss our efforts to design and synthesize macromolecules that are membrane-active including host defense, or antimicrobial, peptide mimics. These novel mimics have potent antimicrobial activity. We will discuss their mechanism of action in solution and self-sterilizing materials including sutures.

COLL 557

Synthesis of high-quality magneto-fluorescent multifunctional nanoparticles

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Nanoparticles exhibit interesting size dependent chemical and physical properties, which have been extensively studied during the last two decades. The methods for synthesizing size- and shape-controlled, monodisperse, single component nanoparticles have been well developed. In recent years, multifunctional assembled nanoparticles which contain more than one type of nanoparticle inside each assembled construct have become attractive due to their combined properties. However, synthesizing high-quality multifunctional assembled nanoparticles with desired size and composition is still challenging. We report a simple method for the fabrication of size and composition controlled magneto-fluorescent multifunctional nanoparticles. Importantly, these assembled particles simultaneously possess good magnetic and fluorescence properties. Moreover, we demonstrate that these particles can be further overcoated with optically transparent thin silica shells that provide added stability, functionality and biocompatibility.

COLL 558

Design and fabrication of novel nanoparticle-porous shell systems

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In this study, three well-developed porous shell templates composed of carbon, crystalline titania, and silica are utilized for the development of heterogeneous structures by the incorporation of novel nanoparticles during their growth. Each porous shell system offers its own unique advantages and disadvantages for use with specific nanoparticles. For instance, the degrees of hydrophobicity for each shell system afford different chemical interactions in the various solvents used in nanoparticle synthesis. Depending on factors such as solubility and surface charge, the nanoparticles can decorate the surfaces, grow inside the shells, or have no interaction. Additionally, by using well-developed synthetic techniques, the focus can be concentrated on the interactions between the materials, and not the synthetic protocols necessary to synthesize uniform, monodispersed nanoparticles. It is our hope that through this investigation, optimized heterogeneous structures will be achieved, and particularly favorable shell and nanoparticle combinations will be discovered that may find practical applications

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COLL 559

Novel synthesis of the monodisperse mesoporous silica nanoparticles under reflux condition

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In this contribution, we propose a novel method combined the advantages of the Stöber's method with the homogenous precipitation. A key feature of the synthetic strategy is use of urea as a substitute for commonly used NaOH or NH4OH under reflux condition. The product possesses well-ordered mesoporous structure, narrow pore size distribution, particle size of ca. 100-500 nm and high monodispersity and spherical morphology. Compared the present reported method, the yield of product can be increased to about 8 times based on the same solution volume. The nanoparticle solutions are very stable with lifetimes of more than one month without indication of agglomeration. The results show the present method is suitable as a direct synthesis route to monodisperse mesoporous silica nanoparticles on a large scale. The size of nanoparticle could be tuned in controlled manner depended on the preparation parameters.

COLL 560

Shaping of metal-organic framework gels into monolithic moulds with high porosity

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Coordination polymers (MOFs) are fine, crystalline powders normally and appropriate shaping is of crucial importance for nearly each process in the chemical industry. Combining the modular building concept of MOFs with classical sol-gel chemistry leads to a new class of porous materials with hierarchical structure.

Two easily scalable procedures for preparing millimeter-sized compact, spherical and binderless MOF particles are presented. In the first case, a MOF precursor is gelated inside a macroporous *exo*-template like metal foam. Upon drying the gel loses the solvent and undergoes a considerable shrinkage, resulting in particles with size and shape as determined from the foam voids. The template can be recycled.

The second way, to produce stable MOF spheres is adding the precursor solution drop-wise to an immiscible solvent at higher temperature. Each droplet gelates individually, resulting in perfectly shaped spheres. In contrast to classic inorganic xerogels, the MOF particles retain their porosity upon shrinkage.

COLL 561

Improve the yield of silver nanoplates by using H_2O_2 as an effective etchant

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In this presentation we will focus on our recent work in the synthesis of silver nanoplates through a simple seeded-growth route. Seeded-growth method has been widely used to synthesize silver nanoplates. However, this method suffers from low yield and long reaction time. On the basis of our recent study, we found that hydrogen peroxide plays a vital role in the chemical reduction of silver nanoplates by favoring the formation of planar twin defects and removing less stable silver nanostructures. Herein, we extend our concept to seeded growth method and found that H2O2 could also be used to effectively improve the yield. In addition, contrary to the previous conclusion that citrate is the key component, we have determined that many di- and tri-carboxylate compounds whose two nearest carboxylate groups are separated by two or three carbon atoms can also be used to make silver nanoplates with high yield and high quality.

COLL 562

Microfluidic synthesis of monodisperse metal nanoparticles using a room temperature ionic liquid solvent

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We present the novel application of vapor phase polymerization to modify the surfaces of pre-assembled microfluidic channels. These coated devices are used for the continuous synthesis of monodisperse metal nanoparticles in a room temperature ionic liquid solvent. This designer solvent can be recycled and has favorable properties that stabilize the nanoparticles in solution. Manipulation of droplet flows presents an optimal platform for controlling mixing and particle size and morphology. Deterministic flow patterns produce particles with a localized surface plasmon resonance.

COLL 563

Shape-shifting of anisotropic microcylinders

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Anisotropic particles with non-spherical shape and distinct compartments are currently under development for a broad range of emerging applications, because of their promising benefits for drug delivery carrier, molecular imaging, optical device, and self-assembly. We have previously developed electrohydrodynamic (EHD) co-jetting as an effective method to fabricate multicompartmental anisotropic particles. Here, we introduce shape-shifting process that can further control the shape of particles using ultrasound. Multicompartmental poly(lactide-co-glycolide) (PLGA) microcylinders produced from EHD co-jetting were treated with ultrasound in water, and when the particle temperature increased above their Tg they were converted into spheres due to surface effect. Moreover, we incorporated polymers with different properties such as poly(methyl methacrylate), poly(vinyl cinnamate). Shape-shifting of such particles resulted in various shapes, which, in turn, can affect future applications such as particle degradation, functionality, flow properties, and targeted efficiency of biomolecules.

COLL 564

Polyelectrolyte microcapsules as carriers of redox materials

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Microcapsules have received a wealth of interest as materials for the encapsulation and controlled release of small molecules. Much of the focus has been on the use of microcapsules for drug delivery and ultrasmall volume reaction vessels. This presentation examines approaches to the construction and characterization of polyelectrolyte microcapsules loaded with redox-active molecules. The microcapsules were synthesized using layer-by-layer assembly of alternating polyelectrolyte layers on polystyrene bead templates ranging from 200 nm to 4.5 μm in diameter. Results of reactivity testing of a series of ferrocene derivatives after encapsulation and release will be described. Studies to determine loading and release levels and loading capacity will also be detailed. Potential applications will be briefly discussed.

COLL 565

Separation of pharmaceuticals by selective surface adsorption

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Mobile condensed matter (MCM) are a known[1] class of sol-gel materials prepared by mixing a solution of silica and a surfactant together and polymerizing the silica in a sol-gel process, where silica polymerizes around the surfactant micelles and afterwards undergoes a hardening process known as gelation. MCM-41 possesses hexagonally packed arrays of channels with very high surface area and narrow pore size distribution compared with amorphous silica, whereas MCM-48 are cubic packed arrays with a 3-D array of the pores, where the silica/surfactant ratio determines the symmetry of the pores.

MCM sol-gel materials can be functionalized[2] by synthesizing the silica with an organic side chain, in order to attain specific chemical residues in the pores. Herein we report the synthesis of a nonafluorohexyl functionalized porous sol-gel material, which exhibits selective adsorption towards molecules with close chemical structure and properties which were difficult to separate by other known techniques. Isothermal titration calorimetry (ITC) was used to measure the adsorption isotherms of the organic molecules to our functionalized silica material. Enthalpies of adsorption for the different molecules were obtained from our adsorption curves, and demonstrated their selectivity towards this porous material.

Future prospects for these functionalized silica materials is to incorporate them in a separation step between the active pharmaceutical ingredient (API) and impurities in a continuous manufacturing process of the desired drug compound.

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COLL 566

Enhanced stability of metal organic frameworks via perfluorohexane plasma chemical vapor deposition

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Metal organic frameworks (MOFs) have become a leading class of porous materials for applications such as gas storage, catalysis and toxic gas removal. However, the pitfall of many of these materials has been their instability in the presence of moisture. Through perfluorohexane plasma chemical vapor deposition (CVD) we have shown a dramatic increase in the water stability of $Cu_3(BTC)_2$ [BTC - 1,3,5-benzenetricarboxylic acid], as evidenced by XRD patterns and SEM images. Also, the addition of perfluorohexane plasma enhances the amount of ammonia adsorption (on a g/g basis) as measured through breakthrough testing under both dry (0% RH) and wet (80% RH) conditions. This unforeseen enhancement is further evidence of the increased stability and a decrease in collapsing pores (as seen in untreated Cu-BTC) when exposed to ammonia and/or water. This increase in water stability can open the door to a wide array of applications that were previously inaccessible to MOFs.

COLL 567

Mesoporous metal nitride materials prepared from bulk oxides

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A simple process for preparing mesoporous transition metal nitrides by the ammonolysis of bulk ternary oxide powder that contain Zn is going to be presented. Mesoporous VN, TiN, CrN, Ta_3N_5, TaN, NbN, WN, MoN and Mo_2N powder have been obtained, as well as mesoporous nitrides containing more than one transition metal as shown in [Figure 1]. Chemical analysis shows some residual oxygen remains in the products, as has been observed previously in the preparation of nitrides by ammonolysis of oxides. The products were characterized by Rietveld refinement of powder X-ray diffraction (PXRD) patterns and by scanning electron microscopy (SEM). Pore sizes ranging from 10 to 50 nm were commonly observed. Under compression at a low pressure of 35 bar, powder conductivities of 76 S/cm (VN), 464 S/cm (TiN) and 1.8 S/cm (WN) were obtained. These conductivities are much higher than carbon black at a similar pressure, for instance. These materials may have applications in a variety of electrochemical devices where high surface area and good electrical conductivity are important.

COLL 568

Comparative dynamics of Ar and CO_2 scattering on liquid and self-assembled monolayer surfaces

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We have investigated the energy transfer dynamics of CO_2 and Ar scattering from both hydrocarbon and fluorocarbon liquid and SAM surfaces, using the direct comparison of the scattering behavior from the liquid and semi-solid surfaces to allow new insight into the pivotal initial step in gas-surface reaction dynamics. Specific interests are to probe the influence of surface structure vs. mass effects on the scattering dynamics and the role of the structure of the incident projectile. Molecular beams of CO_2 and Ar were directed onto the surfaces, and velocity and angular distributions of inelastically scattered species were determined from time-of-flight distributions collected for various initial and final angles with the use of a rotatable mass spectrometer. We appraise the applicability and value of the surface analog of the gas-phase kinematic analysis, known as the Newton diagram, which might in principle be used as a one-parameter basis to obtain effective surface masses for collisions of gas-phase species with surfaces. We have applied this analysis to the new data, and we have re-examined myriad existing datasets of both molecular-beam experiments and molecular dynamics simulations in this light. Included in our investigation are previous data on inelastic and reactive (oxygen-atom) collisions with organic liquids, ionic liquids, polymers, and SAMs. We seek to identify trends that could lead to a robust general understanding of energy transfer processes induced by collisions of gas-phase species with liquid and semi-solid surfaces.

COLL 569

Chemical dynamics simulations of projectile/surface collisions: Comparisons with experiment and unifying models of the energy transfer dynamics

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Classical trajectory simulations have been used to study the energy transfer dynamics for projectiles colliding with organic surfaces. The projectiles considered are rare gas atoms, CO_2, and projectile ions including protonated peptides, while the surfaces studied are self-assembled monolayers (SAMs), diamond {111}, and liquid squalane. The simulation results are in near-quantitative agreement with experimental studies. Unifying models emerge by comparing the results for the different projectile/surface systems. The simulations were assisted and, in part, motivated by experiments of the Steve Sibener research group.

COLL 570

Reactive scattering of oxygen atoms with unsaturated hydrocarbons: Primary products, branching ratios, and role of intersystem crossing

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We have investigated the combustion relevant reaction dynamics of ground state oxygen atoms with small unsaturated hydrocarbons (acetylene, ethylene and allene) using the crossed molecular beams method with “universal” mass spectrometric detection and time-of-flight analysis. By exploiting “soft” electron-ionization detection we have identified and characterized the dynamics of the energetically allowed channels in each of the above reactions. In particular, we have explored how the dynamics, branching ratios and extent of inter-system-crossing (ISC) from triplet to singlet potential energy surfaces (PESs) vary with collision energy. The role of ISC is found to increase strongly with increasing complexity of the hydrocarbon. The experimental results have been compared with theoretical predictions (when available), both statistical calculations and quasiclassical-trajectory surface-hopping computations on coupled *ab initio* triplet and singlet PESs, carried out in other laboratories.

COLL 571

Interactions of open shell atoms and molecules with surfaces

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A large and fascinating array of possible pathways for energy transfer and chemical reaction are exhibited when open shell atoms, molecules or reaction intermediates interact with surfaces. The interplays that can occur among direct scattering vs. trapping-desorption, phonon vs. electronic excitations, electron transfer, spin transitions, and localized molecular electronic transitions are just beginning to be sorted out. Recent theoretical progress towards addressing these issues will be presented.

COLL 572

Impact of particle shape on mineral dust optical properties

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The interaction of aerosol particles with solar radiation is one of the least understood aspects of the climate system. The optical properties of aerosol particles depend upon their size, shape, composition, and internal structure. We use one of the most sensitive techniques available to measure aerosol optical properties, Cavity Ring-Down Aerosol Extinction Spectroscopy (CRD-AES), to obtain the extinction cross sections of size-selected mineral particles. Our first studies have focused on calcium carbonate, calcium nitrate, calcium acetate, and other calcium salts. To determine the effect of shape on the optical properties, we explore the use of microscopy techniques, such as Transmission Electron Microscopy, to image single particles. We correlate the measured extinction cross sections with particle images by applying Mie scattering theory and the discrete dipole approximation. We find that the combined use of CRD-AES with complementary microscopy techniques allows us to determine the effect of shape on the optical properties.

COLL 573

Studies of electron-hole pair behavior in photoexcited TiO_2

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We report studies of band bending in TiO_2 caused either by adsorption or by UV illumination. Measuring the photodesorption of chemisorbed O_2 from TiO_2(110), which is mediated by holes, we have been able to measure band bending effects due to the adsorption of various atoms and molecules. We also have studied photoluminescence from TiO_2 under high vacuum conditions and have combined these studies with IR spectroscopy of adsorbed species, allowing control of surface species concentration. Adsorbed species strongly affect the photoluminescence yield as a result of band bending which modifies electron-hole recombination.

COLL 574

Probing the liquid/solid interface with neutrons and non-linear optical techniques

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In this talk we will present two new approaches to study interfaces of biological relevance in situ and in vivo. The first is the investigation of phospholipid multilayers under pressure and shear stress. We built a dedicated Neutron Reflectometer "BioRef" at the Neutron source at Helmholtz Center Berlin for Materials and Energy which combines neutron reflectivity and IR Reflection Spectroscopy to probe the mechanical and temperature effects on the stability and phase transitions in lipid multilayers. The second example refers to the use of Sum Frequency Generation Spectroscopy to measure ordering phenomena within the extracellular matrix of living adherent cells.

COLL 575

Nanoplasmonic sensing- applications for catalysis, hydrogen storage and nanomaterials science

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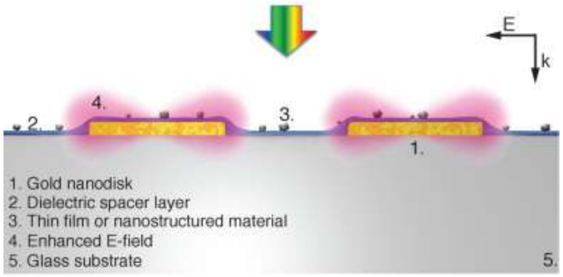
Indirect NanoPlasmonic Sensing (INPS) is a robust, low cost, highly sensitive and fast method for recording processes in/on thin films and nanostructured materials. Metallic and non-metallic systems can be studied in liquid or gas (UHV to high pressure) environments. INPS utilizes the optical signal from state-of-the-art nanofabricated sensor chips decorated with plasmonic (LSPR) gold nanodisks, which act as nanoscale optical antennas and detect events in their proximity, onto which the nanomaterial to be studied is deposited (see figure). INPS case studies including nanoparticle catalyst sintering[1], catalytic activity[2], NOx storage and release in/from barium compounds[3], hydrogen storage in nanoscale systems[2,4] and molecular diffusion through porous layers are presented.



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COLL 576

Grazing incidence small angle scattering and atomic force microscopy studies of interfaces in conducting polymer systems

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This presentation will describe recent results of our studies of interfaces in single and multiple component conducting polymer systems carried out using the combination of grazing incidence x-ray scattering (GIXS) and atomic force microscopy (AFM). Real space AFM images will serve as a basis for models of polymer packing used as an input for simulations of GIXS patterns to be matched to experimental data. Examples illustrating the use of this approach in single-component systems will be focused on regioregular poly(3-alkylthiophenes) (rr-PATs) and their derivatives, and will include: (1) polymer-dielectric interfaces of importance in field effect transistors; (2) impact of polymer backbone and side chains on molecular layering effects, and (3) elucidation of molecular packing in interfibrillar boundaries in rr-PATs. Multicomponent systems will be illustrated with the blends of rr-PATs with fullerene derivatives functioning as organic photovoltaics.

COLL 577

X-ray studies of polymer/polymer interfaces

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Due to the presence of thermally excited capillary waves, the free surfaces of fluids, complex fluids, and other generically soft materials are fluctuating structures. Examining the surface dynamics of such soft materials provides a window into their rheology. In this talk I will present results for more complex polymer bilayer films. X-ray photon correlation spectroscopy was employed in a surface standing wave geometry in order to resolve the thermally driven in-plane equilibrium dynamics at both the surface/vacuum (top) and polymer/polymer (bottom) interfaces of a thin polystyrene (PS) film on top of poly(4-bromo styrene) (PBrS) and supported on a Si substrate.

The non-equilibrium behavior of the top surface of a bilayer was also investigated. The two-time correlation function provides the *in-plane* dewetting velocity of large single holes as a function of time. The dewetting velocity decreases continuously with time according to a power law with exponent ½. This reduction of the dewetting velocity with time is related mainly to interface friction of the viscoelastic film.

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3 A. Fluerasu, S. Malkova, D. Liang, M. Mukhopadhyay, S. Narayanan, S. B. Darling, M. B. Sutton, L. B. Lurio and J. Lal “Depth Dependent Mechanism of Polymer-Polymer Dewetting (to be submitted to Physical Review Letters).

COLL 578

Surface-bound DNA interactions with metal cations studied by nonlinear optics and atomic force microscopy

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Understanding metal cation interactions with oligonucleotides at liquid/solid interfaces is essential for a variety of applications ranging from the development of accurate and reliable biosensors to material directed synthetic strategies. Here, we combined nonlinear optical spectroscopy and atomic force microscopy (AFM) for a uniquely sensitive, label-free approach to detect and quantify single-stranded DNA structural changes and binding interactions in the presence and absence of Mg^{2+} at an aqueous/silica interface. Sum frequency generation (SFG) directly probed vibrational resonances and reordering of surface-bound DNA on silica surfaces with the addition of Mg^{2+}, while second harmonic generation (SHG) quantified binding constants and metal ion coverage per DNA strand over a range of oligonucleotides lengths. Through statistical analysis, AFM was used to quantify shifts in the DNA height and tilt angle distributions before and after the addition of Mg^{2+}. The implications of structural changes due to surface-bound DNA-metal ion binding are discussed.

COLL 579

Molecule and fluid properties probed by analysis of the correlations between the fluctuations in deflection of two cantilevers

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Correlation force spectrometry (CFS) characterizes fluids and molecules through measurement of the correlations between the thermally-stimulated vibrations of two closely spaced micrometer-scale cantilevers in fluid. Two major applications are discussed: measurement of the rheological properties of fluids at high frequency and high spatial resolution, and characterization of the properties of individual molecules. Use of CFS as a rheometer is validated by comparison between data and finite element modeling of the deterministic ringdown of cantilevers using the known viscosity of fluids. The data can also be accurately fit using a harmonic oscillator model, which can be used for rheometry after calibration. The method is non-invasive, uses a very small amount of fluid and has no actively moving parts. It can also be used to analyze the mechanical properties of individual molecules tethered between the cantilevers.

COLL 580

Combined experimental and computational approach for studying solvent and biomolecular structure at solid-liquid interfaces

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The structure of proteins adsorbed at the solid-liquid interface is critical to understanding the biocompatibility of materials, design of biosensors, antimicrobial activity, and chemical separations. Yet despite these wide-spread applications, there is a paucity of techniques that are capable of characterizing surface-adsorbed molecules with sufficient selectivity and structural sensitivity. Our group has been working on combined optical probe and molecular modeling approaches to provide a description of solvent and solute structure at solid-liquid interfaces. In particular, techniques based on vibrational spectroscopy provide an opportunity to target specific chemical moieties without extrinsic labeling. Our work in this area has been a multi-faceted effort: (1) Spectroscopic measurements utilizing the surface-sensitivity of vibrationally-resonant three-wave mixing allows us to measure the ensemble-averaged local structure of

adsorbed molecules, including solvent. (2) Dipole and polarizability calculations provide information on the molecular-frame vibrational hyperpolarizabilities. (3) Molecular dynamics simulations provide additional details of the orientation distribution that can be used to enhance our understanding of the experimental results. Furthermore, a unique aspect of our experimental effort is the ability to resolve the polarity of chemical bonds, distinguishing functional groups pointing up or down at the surface in an absolute sense. For this we employ optical heterodyne detection in a manner that offers particularly-high phase stability.

COLL 581

Immobilization of palladium nanoparticles within electrospun polymer nanofibrous mats for catalytic applications

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We report a facile and economic approach to fabricating palladium (Pd) nanoparticles (NPs)-immobilized electrospun polyethyleneimine (PEI)/polyvinyl alcohol (PVA) nanofibers for catalytic transformation of Cr(VI) to Cr(III). PEI/PVA nanofibrous mats were first formed by electrospinning the homogeneous mixture solution of PEI and PVA, followed by crosslinking with glutaraldehyde vapor to render the fibers water stable. Then, the nanofibrous mats with a large amount of free PEI amines were dipped into a solution of H_2PdCl_4 to allow the ionic interaction between PEI amines and the $PdCl_4^{2-}$ anions, followed by reducing the $PdCl_4^{2-}$ anions using sodium borohydride to form zero-valent Pd NPs. The formed Pd NPs-immobilized PEI/PVA nanofibers were characterized by scanning electron microscopy, transmission electron microscopy, energy dispersive spectroscopy, Fourier transform infrared spectroscopy, and thermal gravimetric analysis. The catalytic activity and reusability of the fabricated Pd NPs-containing fibrous mats were evaluated in the transformation of Cr(VI) to Cr(III). We show that the Pd NPs-containing nanofibrous mats with Pd NP size of 2.6 nm display good water stability, excellent catalytic activity, and reusability in the reductive transformation of Cr(VI) to Cr(III) in the presence of formic acid as the reducing agent. With the high surface area to volume ratio of the nanofibers, excellent reusability, and the facile NP immobilization approach, a range of different catalytically active monometallic or multimetallic NPs-based fibrous materials may be fabricated for various catalytic applications.

COLL 582

In situ synthesis and immobilization of metal organic frameworks (MOFs) onto functionalized polymer and ceramic nanofiber membranes

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Metal organic frameworks (MOFs) are well known for their outstanding sorption properties and are being considered for application in different fields, *e.g.*, gas storage, catalysis,and purification. It is possible to control morphology of particles for integration of different materials to enhance applications. The MOFs could find broader applications in purification processes if their transport kinetics is enhanced through effective control of their morphology to ensure low pressure drop and high performance. This can be achieved through organization of MOF particles to form a wire-like assembly or formation of particle/fiber composites. We will present the use of electrospinning for *in-situ* synthesis via covalent attachment and immobilization of MOF particles in fibers. In addition, ceramics and polymer nanofiber functionalization strategies for attachment of MOFs will be presented. These new nanocomposites could find applications in removal of toxic chemicals in protective clothing where chemical, thermal and mechanical integrity is paramount.

COLL 583

Effect of solvent interactions on reinforcement of functionalized gold nanoparticles and polymers

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Polymer-nanoparticle composite materials already won their place in various industrial applications. However, the interfacial properties between polymers and nanoparticles and nanoparticle spatial arrangements affect nanocomposite performance. In this study, we investigate the interfacial properties of polymers (polystyrene (PS), poly-(methyl methacrylate) (PMMA)) and diblock copolymers PS-PMMA) and gold nanoparticle functionalized with alkanethiol ligands (AuNP) in polar and non-polar solvent using atomistic MD simulations. We observed that the presence of AuNP changes polymers flexibility and interactions. We found that PMMA will wrap around AuNP more efficiently in a non-polar solvent and interact with AuNP stronger that PS. Whereas, PS tend to fold onto itself through formation of pi-pi interactions and is much less affected by the presence of AuNP. Apart from conformational change the polarity of the solvent significantly influence the flexibility of the polymer and interfacial binding free energy of polymers and AuNPs. Interestingly, in the case of diblock PS-PMMA, the PMMA block coats the AuNP while leaving the PS block on the surface. The results of this study will provide better insight into structural ordering of nanoparticles in these composites.

COLL 584

Long-range alignment of gold nanorods in electrospun polymer nano/microfibers

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A scalable fabrication technique for controlling and maintaining the nanoscale orientation of gold nanorods (GNRs) with long-range macroscale order has been achieved through electrospinning. Low aspect-ratio GNRs were dissolved in aqueous poly(ethylene oxide) solutions and electrospun to generate fibers possessing different GNR concentrations (up to 4.5 vol%) and diameters measuring between 40 and 3000 nm. The GNRs aligned within the fibers with their long axes parallel to the fiber axis. The average deviant angle between the GNR long axis and the fiber axis increases modestly as the fiber diameter increases. Complementary electron diffraction measurements confirm preferred orientation of the GNR crystal planes. Optical absorbance spectroscopy measurements reveal that the longitudinal surface plasmon resonance bands of the aligned GNRs depend on the polarization angle and that maximum extinction occurs when the polarization is parallel to the fiber axis.

COLL 585

Enabling of nanoparticle application and function on the surface of fibrous textiles by atomic layer deposition

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Nanoparticle ink modification of a polymer surface represents a method to apply unique catalytic or responsive behaviors to textiles. However, incompatibility of the surface tension of many nanoparticle inks with that of the polymer surface energy results in non-uniform distribution of the nanoparticles throughout the fiber matrix. Atomic layer deposition (ALD) is provided as a bridging technology to broaden nanoparticle distribution on both hydrophobic and hydrophilic polymers. After 50 cycles of low temperature ALD alumina surface modification of a hydrophobic surface, such as polytetrafluoroethylene (PTFE), surface energy is increased by 50 dynes/cm to produce a hydrophilic surface. Aqueous-based nanoparticle ink solutions wet the ALD modified fabrics, and uniformity was inspected using time-of-flight secondary ion mass spectroscopy (TOF-SIMS). An ALD ZnO overcoat layer, which embeds the

nanoparticles, results in a platform for enhanced optical absorption and luminescence of the fabric. Ability to control the nanoparticle distribution is presented.

COLL 586

Cellulose-based sensors for detecting chlorine and nitrogen dioxide

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Chemiresistors vapor sensors composed of single-walled carbon nanotubes inkjet printed on paper and cloth (cellulosic substrates) can reversibly detect aggressive oxidizing vapors like nitrogen dioxide or chlorine at sub-ppm levels in ambient air at room temperature without the aid of a vapor concentrator. Lightweight and highly flexible, these all-organic sensors can be bent to a crease without any significant loss of sensor function.

COLL 587

Protein resistant surface with micro/nano scale topographical features and GRGDY modification: A highly efficient cell specific surface

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Surface chemical composition and physical topographical features are two predominant factors in determining protein adsorption and cell responses; hence, surface-protein/cell interactions may be fine-tuned by controlling both of these factors. In this research, we fabricated surfaces consisting of layers of gold particles on gold films. A series of films with increasing surface roughness were prepared via deposition of gold nanoparticles. Polymer brushes (poly(oligo (ethylene glycol) methacrylate) (POEGMA)) were grafted from these surfaces by surface initiated atom-transfer radical polymerization (SI-ATRP) and GRGDY peptide was conjugated to the brushes. Compared to smooth gold films (no particles) modified with POEGMA-GRGDY, the particle-decorated (rough) modified surfaces showed significantly greater protein resistance and specificity for L929 fibroblast adhesion and proliferation. These bioresponses were also dependent on surface roughness. These results suggest that non-fouling micro/nano structured surfaces functionalized with biospecific ligands may be useful in the design of biomedical devices.

COLL 588

Understanding protein-surface interactions at the submolecular level through the synergistic combination of experiment and molecular simulation

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Despite decades of study, very little is yet understood regarding the submolecular events that mediate protein-surface interactions. Experimental methods alone are too limited to provide the atomic level of detail that is needed to characterize the molecular interactions that are involved and could use the assistance of molecular modeling to help describe these processes. On the other hand, while molecular modeling methods possess the potential to provide this level of detail, these methods require experimental data for tuning and validation before they can be confidently applied. In order to solve this chicken-or-the-egg type of problem, we have been synergistically developing experimental methods to provide the data that are needed to both tune and validate molecular simulation methods for the accurate prediction of protein adsorption behavior. Once properly developed, these methods have the potential to provide a valuable tool to help understand, predict, and control protein-surface interactions for material surface design.

COLL 589

Probing the structure of statherin on hydroxyapatite surfaces with SFG and NEXAFS spectroscopy

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Biomineralization proteins act as nature's crystal engineers and adsorb onto crystal surfaces with precision. The human salivary protein statherin regulates the growth of hydroxyapatite (HAP) in bone and tooth enamel. We have used sum frequency generation (SFG) spectroscopy to probe the orientation and secondary structure of the binding domain of statherin, SN15, on HAP surfaces in situ. The data showed an α-helical secondary structure of SN15 on HAP with the helix axis parallel to the surface. Site selective isotope labeling allows the analysis of specific protein regions with atomic resolution (1) and we have used this method to determine the orientation of all hydrophobic side chains of SN15 on HAP (leucine, isoleucine, phenylalanine). We have also combined SFG with near edge X-ray absorption fine structure (NEXAFS) analysis of site-selectively fluorinated SN15 to complement our structural analysis.

1. Weidner et al. (2010) *Proc. Natl. Acad. Sci. U. S. A.* 107:13288.

COLL 590

Quantifying and modeling the adsorption kinetics of glucose oxidase utilizing a whispering gallery mode biosensor

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A whispering gallery mode (WGM) biosensor was used to quantify the kinetics of adsorption of glucose oxidase (GO) on native glass (negatively charged hydrophilic) and resonators modified with silane self-assembled monolayers to form a hydrophobic surface (13F), a positively charged hydrophilic surface (DETA), and an uncharged hydrophilic surface (SiPEG). An enzymatic activity assay was used to assess the function of the adsorbed GO. Five kinetic models of protein adsorption were fitted to the WGM measurements, used to predict the activity of the adsorbed enzyme, and compared to experimental results. The adsorption of GO on glass and 13F was best fitted by a model incorporating denaturation, while GO on DETA was best fitted with a two-layer adsorption model. Adsorption on SiPEG could be fitted with a simple Langmuir or RSA model. The kinetic data, activity data and model fitting results yielded new insights about the adsorption of GO onto each surface.

COLL 591

Accurate simulation of peptide adsorption to polyethylene, poly(methyl-methacrylate), and silica surfaces using a modified CHARMM force field

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All-atom molecular dynamics is the most direct method to predict the molecular-level events associated with protein-surface interactions. However, current force fields have not been validated for this application. The free energy of adsorption (ΔG_{ads}) provides the most direct thermodynamic measure of the dominating events governing peptide-surface interactions. The objective of our study was to calculate ΔG_{ads} of small host-guest peptides (TGTG-X-GTGT, where T=threonine; G=glycine; and X being asparagine, aspartate, glycine, lysine, phenylalanine, threonine, tryptophan, or valine) and to compare these ΔG_{ads} values with experimental results. Simulations were performed on three types of surfaces (high-density polyethylene, poly(methyl-methacrylate), and silica glass) with explicitly represented water molecules utilizing the CHARMM force field. Simulation results indicate that corrections in non-bonded force-

field parameters are necessary to provide ΔG_{ads} values that closely match the experimental data. Following force field parameter adjustment and validation, simulations can be conducted with the potential to accurately predict protein adsorption behavior.

COLL 592

Critical role of protein immobilization in micro and nanomechanical biosensors

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Advances in micro/nanofabrication technologies are enabling the development of mechanical devices with nanosized moving parts. Micro/nanocantilever sensors respond to changes on their surface with a mechanical bending in the order of nanometers which can easily be detected. For sensing applications, when a specific biomolecular binding like protein-protein interactions occurs on one surface of the microcantilever, a change of the surface stress is induced. The oriented immobilization of antiperoxidase from horseradish antibody on a microcantilever was used as model and the specific antigen-antibody interaction was detected by a simple and fast measurement of the microcantilever profile in air for the first time. 3000 measurements conducted to statistically significant results. This specific and sensitive protein biosensor is a potential candidate for the detection of disease-related proteins at clinically relevant conditions and concentrations. Unfortunatelly, label-free protein biosensors still present poor reproducibility and specific immobilization methods must be developed relying on high throughput methodologies.

COLL 593

Protein-polymer assemblies generate nanoreactors and processors for medical applications

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Combining biological molecules, such as proteins, enzymes, DNA and synthetic carriers/templates, such as polymer supramolecular assemblies, represents a very promising strategy for development of efficacious therapies with minimum side effects, diagnostic methods featuring significantly higher sensitivity and selectivity, and personalized diagnostics and therapeutics for theragnostic approaches. In this respect, suitable amphiphilic block copolymers self-assemble into supramolecular structures in aqueous media with membranes mimicking biological membranes. The properties of such membranes can be extensively controlled via chemical composition, molecular

weight and the hydrophilic-to-hydrophobic block length ratio of the polymers and have the advantage of superior stability and robustness. Other well-defined functions, such as molecular recognition, cooperation, and catalytic activity can be introduced by combining these polymeric superstructures with suitable biological entities, e.g., by incorporating integral membrane proteins or by enzyme encapsulation.

We exploited the concept of bio-synthetic combination to develop polymer nanoreactors that encapsulated water-soluble enzymes in the aqueous cavities of vesicles generated by the self-assembly of amphiphilic copolymers. Channel proteins inserted into the polymer membrane selectively controlled the exchange of substrates and products with the environment, supporting the *in situ* activity of the enzymes. A step further was made by co-encapsulation of enzymes that act in tandem inside the polymer cavity.

By synthesizing appropriately functionalized polymers (e.g. biotin, antibody) we successfully immobilized the nanoreactors on solid support to follow the folding/unfolding of single proteins, and to monitor enzymatic reactions down to the scale of a few molecules.

After cellular uptake, the nanoreactors retained their function over extended periods of time, thus acting as artificial organelles that continuously exchanged molecular information with the host cell. This opens new avenues in protein therapy as well as intracellular sensing approaches.

COLL 594

Complement sensing of PEGylated carbon nanotubes

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As a result of their unique thermal and spectroscopic properties as well as their ability to traverse cellular membranes, carbon nanotubes have attracted considerable attention as entities for disease diagnosis and treatment. The interaction of carbon nanotubes with elements of the innate immunity, and particularly the complement system has not received much attention. Complement is the first line of defense against intruders and its uncontrolled activation may induce adverse effects. Our investigations show that both methoxypoly(ethylene glycol) (PEG)-phospholipid coated and PEG functionalized carbon nanotubes can trigger complement system in human serum. Activation is triggered through surface sensing by the pattern recognition molecule L-ficolin, which in turn activate the zymogen mannose-binding lectin associated serine protease-2. Complement activation by PEGylated carbon nanotubes proceeds regardless of PEG molecular mass and surface packing density. Further treatment of PEGylated carbon nanotubes with serum albumin did not prevent complement activation. The immune safety of carbon nanotubes is therefore questionable.

COLL 595

Nonadsorbing properties of the zwitterion surface

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When derivatized with zwitterions, planar and (nano)particulate surfaces can show exceptional resistance to the adsorption of proteins and cells. In a recent head-to-head comparison of PEG oligomers and short-chain zwitterions, both were found to be roughly equivalent in preventing adsorption and stabilizing colloids (*Langmuir*, **27** , 6794-6800 (2011)). Zwitterion passivation is achieved with only a minimal thickness (< 1 nm) at the surface, which can be critical for nanoparticles' *in vivo* transport and selective excretion. In this presentation we will compare the effectiveness of polymeric and monomeric zwitterions in guiding the selective adsorption of cells on surfaces and in stabilizing suspensions of nanoparticles. A simple mechanism by which both zwitterions and PEG prevent adsorption will be presented. The mechanism is based on removing entropic driving forces caused by the loss of counterions and water molecules at the surface.

COLL 596

Determining peptide and protein orientations at interfaces using sum frequency generation vibrational spectroscopy

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Sum frequency generation (SFG) vibrational spectroscopy has been used to determine peptide and protein orientations at solid/liquid interfaces and in solid substrate supported single lipid bilayers. SFG is a submonolayer surface sensitive nonlinear optical spectroscopy. A variety of peptides with different secondary structures such as alpha helical magainin 2, MSI-78, cecropin, 3-10 helical alamethicin, and beta-sheet tachyplesin I have been examined. In addition, various proteins including fibrinogen, factor XII, cytochrome b5, Gbeta-gamma, Galpha-beta-gamma, and Gbeta-gamma-GRK2 complex have been studied using SFG in situ in real time. Combined with ATR-FTIR, both average orientation and orientation distributions of peptides as well as large proteins at interfaces can be determined.

COLL 597

Mechanism of raft formation and membrane fusion studied in supported planar bilayers

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It can be very challenging to dissect the complex functional properties of biological cell membranes. Supported planar membranes are very helpful by reducing the complexity of real membranes and thereby focusing on certain constituents and functions. Here we report results from studies about trans-membrane phase coupling pertinent to lipid rafts and membrane fusion.

Previously we reported how cholesterol-rich liquid-ordered domains with lipid compositions typically found in the outer leaflet of plasma membranes induce liquid-ordered domains in adjacent regions of asymmetric lipid bilayers with apposed leaflets composed of typical inner leaflet lipid mixtures. We show how binding of Synaptotagmin 1 C2 domains to PS and PIP_2 containing bilayers is modulated by induced inner leaflet lipid phases.

We present results from SNARE mediated single vesicle fusion experiments. Vesicles containing recombinant Synaptobrevin and purified synaptic vesicles are observed during fusion with supported membranes containing the SNARE acceptor complex consisting of Syntaxin1 and SNAP25.

COLL 598

Interpreting neutron spin echo experiments on lipid bilayer membranes

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We present a continuum level theory for NSE measurements on lipid bilayers. The analysis suggests that it is not necessary to introduce the customary rescaling of solvent viscosity to explain experiments, provided that dissipative mechanisms within the bilayer are included within the theoretical description.

COLL 599

Critical dynamics, compositional interface fluctuations, and coarsening dynamics in planar lipid bilayer membranes

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Multicomponent lipid bilayer membranes comprise a class of soft materials with intriguing physical, chemical, mechanical, and biological properties. They are ubiquitous in mammalian cells where, together with proteins, they facilitate the interaction of cells with their surroundings. In this talk, I will first highlight the emerging understanding of the structure and dynamics of bilayer membranes in the vicinity of a critical point. In the

second part of my talk, I will discuss our very recent analysis of compositional interface fluctuations in symmetric bilayer membranes below the critical point. The analysis incorporates the effects of diffusive and advective lipid transport processes within the membrane, viscous or viscoelastic membrane properties, coupling between membrane and solvent, and inertial effects within the membrane and solvent. Finally, in the third part of my talk, I will discuss the role of hydrodynamics on domain formation within multicomponent membranes undergoing phase separation.

COLL 600

Membrane-mediated interactions between carbon nanotubes embedded in a lipid membrane

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Understanding behavior of nanoparticles embedded in lipid membranes is important for development of novel biomedical devices and assessment of potentially harmful effects of nanomaterials on living cells. The current work is focused on theoretical and computational investigation of carbon nanotubes (CNTs) embedded in a dipalmitoylphosphatidylcholine lipid bilayer. Our molecular dynamics (MD) simulations indicate existence of a long-range attractive force between the CNTs. This suggests that the CNTs may form large clusters which may significantly perturb the membrane structure and lead to membrane destabilization. The long range of the CNT-CNT interactions suggests that these interactions are mediated by the membrane. CNTs embedded into the bilayer create a stress in the membrane interior and an impetus to minimize this stress creates a force between the CNTs. We analyze spatial dependence of CNT-induced stresses in the membrane and compare results of the MD simulations with predictions of a theoretical model for membrane elasticity.

COLL 601

Molecular dynamics study of Cytolysin A pore forming toxin in a lipid bilayer membrane

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Understanding the interactions of membrane proteins is important in a wide variety of events that can occur in biological membranes. Pore forming toxins are a unique class of proteins that assemble in biological membranes to form stable pores, ultimately leading to cell lysis. Unravelling the mechanism of pore formation and protein interactions at the membrane interface has potential applications in developing novel drugs and delivery systems. Cytolysin A (ClyA) is a cytolytic protein expressed by Escherichia coli and other enterobacteria. Using a recently reported crystal structure of the dodecameric pore complex formed by ClyA we carried out all-atom molecular dynamics simulations of the assembled pore complex in a POPC membrane. The simulations are carried out with three different salt concentrations, neutral, 0.1 M and 1 M NaCl concentrations with the membrane in the liquid crystalline phase. The pore crystal structure was found to be stable over a 140 ns simulation independent of the salt content. Increasing the salt concentration led to an increase in the sodium content in the pore which has an increased selectivity towards Na ions. This observation is further supported with the adaptive Poisson-Boltzmann solver calculation, indicating that the pore interior has a strong negative potential. Distinct thinning of the bilayer membrane was observed in the vicinity of the pore complex. Simulations indicate a three fold increase in the number of salt bridges in the membrane pore complex when compared with the crystal structure data, suggesting increased stabilization of the pore complex in the presence of the membrane.

COLL 602

Ligand dynamics during microsecond simulations of the A2a adenosine receptor

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Thanks to their diversity of functions and widespread expression in all tissues, activation of G-protein-coupled receptors (GPCRs) upon agonist binding plays a critical role in cell signaling in many contexts. The GPCRs are therefore one of the most important classes of protein as drug targets. Recently, the crystal structure of the A2a adenosine receptor bound to agonist adenosine [G. Lebon et al., Nature 474, 521 (2011)] or UK432097 [F. Xu et al., Science 332, 322 (2011)] has been reported, offering insight into receptor A2a ligand binding and activation. Using the crystal structures as a starting point, we performed microsecond-timescale simulations of the A2a receptors bound to adenosine or UK432097, as well as the antagonist ZM241385. Our data suggest that adenosine is highly dynamic when bound to A2a, which contrasts starkly with the larger ligands UK432097 and ZM241385. Analyzing the simulation data in the context of published mutagensis experimental data suggests that the extra molecular scaffold of the larger ligands serves to stabilize key interactions, perhaps rationalizing the relative efficacy of different agonists.

COLL 603

Conjugated polyelectrolytes: Structures, synthesis, materials and light-activated biocidal activity

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Cationic conjugated polyelectrolytes (CPE) and oligomer electrolytes (OPE) exhibit profound light activated biocidal activity. The presentation will describe various CPE and OPE structures and synthetic methods used to fabricate them into various material formats at interfaces and on the surface of colloids. The light activated biocidal activity is related in part to the ability of the CPE and OPE to efficiently generate singlet oxygen following absorption of a near-UV or visible photon. The mechanism of light activated biocidal activity will be discussed, and structure-property relationships for singlet oxygen generation and biocidal activity will be discussed.

COLL 604

When worlds collide: Interactions at the interface between biological systems and synthetic cationic polyelectrolytes and oligomers

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The dark bactericidal mechanisms of poly(phenylene ethynylene) (PPE)-based cationic conjugated polyelectrolytes (CPE) and oligo-phenylene ethynylenes (OPE) have been investigated using electronic/optical microscopy and small angle X-ray scattering (SAXS). The ultrastructural analysis shows that the polymeric PPE-Th significantly remodels the bacterial cell wall followed by possible collapse of the bacterial cytoplasm membrane. In contrast, the oligomeric End-Only OPE (EO-OPE) possesses potent bacteriolysis activity, which efficiently disintegrates the bacterial cytoplasm membrane and induces the release of cytoplasma content. Using single giant vesicles and SAXS, we demonstrated that the membrane perturbation mechanism of the EO-OPE against model bacterial membranes results from a three-dimensional membrane phase transition. The biocidal pathways of the CPE and OPE compounds function by via compromising the bacterial structural integrity make it difficult for the bacteria to develop resistance. The correlation of quantitative dark biocidal activity with structure and type of perturbation of the cell wall will be reported.

COLL 605

Antimicrobial surfaces for combating marine biofouling and biocorrosion

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The 'beneficial' application of barnacle cement as an initiator anchor for antifouling and antimicrobial polymer brushes was compared to that of dopamine, a marine mussel inspired biomimetic anchor widely used in surface-initiated controlled radical polymerization. The environmentally-friendliness of the surfaces was further enhanced by coupling of natural biocides, such as lysozyme and chitosan. Synthetic poly(dopamine acrylamide)-*co*-poly(propargyl acrylamide) copolymers can also be coupled to a metal surface via coordination interaction of the catechol moieties, yielding a functionalizable metal platform containing 'clickable' alkyne groups on the surface for incorporation of azide-labeled antimicrobial and anti-fouling moieties. Surfaces functionalized with hydrophilic, hydrophobic, cationic, anionic and zwitterionic polymer brushes exhibit different efficacies in preventing protein adsorption, bacterial adhesion and settlement of barnacle cyprids. Finally, imparting of metal surfaces with antibacterial functionality effectively inhibits biofilm formation and biocorrosion in seawater.

COLL 606

Surface modification of biomaterials for directing cellular and bacterial response

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As the use of man-made materials and devices such as catheters, cardiac pacemakers, and prosthetic implants continue to escalate, a corresponding increase in biomaterials-associated infection is expected. It has been estimated that device-associated infections are responsible for ~50% of nosocomial infections. Our work focuses on functionalization strategies to tailor biomaterial surfaces to achieve the desired cellular and bacterial response. Bacterial colonization on implanted materials can be inhibited by grafting highly hydrophilic anti-adhesive polymers on the material surface. This method is applicable where the adhesion of mammalian cells on the material surface is also not desired or required but not for orthopedic implants where tissue integration is necessary to ensure the success of the implant. For such applications, surface functionalization with biomolecules such as peptides or growth factors in addition to anti-adhesive or bactericidal polymers can reduce bacterial colonization with concomitant enhancement of osteoblast functions to promote osseointegration.

COLL 607

Significant *Staphylococcus aureus* biofilm reduction by SAM immobilized antibiotics on implant materials

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Stainless steel (SS316L) is an alloy commonly used for artificial hip and knee replacements. In these applications, bacteria such as *Staphylococcus aureus* can adhere to the implant surface and form a biofilm that is resistant to systemic antibiotic therapy. To combat bacterial adhesion and retard biofilm development, localized presentation of antibiotics on the surface was achieved using amide bond formation between monolayers of 16-phosphonohexadecanoic acid and the antibiotics, gentamicin and vancomycin. Surface localization was confirmed by reflectance infrared spectroscopy and MALDI-MS. Using zone inhibition assays, colony forming unit enumeration, and confocal laser scanning microscopy with COMSTAT analysis, gentamicin was effective at reducing biofilm growth by 99% at short time points (2,6 hours). Vancomycin, alone, exhibited increased effectiveness from 6-48 hours, reducing biofilm formation by 99%. Immobilizing both antibiotics on the surface resulted in overall reduction of biofilm growth from 2-48hrs, indicating the antibiotics were acting synergistically on the surface.

COLL 608

Preparation of novel antimicrobial latexes for cellulose fiber-based packaging materials

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A range of novel core-shell antimicrobial latexes were prepared from butyl acrylate (BA), styrene (St), and guanidine-based antimicrobial macromonomer (GPHGH) via emulsion copolymerization using cetyl trimethyl ammonium bromide (CTAB) as a cationic emulsifier. A two-stage seeded semi-batch polymerization was employed for constructing a core- shell structure with P(BA-co-St) as the core and GPHGH as the shell. Monomer conversion, colloidal particle size, zeta potential and charge density were determined as a function of CTAB levels. The transmission Electron Microscopy (TEM) observation confirmed that the latexes obtained indeed possessed the desired core-shell structure. The latexes exhibited excellent antimicrobial activities against E. coli due to the GPHGH shell which also ensured the strong adsorption of latex particles

on cellulose fibers via electrostatic association. In conjunction with the hydrophobic layer contributed from the core of latex, the core-shell latex-treated fibres lead to the paper which is of great potential as novel food packaging materials.

COLL 609

Bacterial toxin-triggered release of antimicrobials for the treatment of bacterial infections

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We report a novel approach to selectively delivering antimicrobials to the sites of bacterial infections, in which bacterial toxins are utilized to trigger antimicrobial release from nanoparticle-stabilized liposomes for inhibiting the growth of the toxin-secreting bacteria. The binding of chitosan-modified gold nanoparticles to the surface of liposomes can effectively prevent them from undesirable payload release at regular storage or in physiological environments. However, once these protected liposomes “see” bacteria that secrete toxins, the toxins will insert into the liposome membranes and form pores, through which the encapsulated drugs are released. The released drugs subsequently impose antimicrobial effects on the toxin-secreting bacteria. Using methicillin-resistant *Staphycoccus aureus* (MRSA) as a model bacterium and vacomycin as a model drug, we demonstrate that the nanoparticle-stabilized liposomes can completely release the encapsulated vacomycin within 24h in the presence of MRSA bacteria and lead to inhibition of MRSA growth as effective as an equal amount of free vacomycin.

COLL 610

Light and dark antimicrobials: “Roach motel” synthesis by oligomer/polymer conjugated polyelectrolyte deposition

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Layer-by-layer constructs of conjugated polyelectrolytes have been synthesized by step-wise adsorption of conjugated polyelectrolytes (CPEs) supported on colloidal particles followed by core dissolution; their biocidal activity can be attributed to the CPE's generation of reactive oxygen, and the morphology of the layer-by-layer microcapsules. Differentiating the CPE makeup is of importance for further understanding of not only the mechanism of biocidal activity, but optimizing the given CPE's biocidal efficiency. Template particles were coated with alternating poly(phenylene ethylene)-type conjugated polyelectrolytes followed by dissolution of the inorganic template. Studies of the microcapsules in both light and dark environments, roach motel concentration differentials, bilayer counts, and cationic/anionic pair derivatives were carried out against Staphylococcus epidermidis, Pseudomonas aeruginosa, Staphylococcus aureus, and Escherichia coli. Microcapsules containing an oligomer and a polymer were studied for possible release of oligomer into solution. Strong biocidal activity of the capsules was verified via microscopy and staining procedures.

COLL 611

Multifunctional gold nanoparticles for gene silencing

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Small interfering-RNAs (siRNA) show significant potential to down-regulate specific abnormal gene expression in cancerous or viral-infected cells. We have developed effective conjugation strategies to combine biomolecules to the surface of AuNPs with specific functions, such as cell penetrating peptides to overcome the cellular membrane barrier, quaternary ammonium to introduce stable positively charges on the AuNPs' surface and siRNA complementary to a key cell-cycle regulator gene, the proto-oncogene c-Myc. Two approaches were designed for the binding of all these molecules to the nanoparticles: i) the use of a thiolated siRNA for covalently bind to the AuNPs' surface; and ii) ionic interactions generating positive charge on the nanoparticles. The resulting nanoparticles were characterized on their chemical functionalization, ease of cell uptake, cellular toxicity and knockdown of c-Myc expression in a cancer cell line, Hydra and C57BL/6j mice. Results confirmed their high efficiency for the specific silencing of c-Myc expression.

COLL 612

Effect of surface immobilization on the DNA structure and its mechanical properties

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The DNA functionalized surfaces are used in biosensors and for programmed self-assembly of biological, organic and inorganic moieties into novel materials. However, experimental observation show that a large fraction of surface bound DNA is unavailable for hybridization. This study investigates the effect of surface and DNA length on the structure of single stranded DNA (ssDNA). The behavior of surface constrained ssDNA (poly thymines and poly adenines) molecules was compared to the labile single stands in solution. We observed that surface constrain on ssDNA introduces different chain folding pathwaysand reduced intra chain interactions than that of labile strands. Based onthe surface density variance for the duplex samples, we found that 15 bases of single stranded oligonucleotide lengths is most favorable for the film growth applications.We also performed steered molecular dynamics to explain the correlation between the folding and unfolding pathways of oligonucleotides and we found that the mechanical properties of ssDNA were sequence and folding pathway dependent. The length and sequence dependence of ssDNA together with surface effects are important for the understanding of self-assembly of nucleic acid based materials.

COLL 613

Nanomaterial for targeted capture and photothermal killing of antibiotic-resistant bacteria

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Since last two decades several human pathogens became resistant to most of the clinically approved antibiotics and they are easily spread across continents. As a result, antibiotic resistant bacteria have become an emerging threat worldwide. Recent advancement in nanoscience and nanotechnology has expanded our ability to design and construct nanomaterials with targeting, therapeutic, and diagnostic functions. These multifunctional materials have attracted our attention to be used as promising tool for selective MDRB sensing and therapy without the current drugs. In this talk we will provides the basic concepts and critical properties of different nanostructures that are useful for pathogen detection and photothermal applications from our groups. In addition, bio-conjugated nanomaterials based strategies have been employed for photothermal therapy of MDRB will be discussed by aiming to provide an overview on exciting opportunities and challenges in this field

COLL 614

Polyvalent display of RGD motifs on turnip yellow mosaic virus for enhanced stem cell adhesion and spreading

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Turnip yellow mosaic virus (TYMV) is a stable 28 nm icosahedral plant virus that can be isolated in gram quantities. In order to study the polyvalent effect of Arg-Gly-Asp (RGD) clustering on the response of bone marrow stem cells (BMSCs), an RGD motif was genetically displayed on the coat protein of the TYMV capsid. Composite films composed of either wild-type TYMV or TYMV-RGD44, in combination with poly(allyamine hydrochloride) (PAH), were fabricated by a layer-by-layer adsorption of virus and PAH. The deposition process was studied by quartz crystal microbalance, UV-vis and atomic force microscopy. BMSC adhesion assays showed enhanced cell adhesion and spreading on TYMV-RGD44 coated substrates compared to native TYMV. These results demonstrate the potential of TYMV as a viable scaffold for bioactive peptide display and cell culturing studies.

COLL 615

Polymer-based biomimetic membranes on solid supports

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The ability for model systems of cellular membranes to mimic complex natural functions is of great interest to both biomaterials and biophysics. Specifically, there is need for membranes that allow and stabilize the *in vivo* activity of imbedded components. While this field traditionally utilizes lipids to create such architectures, recent progress has been made in synthesis and creation of polymer assemblies that improve on several aspects of biomimetic membranes. Our group is specifically interested in the creation and characterization of polymer membranes on solid supports.

The deposition of amphiphilic poly(ethylene oxide)-*block*-poly(butadiene)(PEO-*b*-PBD) copolymer micelles is demonstrated on solid substrates. Depending upon surface chemistry, adsorption creates either bilayers or monolayers. Lateral diffusion measurements reveal that strong coupling between hydrophilic surfaces and PEO moieties creates immobile bilayers, while monolayers retain the fluidity observed in vesicles. These membranes may be capable of meeting the requirements for hosting biological molecules and maintaining their native functions.

COLL 616

Effect of nanoparticle shape and charge on cytotoxicity

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Nanoparticles of non-spherical shape exhibit plasmon resonance in the infrared region (IR) of the electromagnetic spectrum. Hence they are ideal candidates for biomedical

applications in targeted vivo imaging, diagnostics, and cancer therapy since the biological tissue is transparent to near IR radiations. For this purpose, we perform MD simulation of the gold nanoparticles as nanocube, nanocage, nanocylinder, nanocone, nanostar, and nanorice among others and study their interaction with model lipid bilayer. It is known that charged nanoparticles penetrate the lipid bilayer forming holes leading to cyotoxicity. We will provide estimates of the cell-membrane damage and the energy barrier for the penetration of the nanoshapes. Combined effect of nanoshape and charge on the translocation of these particles and membrane damage will be discussed.

COLL 617

Library of the nanoscale self-assembly of amino acids on metal surfaces

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The self-assembly of amino acids on surfaces represents a unique test-bed for the origin of enantio-favoritism in biology and the transmission of chirality from single molecules to complete surface layers. These chiral systems represent a direct link to the understanding of certain biological processes, specifically the preference for some amino acids to form alpha helices vs. beta-pleated sheets in the secondary structure of proteins. Scanning tunneling microscopy (STM) is used to study the self-assembly of amino acids on Cu(111) to build a library of their two-dimensional structure with molecular-scale resolution. Both enantiopure and racemic structures are studied to elucidate how chirality can affect the self-assembly. The advent of such a library with fully resolved structures at different molecular coverages would address some of the complex questions surrounding the secondary structure of proteins and lead to a better understanding of the key role played by these amino acids in protein sequencing.

COLL 618

Multiplexed sensing of ions with barcoded polyelectrolyte capsules

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Multiplexed detection of analytes is a challenge for numerous medical and biochemical applications. Many fluorescent particulate devices are being developed as ratiometric optical sensors to measure concentration of intracellular analytes. The response of these sensors is based on changes of the emission intensity of analyte-sensitive probes, entrapped into the carrier system, which depends on the concentration of a specific analyte. However, there are a series of technical limits that prevent their use for quantitative detection of several analytes in parallel (e.g., spectral overlap between different sensor molecules). Here we demonstrate that double wall barcoded sensor capsules can be used for multiplexed analysis of proton, sodium and potassium ions. The sensor detection methodology is based on porous microcapsules which carry ion-

sensitive probes in their inner cavity for ion detection and a unique QD barcode in their outermost wall as tag for identification of individual sensors. The engineering of QD barcodes to capsules walls represents a promising strategy for optical multi-analyte determination.

COLL 619

Synthesis and characterization of PEGylated dendrimer-entrapped gold nanoparticles for molecular imaging applications

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We report the synthesis and characterization of dendrimer-entrapped gold nanoparticles (Au DENPs) modified by polyethylene glycol (PEG) with enhanced biocompatibility for computed tomography (CT) imaging applications. In this study, amine-terminated poly(amidoamine) dendrimers of generation 5 ($G5.NH_2$) modified by PEG monomethyl ether ($G5.NH_2$-*m*PEG_{20}) were used as templates to synthesize Au DENPs, followed by acetylation of the remaining dendrimer terminal amines to generate PEGylated Au DENPs. The partial PEGylation modification of dendrimer terminal amines allows high loading of Au within the dendrimer interior, and consequently by simply varying the Au salt/dendrimer molar ratio, the size of the PEGylated Au DENPs can be controlled at a range of 2-4 nm with a narrow size distribution. The formed PEGylated Au DENPs are water-dispersible, stable in a pH range of 5-8 and a temperature range of 0-50 ^{o}C, and non-cytotoxic at a concentration as high as 100 mM. X-ray absorption coefficient measurements show that the attenuation intensity of the PEGylated Au DENPs is much higher than that of Omnipaque with iodine concentration similar to Au. The PEGylated Au DENPs enabled not only X-ray CT blood pool imaging of mice and rats after intravenous injection of the particles, but also effective CT imaging of a xenograft tumor model in nude mice. These findings suggest that the designed PEGylated Au DENPs can be used as a promising contrast agent with enhanced biocompatibility for CT imaging of various biological systems, especially in cancer diagnosis.

COLL 620

Self-powered microscale pumps based on analyte-initiated depolymerization/degradation reactions

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Microscale pumps that provide precise control over flow rate without the aid of batteries or electronics and that are capable of turning "on" in response to specific analytes in solution, such as an enzyme, are needed for use in many types of smart micro- and nano-scale devices, such as implantable medical devices. The ideal pump for such applications should be capable of functioning autonomously, with pumping action controlled both by the presence and concentration of a specific analyte. Herein we describe the first examples of microscale pumps that display these desirable characteristics. These pumps consist of insoluble polymer films that depolymerize to release soluble monomeric products when exposed to a specific analyte. Products formed as a result of the depolymerization reaction amplify the signal and create a concentration gradient that pumps fluids (and insoluble particles) away from the bulk polymer due to a diffusiophoretic mechanism. These pumps are capable of turning "on" in response to specific analytes and are tunable to respond to a variety of analytes, ranging from small molecules to enzymes.

COLL 621

Hyperthermal gas-surface collisions: Theoretical studies

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In this talk I will describe theoretical studies of gas-surface collision processes in which the colliding gaseous species have hyperthermal energies, and we want to determine information about the surface structure and reactivity that is provided by examining species that emerge from the surface after collision. Much of the emphasis will be on studies of hyperthermal CO2 collisions with ionic liquid surfaces, but other examples of atoms or molecules colliding with liquids or solids will be provided. Detailed comparisons with experiment will be provided.

COLL 622

Polymer molecular engineering: Vignettes from lithography and photovoltaics

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This talk will cover two topics based on applications of polymers: sequential infiltration synthesis (SIS) and organic photovoltaics. SIS is a new materials synthesis technique, derived from atomic layer deposition, with applications ranging from advanced lithography to separation membranes. Coupled with block copolymer self-assembly, SIS

provides a unique pathway to complex 2-D and 3-D nanostructures. Self-assembly can also be utilized to begin deciphering structure-property relationships in OPVs. A few examples of rationally designed assembly in OPV systems will be discussed, along with recent results that point to a rethinking of the idealized morphology in OPVs.

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COLL 623

Precise assemblies, clusters, superatoms, and cluster-assembled materials

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Precise clusters offer a new set of building blocks with unique properties that can be leveraged both individually and in materials in which their coupling can be controlled by choice of linker, dimensionality, and structure. Initial measurements in both of these worlds have been made. Isolated adsorbed or tethered clusters are probed with low-temperature scanning tunneling microscopy and spectroscopy. Even closely related elements behave differently on identical substrates. Surprising spectral variations are found for repeated measurements of single isolated, tethered clusters. In periodic solids, precise clusters joined by linkers can be measured experimentally and treated theoretically with excellent agreement, in part due to the relatively weak coupling of the clusters. This coupling can be controlled and exploited to produce materials with tailored properties. Some of the rules of thumb for predicting these properties are being developed through these initial studies and the limit to which they can be applied is being explored.

COLL 624

Mechanism of structural transformations indcued by antimicrobial peptides in lipid membranes

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Antimicrobial peptides are a class of small (<100 residues) host defense peptides that induce selective membrane lytic activity against microbial pathogens. The permeabilizing behavior of these diverse peptides has been commonly attributed to the formation of pores, and such pore formation has been categorized as barrel-stave,

toroidal, or carpet-like. Using atomic force microscopy, the disruption of supported lipid bilayer patches by protegrin-1 has been studied in a concentration-dependent manner. PG-1 acts to lower the interfacial energy of the bilayer in a way similar to detergents, stabilizing pore formation. The intercalation of PG-1 into the bilayer results in structures beyond that of pore formation, giving rise to worm-like micelles at high peptide concentrations. The interaction depends not only on the charge of the peptide, but also on the composition and state of the membrane. Antimicrobial peptides with structural differences, magainin-1 and aurein 1.1, exhibit a mechanistic commonality.

COLL 625

Using nanoscale amorphous solid films to create and study deeply supercooled liquids

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Molecular beam vapor deposition on cryogenic substrates is known to produce amorphous solid films. When heated above their glass transition these films transform into deeply supercooled liquids. These nanoscale liquid films can be used to study kinetic processes such as diffusion, isotope exchange, and crystallization in unprecedented detail. This talk will highlight our recent advances in this area with a focus on hydrogen-bonded liquids such as water and alcohols.

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COLL 626

Non-Maxwellian evaporation of gases from liquids

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Vacuum experiments indicate that gases generally evaporate from liquids in Maxwellian velocity and cosine angular distributions. Using liquid microjets, however, we find that dissolved helium atoms evaporate in non-Maxwellian distributions from liquid dodecane, squalane, and ethylene glycol. While the energy distributions of O_2, H_2O, and Ar follow a Maxwellian distribution with an average kinetic energy of $2RT$, the energy distribution of He is broader and shifted to higher average energies up to $2.8RT$ for ethylene glycol. This higher energy evaporation implies that some He atoms exit over an interfacial

potential energy barrier or plateau and do not re-equilibrate at the surface before leaving the liquid. This barrier may arise from the energy required for He atoms to move between surface molecules or from energy released as He departs from a surface cavity. By detailed balance, high energy He evaporation implies preferential entry by impinging high energy He atoms.

COLL 627

Missing link: Surface freezing meets self-assembly

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Using atomic-resolution x-ray reflectivity we have investigated monolayers formed at the bulk alkanol-sapphire interface. Measurements were performed using high energy x-rays at 71 and 32 keV, sufficiently high that there is little absorption through the liquid. This system, with its relatively balanced inter-molecular and molecule-substrate interactions bridges the gap between self-assembled and surface-frozen monolayers, each dominated by only one interaction. For octadecanol the monolayer is comprised of densely packed surface-normal molecules, hydrogen-bound to the sapphire. Mediated by a partial desorption of the alkanols, the monolayers melt reversibly at a temperature about 30°C above the bulk, which we rationalized within a thermodynamic model comprising interfacial interactions, molecular elasticity, and entropic effects. Separating the substrate from the alkanol melt leaves the monolayer structurally intact. Additional studies show that the monolayer is epitaxial with the sapphire substrate. The interfacial surface freezing behavior found is expected to be generic to weakly bound, self-assembled monolayers.

COLL 628

Analysis of graft compositions in surface modified nanoparticles

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Chemical modification of nanoparticles or particlelike systems is ubiquitously being used to facilitate specific pharmaceutical functionalities or physicochemical attributes of nanocrystals, proteins, enzymes, or other particlelike systems. Often the modification process is incomplete and the functional activity of the product depends upon the distribution of functional ligands among the different particles in the system. Here, the distribution function describing the spread of ligands in particlelike systems undergoing partial modification reactions is derived and validated against a conjugated enzyme model system by use of matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF). The distribution function is shown to be applicable to describe the distribution of ligands in a wide range of particlelike systems (such as enzymes, dendrimers, or inorganic nanocrystals) and is used to establish guidelines for the synthesis of uniformly modified particle systems even at low reaction efficiencies.

COLL 629

Assessing the differentiation status of individual hematopoietic cells from mouse bone marrow with multivariate analysis of TOF-secondary ion mass spectrometry data

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Hematopoiesis is a process where the blood and immune cells are generated from a small number of hematopoietic stem cells (HSCs). Though their self-renewal ability renders HSCs of significant value for tissue engineering, the combination of chemotactic and micromechanical properties that need be included in *ex vivo* culture systems remain to be elucidated. New experimental approaches that permit identifying the differentiation stage of individual cells would facilitate this task. Because the surface antigens on HSCs change during differentiation, the chemical information about the cell surface that can be acquired with TOF-secondary ion mass spectrometry (TOF-SIMS) might be exploited to identify differentiation status. We demonstrate that multivariate analysis of TOF-SIMS data enables classifying individual hematopoietic cells from mouse bone marrow according to their distinct lymphopoiesis phenotype, specifically HSCs, common lymphoid progenitors, or mature B cells. This approach may enable correlating cell differentiation status with location within a colony or engineered environment.

COLL 630

Folate-conjugated luminescent nanoporous silica spheres for bio-imaging

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Bio-imaging to visualize specific cells are important for diagnosis and medical treatment. In this study, the folic acid (FA), which is used as the targeting ligand for tumor cells, was immobilized on the luminescent europium(III)-doped nanoporous silica spheres (Eu:NPS) through a mediation of 3-aminopropyltriethoxysilane (APTES). The immobilization of APTES and FA occurred on the Eu:NPS. The ordered nanopores were preserved with the immobilization. The surface area decreased only with the APTES immobilization, and the FA was immobilized only on the outer surface of the pore. The photoluminescence of the immobilized spheres showed the characteristic luminescence peak due to interactions between the FA and Eu^{3+}, which can be observed using a fluorescent microscopy. The immobilized spheres showed the highly dispersed stability in phosphate buffered saline to easily react tumor cells. Thus, the FA was successfully immobilized on the luminescent Eu:NPS spheres through the APTES adlayer to show the highly targeting ability.

COLL 631

Investigating solid-fluid interfaces using forced dewetting

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Forced dewetting is a strategy for physically isolating ultrathin regions of the solid-fluid interface that can be probed directly with optical spectroscopies. Under the proper conditions, this approach results in residual thin films whose thicknesses are in the several nm regime and are dictated by long range as opposed to hydrodynamic forces. These thin film environments have been shown to replicate interfacial behavior of in-situ systems, while excluding the relatively thick, opaque bulk solvent layers that traditionally complicate interfacial spectroscopy. Examples of the applicability of this approach will be presented that include an analysis of interfacial molecular structure at bare metal substrates and at substrates covered by either self-assembled monolayers or thin polymer films.

COLL 632

Molecular mechanisms of fouling in polyamide membrane

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Nanofiltration (NF) and reverse osmosis (RO) membranes are recognized as one of the best technologies for water treatment. Most fouling phenomena on membrane surface are originated from bacteria activity and organic matters in feed water and can decrease the performance of NF and RO membranes. The molecular interaction mechanisms of

membrane bio- and organic fouling are not well understood, but are important as the guidance to optimize the membrane reactivity. In this study, surface forces apparatus (SFA) technique was applied for measuring the interaction forces and adsorption behaviors of bio- and organic matters on the polyamide (PA) membrane, which is a polymer composition of thin-film composite (TFC) NF and RO membranes. Alginate, bovine serum albumin (BSA), Aldrich humic acid (AHA), lipopolysaccharides (LPS) and extracellular polymeric substances (EPS) were used as representative organic and biological matters. PA thin-film layer was prepared by interfacial polymerization using *m*-phenylenediamine (MPD) and 1,3,5-benzenetricarbonyltrichloride (TMC).

COLL 633

Mechanically addressable smart surfaces

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In this contribution we show how a mechanically addressable surface with excellent promise for further applications, e.g. bio adhesion studies, can be created on the basis of a cationic, fluorescently labeled polyelectrolyte brush. These surfaces have outstanding properties with pressure sensitivity in the order of human skin (1 kPa) and a lateral resolution better than 1 µm (50X better than human skin).The experimental setup is based on the soft colloidal probe technique [1], where a defined force was applied to the brushes using an atomic force microscope (AFM). Due to mechanical deformation of the soft colloidal probe the response of the system in the contact area can be monitored with a confocal laser scanning microscope (CLSM) in situ. In order to understand the behavior of the observed response, we model the contact situation underneath the PDMS bead with the theory developed by Johnson, Kendall and Roberts.

We find a decrease in fluorescence intensity (as compared to the background intensity) in areas of compression and a slight increase of fluorescence in areas of tension. Also we could show that the response is stabilized well before acquisition times of 1-2 seconds, is constant over several minutes and is completely reversible.

The key advance in the present work [2] is the quantitative characterization of the mechanoresponsive surfaces. We have determined a response function I(p), which correlates local fluorescence intensity (I) to local pressure (p).

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COLL 634

Smart shape-memory interfaces for mechano-structual control of cell function

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Shape-memory surfaces (SMSs) with on demand, tunable nano-patterns have been developed to observe time dependent changes in cell alignment using temperature-responsive poly(e-caprolactone) (PCL) films. Permanent surface patterns were generated by crosslinking the PCLs in a mold. Temporary surface patterns were later embossed into the crosslinked SMSs. The application of body heat quickly and completely transitioned temporary surface patterns to permanent patterns. To observe the effects of a shape-memory-activated change in surface topography on cell behavior, surfaces with a temporary grooved pattern were used as a cell culture substrates and subsequently triggered to revert to a permanent flat surface in the presence of growing cells. A time-dependent decrease in cell alignment was observed as a result of remodeling of the actin cytoskeleton. Dynamically tunable nano-structured surfaces, therefore, can be used to study the effects of surface nano-geometries on time-dependent cytoskeleton remodeling under biological relevant conditions.

COLL 635

Silver nanoparticle incorporated novel polyelectrolyte composite nanofibers with antimicrobial and anti-infective properties for protective clothing applications

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To overcome the current activated charcoal impregnated protective clothing and face masks, we attempted polyelectrolyte composite nano-fibrous materials for protective clothing applications. The current material has the disadvantages such as wearer discomfort, moisture absorption and heaviness. Nanofibers possess high surface area to volume ratio and the pores present in the nanofibers have the capability to exchange moisture together with selective blocking of chemical vapors. Hence they are tested as non-woven fabrics for protection against chemical and biological (CB) warfare agents. We achieved polyelectrolyte membranes through eco-benign water mediated green electrospinning further enhancing their usage with cheaper production cost. The usage of water soluble poly-electrolytes along with nanoparticle composite enables synergistic antimicrobial activity. The nano-composite nanofiber membrane was fabricated by the method of layer-by-layer electrospinning and layer-by-layer deposition of poly-electrolytes. Comparison of antimicrobial activity against Escherichia Coli with varying concentrations of polyelectrolytes and incorporated silver nano-particles is done which showed that the nanofiber material as a versatile antimicrobial membrane. Thus

fabricated silver nanoparticle composite functionalized polyelectrolyte nanofibers can be applied as filters to protect the wearer from bacterial contaminants. The application of the nanofiber material for broad spectrum antibacterial activity and for anti-infective protective wear needs is ongoing.

COLL 636

Electrospun green nano fibers: Processing, properties, and applications

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Electrospun fibers have a large surface area to volume ratio which is over 1000 times higher than the micro fibers. Their high porosity, inherently large surface area, flexibility in surface functionalities and superior mechanical performance make these nonwovens the optimal candidates for applications in batteries and biomedicine. The government's push for green products, consumers' desire, and energy conservation are some of the key factors that drive research towards the development of renewable resource-based materials. This paper will highlight the current status of preparation, properties and applications of electrospun green nanofibers derived from renewable resource based plastics and their nanocomposites. This research is financially supported by the *Natural Sciences and Engineering Research Council* (NSERC) Canada, Discovery grant individual to MM; NSERC USRA granted to NK and MS; and the Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA)-University of Guelph (Bioeconomy for Industrial Uses) research program.

COLL 637

Development and investigation of functional textiles

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My research focuses on the development of textiles with multifunctional properties, emphasis given to hydrophobicity, self-cleaning, and photoactivity. In this talk I will describe the methods used to functionalize textile materials in our lab. One of the methods is the layer-by-layer deposition of nanoparticles of various sizes onto textile surfaces. Another widely used method is the electrospinning of functional polymers onto textile surfaces to develop reagentless surface modification techniques. Textiles are plasma treated prior to electrospinning to generate reactive groups for further functionalization. Last method to be explained is the development of ZnO nanorods on cotton and electrospun cellulosic substrates to generate UV-blocking, photoactive, and hydrophobic surfaces.

COLL 638

Effect of nano-fiber cellulose addition on the mechanical properties of epoxy resin

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The effect of the addition of nano-fibers cellulose (NFC) to enhance the tensile properties of the epoxy resin was investigated. NFC was added to the epoxy resin at different weight percentages (0.25, 0.5 and 1%). Tensile properties including, strength, elongation, toughness and young modulus were investigated. In addition the pull of strength, the weight lost by the abrasion test and the weathering results were reported.

Addition of NFC to the epoxy resin causes massive improvements in the tensile properties of the epoxy composite. The highest increase was found at the optimum addition ratio of 0.5% of NFC. At this ratio, the epoxy composite strength increased by 99%, the elongation and the toughness increased by 150%, and the young modulus increased by 50% in comparison to the pure epoxy resin. The epoxy composite show discoloration after the weathering test in comparison to the pure epoxy, both samples shows perfect bond adhesion.

COLL 639

Functionalization of wood pulp fibres with layered double hydroxide particles

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Hydrogen peroxide bleached Spruce (Picea abies) Thermo Mechanical Pulp (BTMP) fibres were modified with Layered Double Hydroxides (LDH). The LDH particles were precipitated onto the BTMP fibre surfaces from aqueous solutions of urea and sodium hydroxide. The BTMP that had been modified in alkaline sodium hydroxide was further functionalized with sodium dodecyl sulphate (SDS) surfactant to produce pulp with hydrophobic character. The contact angle measurement with water on paper showed that the functionalization with SDS was successful. The apparent contact angles varied in between the initial θ = 75° of the reference pulp up to θ = 135° of the SDS functionalized pulp. A hydrophobic surface was obtained already with 2.0% weight to weight ratio of SDS in pulp suspension. A high affinity between the LDH particles and the BTMP fibres was found as well. The investigated fibre modification route offers a new feasible tool in fibre surface treatment.

COLL 640

BC whisker/P (NIPAM-co-BMA) nanogel complex for interventional therapy of hepatocellular carcinoma

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Bacterial cellulose (BC) consists of ribbon-shaped nano-fibers in web-like structures. Poly (*N*-isopropylacrylamide- *co*- butylmethacrylate) (PNB) nanogel dispersion exhibited reversible thermosensitive sol-gel phase behaviors and it could be used as a new material for interventional therapy. In this paper, BC whiskers were nanosized and then utilized to prepare BC whisker/PNB nanogel complex, which could enhance the bloodvessel-embolization property of PNB nanogel.

The morphology and average size of the nanogel complex were characterized by transmission electron microscope (TEM) and dynamic light scattering (DLS). The vial inverting with visual method and differential scanning caborimetry (DSC) ware utilized to study the thermosensitive behaviors of concentrated BC whisker/PNB nanogel complex Iohexol dispersion.

The kinetics of the thermosensitive volume phase transition of BC whisker/PNB nanogel complex was evaluated by rheological tests. The concentrated dispersion showed good shear thinning behavior, which plays a key role on the interventional therapy for hepatocellular carcinoma.

COLL 641

Incorporating carbon fiber papers as conductive scaffolds in carbon inverse opals

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The physical inflexibility and modest electronic conductivities of carbon inverse opal monoliths limits their prospects as electrodes in portable electronic devices. We hypothesize that carbon inverse opals that are fabricated within carbon fiber paper scaffolds will exhibit mechanical flexure and increased electronic conductivity, and will therefore discharge greater magnitudes of electrochemical capacitance than comparable carbon inverse opal monoliths in response to increasing current densities. We fabricate carbon inverse opal papers by assembling polymer colloidal crystals within the fiber matrix, infiltrating the colloidal template with resorcinol-formaldehyde monomer, and subsequently pyrolyzing the composite to create the inverse opal pore geometry. The resulting nanoarchitectured fabric has a four-point electronic conductivity that is at least two orders of magnitude greater than that for monolithic carbon inverse opals. Carbon inverse opal monoliths and papers discharge statistically similar magnitudes of

electrochemical capacitance, which indicates that ionic transport through the tortuous pore networks is the rate-limiting factor.

COLL 642

Surface and chemical degradation mechanism of silk by radicals

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The degradation of silk protein by radical induced chemicals under the UV light was studied. The EPR test results confirmed that anthraquinone based structure chemicals including dyes are able to produce radical under UV-A, UV-B and fluorescent light and attack protein chemical structure. Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy were used to study the photo-initiated degradation of silk by radicals. Scanning electron microscopy (SEM) and AFM were applied to investigate the damages on the silk surface. The Raman spectra of UV irradiated dyed silk showed that some changes in the ratio of amide I (1667 cm^{-1}) and amide III (1230 cm^{-1}) groups has occurred, suggesting the possible breakage of peptide links in the protein. The intensity reduction of peaks in area 821 cm^{-1} to 930 cm^{-1} revealed the possible loss of amino acids in soft segment of fibroin fibers. SEM and AFM pictures confirmed the specified damages on the silk surface.

COLL 643

Effect of surface functional group on adsorption of cell adhesive proteins and subsequent cell adhesion using self-assembled monolayers

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Cell adhesion onto biomaterial surfaces are mediated by adsorbed protein layer. Cell adhesive proteins such as fibronectin (Fn) and vitronectin (Vn) plays an important role in cell adhesion. To elucidate the effect of surface chemistry on adsorption of cell adhesive proteins and subsequent cell adhesion, we examined adsorption of Fn and Vn and cell adhesion to self-assembled monolayers (SAMs) of alkanethiols carrying methyl (CH_3), hydroxyl (OH), carboxylic acid (COOH) and amine (NH_2). Larger amount of Fn and Vn was adsorbed to COOH- and NH_2-SAMs than to CH_3- and OH-SAMs in both mixture with bovine serum albumin (BSA) and 2% fetal bovine serum, indicating that Fn and Vn is preferentially adsorbed to these SAMs. Human umbilical vein endothelial cells adhered to COOH- and NH_2-SAMs preadsorbed with Fn or Vn even in the presence of 1000-times BSA. These results suggest that competitive adsorption of cell adhesive proteins greatly affects subsequent cell adhesion.

COLL 644

Cadherin interactions at the adhesive interface

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The functional organization of cells within tissues is determined by cell-cell adhesion, a two-part mechano-chemical process that maintains tissue architecture and organizes intracellular proteins for downstream cell signaling. Initially, cell-cell adhesion is characterized by dynamic chemical interactions that tightly regulate protein-ligand binding events. The second step, which encompasses the dynamics of how weak interactions in the initial protein binding stage are strengthened spatiotemporally, remains poorly understood for lack of robust quantitative platforms for analyzing these interactions. Protein orientation at the adhesive interface during ligand recruitment may be critical to cadherin binding dynamics and activity. We investigate the binding dynamics and activity of vascular endothelial cadherin ligands on bio-adhesive surfaces as a function of protein orientation using a quantitative, label-free real-time molecular interaction biosensor. Surface plasmon resonance data could inform the rational design of ligand-conjugated 'biomimetic' biomaterials that have potential to promote tissue integrity in various disease contexts.

COLL 645

Protein PEGylation: Conformation of the poly(ethylene glycol) conjugate and effect on protein adsorption to the solid-liquid interface

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Covalent conjugation of poly(ethylene glycol) to proteins is an effective strategy to enhance in vivo circulation time and efficacy of protein therapeutics. The configuration of the protein-bound PEG conjugate and the effects of these conjugates on protein adsorption to surfaces they encounter during purification, storage or delivery are only just beginning to be understood. With chicken egg lysozyme as a model protein, we used small angle neutron scattering to determine that a 20 kDa PEG conjugate exists as a modestly perturbed random coil adjacent to the protein. In a study of three model proteins, we find that PEGylation tends to decrease the extent of adsorption and to increase adsorption reversibility. PEGylation tends to inhibit surface-induced aggregation and alters the organization of an adsorbed layer. The latter is indicated by neutron reflection measurements that resolve the surface concentration-dependent distribution of PEG segments in adsorbed layers of PEGylated lysozyme.

COLL 646

Rational development of biosensors based on enzymes adsorbed onto carbon nanotubes

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Electrochemical biosensors based on enzyme electrodes are attractive because they integrate the specificity of enzymatic reactions with a sensitive signal transduction. Although considerable progress has been made by encapsulating or cross-linking enzymes, the analytical performance of biosensors still suffers from fundamental deficiencies such as slow response (≥ 10 sec) and limited sensitivity (~uM). In order to overcome these drawbacks, our group is focused on the development of biosensors based on enzymes *adsorbed* onto carbon nanotubes. Our hypothesis is that experimental conditions and adsorption kinetics can be rationally selected to maximize the amount, integrity of structure, enzymatic activity, and stability of adsorbed proteins. Our experimental design includes the employment of spectroscopic ellipsometry for evaluating the nanotube substrates, developing optical models, and investigating the kinetics and effects of varied adsorption conditions (protein concentration, solution pH, ionic strength, etc.) on enzyme interactions with carbon nanotubes. Our most significant results will be highlighted.

COLL 647

Interaction of integral membrane proteins with lipidic cubic nanoparticles

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Self-assembled lipidic cubic phases are attracting increasing interest as biocompatible carriers of large biomolecules including proteins, peptides, DNA and drugs [figure 1].[1] The interaction between the dopamine D2 receptor, a membrane protein drug target, and cubic nanoparticles is described. Agonist-receptor interactions may be exploited to increase the interaction between the membrane protein and the nanoparticles.[2] A suite of new high-throughput techniques, to both formulate and structurally characterize lipidic phases, and assess functionality for membrane proteins contained within them, are described.[3]

COLL 648

Protein adsorption to planar polymer brushes – the effects of charge and grafting density

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Polymer brushes provide a soft micro-environment for adsorbed proteins preventing changes or even enhancing the functionality of the immobilized species. We present a neutron reflectivity study on the adsorption of bovine serum albumin (BSA) to polyacrylic acid (PAA) brushes of varied grafting density. The PAA brushes are prepared by a Langmuir-Schaefer based grafting of perdeuterated poly(styrene)-b-poly(acrylic acid) block copolymer (dPS-PAA) to dPS pre-coated silicon supports. The grafted brushes are characterized in their collapsed state at the air-solid interface by x-ray reflectometry. Subsequent neutron reflectivity measurements at the solid-liquid interface after incubation in buffered D_2O and adsorption of BSA reveal detailed volume fraction profiles of the swollen brush, $\Phi_{PAA}(z)$ and the immobilized protein, $\Phi_{BSA}(z)$, respectively, where the amount of adsorbed BSA scales linearly with grafting density. We show that $\Phi_{BSA}(z)$ differs substantially from $\Phi_{PAA}(z)$. Experiments at elevated hydrostatic pressure prove full stability of the plain and BSA-loaded brushes up to 90MPa.

COLL 649

Interaction between saliva proteins and Streptococcus mutans with and without antigen I/II at its surface

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Adhesion of proteins to bacteria may be controlled by non-specific and/or specific interactions. The latter ones are mediated by antigens on the bacterial surface. This paper reports on the interaction between saliva proteins and Streptococcus mutans, an oral bacterium that is involved in tooth decay, by comparing two strains of S. mutans, one with and one without antigen I/II on its surface. Bacterium-saliva interaction is characterized in terms of enthalpy (calorimetry), strength of adhesive bond (AFM), and kinetics of adhesion of the bacterial strains to a saliva-coated surface (parallel plate flow chamber). The study shows that the presence of antigen I/II at the streptococcal surface adds favorable adsorption sites for (a number of) saliva proteins, resulting in an increased adhesion of S. mutans to salivary coatings, such as the acquired pellicle at tooth surfaces.

COLL 650

Protein adsorption on surfaces is a thermodynamically irreversible process

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As a rule protein binding to surfaces occurs on a two-dimensional lattice of binding sites (for review see [1]). Present evidence strongly indicates that the fundamental postulates of Langmuir [2] for monolayer adsorption are invalid in such systems. Typically the consequences of lattice binding are multivalence, negative cooperativity (Freundlich-type isotherms) and adsorption-desorption hysteresis [1,3]). We have detected protein adsorption hysteresis on surfaces of agarose, quartz glass, PDLLA and titanium with or without covalent surface modifications e.g. with alkyl silanes or biotin. As proteins phosphorylase b (m_r = 196 kDa), fibrinogen (m_r = 340 kDa), bone morphogenetic protein 2 BMP-2 (m_r = 26 kDa) and avidin (65 kDa) were studied (see also [4]). Characteristic for protein adsorption hysteresis are long-lived metastable states attributed to local energy minima, which can be evaluated for apparent thermodynamic state functions of the thermodynamically irreversible process. The hysteresis cycle itself generates entropy (DiS) from which the DiG associated with the conformational change of the protein on the surface can be calculated [3]. As will be shown the binding constants (K_A) for the desorption branch of proteins lie in the range of 10^9-10^{13} M^{-1} and the apparent molar Gibbs free energies of the irreversible process (D_iG) in the range of -9 to -40 kJ Mol^{-1}.

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COLL 651

Cylindrical bubbles and blobs of the protein *Cerato ulmin*, conditions for stability and applications

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Cerato ulmin is a class II hydrophobin. On suitable treatment, it easily forms cylindrical air bubbles and cylindrical oil blobs. The conditions for formation of these unusual structures will be discussed, along with their stability and possible applications in diverse fields including polymer synthesis and oil spill remediation. Acknowledgment is

made to Dr. Wayne C. Richards of the Canadian Forest Service for the gift of *Cerato ulmin*, and to The Gulf of Mexico Research Initiative for financial support.

COLL 652

Multicomponent 3D protein arrays by electron beam lithography

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Multi-component micro-aligned patterns have been constructed and 3-D spatial control for hydrogels fabricated by e-beam lithography has been demonstrated. Cross-sectional analysis has confirmed that these microstructures have been produced such that an alkyne terminated 8-arm polyethylene glycol (Alkyne-PEG) is patterned inside a contiguous outer shell with 8-arm PEG of aminooxy functionality (AO-PEG) completing encapsulation of the hydrogel (Figure 1). This strategy has been extended to achieve 3-D spatial control of immobilized proteins including two different enzymes, horse radish peroxidase (HRP) and glucose oxidase (GOx). Activity of both immobilized enzymes has been confirmed in this encapsulated configuration via the reaction series between GOx and HRP.

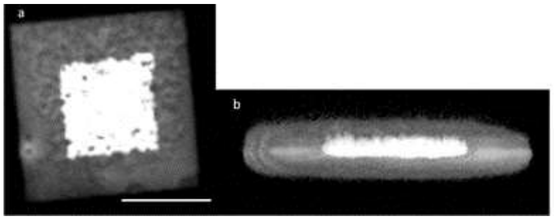

Figure 1: a) Top down view of Alkyne-PEG stained with azide functionalized AlexaFluor® 488 (white) patterned inside AO-PEG stained with maleimide functionalized coumarin (gray). b) xz through y transparency projection illustrating complete encapsulation of the alkyne-PEG core. Scale bar is 20µm.

COLL 653

Kinetics of phosphatidylserine lipid flip-flop measured by sum-frequency vibrational spectroscopy and the implications for membrane compositional asymmetry

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The plasma membrane of eukaryotic cells contains a variety of phospholipids which are not equally distributed between the cytosolic and extracellular leaflets of the membrane. For example, the location of the negatively charged phosphatidylserine (PS) headgroup

lipids has drastic effects on cell function, ranging from coagulation to apoptosis. The localization of PS in 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. Sum-frequency vibrational spectroscopy (SFVS) has been used here 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, dependence on bilayer composition, and the impact on compositional asymmetry will be discussed in detail.

COLL 654

Dynamic imaging of membrane domains through plasmon coupling microscopy

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The surface receptors on the plasma membrane of living cell are targeted with gold nanoparticles (NPs) through multivalent labeling strategy. We observe the clustering of individual particle labels on the membrane even at low bind efficiency indicative of local enrichment of receptors on specific areas (domains). We monitor the translational motions of the particle labeled domains and investigate the dynamic interactions of individual particle labels co-localized within the confinement by applying the plasmon coupling based imaging approach. The ability to characterize the relative motions of labeled receptors in the confinement on subcellular length scales with a conventional single NP imaging techniques opens up new opportunities to study the structural dynamics of living cell membrane domains as a function of time and space.

COLL 655

Molecular photovoltaic system based on solid-supported lipid structure: Photocurrent generation and modulation

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There has been a lasting research interest in mimicking natural photosynthesis using synthetic approaches and for over three decades, lipid-bilayer based structures have been employed in building such biomimetic systems. Studies of lipids based artificial photosynthetic systems have greatly advanced our understanding in photoinduced electron transfer in biological environment. Here, we present a molecular photovoltaic system based on either a phospholipid bilayer or phospholipid/alkanethiol hybrid bilayer system in aqueous media. By quantitatively controlled the amount of photoactive species such as fullerene,ruthenium tris(bipyridyl) (Ru(bpy)32+) and porphyrin in each

leaflet of the bilayer, we demonstrate both photocurrent generation and modulation in these model lipid systems.

COLL 656

Interactions between vascular endothelial cells and nanoparticles investigated by single-cell mechanics

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Inhalation of airborne nanoparticles (NPs) has been correlated with cardiopulmonary disease. To better understand the underlying mechanisms, human aortic endothelial cells (HAECs) were exposed *in vitro* to zinc oxide (ZnO) and silicon dioxide (SiO_2) NPs at various doses. By using atomic force microscopy based single-cell compression, we observed that ZnO NPs at 10 µg/ml produced stiffening of the cellular membrane and cytoskeleton. At higher ZnO NP doses, cell volume increased by up to 280%. SiO_2 NPs had a similar but milder effect. A simple balloon model based on Hertzian mechanics yielded a membrane Young's modulus (E_m) increase from 5.0 ± 2.1 MPa to 7.7 ± 1.8 MPa for ZnO NPs and to only 5.49 ± 0.75 MPa for SiO_2 NPs. The results can be rationalized by unregulated ion influx leading to increased intracellular osmotic pressure. Single-cell mechanics provides sensitive and quantitative measurements that yield insight into NP – cell interactions.

COLL 657

Integrated optical tweezers with broadband quantitative phase microscopy for high resolution characterization of lipid bilayer nanostructures

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Membrane tether formation is used in a range of biophysical investigations including plasma membrane studies and the study of membrane-cytoskeleton interactions. Tethers are lipid bilayer nano-tubes formed from membranes. Accurate characterization of tether structure is essential in applications such as measuring membrane's apparent tension and drug related modulations in membrane-cytoskeleton interaction. However, tether structure and changes in tether diameter often cannot be accurately measured by conventional microscopy. While the lateral resolution of conventional optical microscopy is diffraction limited, quantitative phase imaging techniques allow for nanometer resolution of structures along the propagation axis of illumination. In this study, we

formed membrane tethers from HEK293 cells using an optical tweezers setup. To measure tether structures, we employed spatial light interference microscopy (SLIM) as a quantitative phase imaging method employing broadband illumination. For the first time, we report simultaneous tether formation from cell membranes and measurement of tether diameters at 40 nm resolution.

COLL 658

Membrane phase behavior in lipid curvature sorting

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The curvature of the cell membrane is thought to play an important role in spatial sorting of lipids, and modulating the function of membrane-bound proteins. We investigate the effect of the curvature using a model lipid membrane containing a ternary lipid mixture of two phospholipids and cholesterol. The biomembrane is spin-coated onto a homogeneous Poly(methyl-methacrylate) support with curved array features. We systematically vary the curvature by decreasing the radius of the features from 5µm – 100nm, and the distance in between. We find that this nanofabricated support promotes a curvature controlled sorting of the lipid phases with a clearly distinct pattern formation. It is shown how the lipid phases balance the line energy over the bending energy in a percolated system and also, the curvature preference of a certain phase when changes in the geometry of the arrays are introduced. This homogeneous surface allows examination of large-scale demixing which resembles to the scale of demixing of the plasma membrane.

COLL 659

Quantitative fluorescence imaging of intermembrane ligand-receptor complexes

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Juxtacrine signaling systems require direct interaction between ligand and receptor molecules on apposing cell surfaces. Physical contact between ligand and receptor cells triggers the transduction of chemical signals. We describe the development of a method to recapitulate the cell-cell interface of a juxtacrine system. This platform is composed of: (1) fluorescently tagged ligand molecules tethered to a supported lipid bilayer and (2) receptor-eGFP expressing cells. Ligand and receptor molecules are observed in separate channels using total internal reflection fluorescence (TIRF) microscopy, where each channel is quantitated by comparing fluorescence signal with calibration standards. This method can be used to determine the stoichiometry of binding in live cells and can be widely utilized to study any juxtacrine system. This

presentation will describe how this method was specifically applied to the Notch signaling pathway.

COLL 660

Effects of membrane composition and cytoskeletal proteins on membrane mechanical properties

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Cell plasma membrane is a composite nanostructure containing mainly proteins and lipids. The interaction between membrane and the cytoskeleton is important in various cellular processes such as membrane diffusion, membrane tension, cell shape and volume regulation.

To study plasma membrane mechanics and its local interaction with underlying cytoskeleton, we pull plasma membrane nanotubes (tethers) from human embryonic kidney (HEK) cells using optical tweezers. Temporal force plots of membrane tethers are obtained and membrane mechanical properties such as stiffness, viscosity, and tension are estimated from those data. We modulate the membrane composition by modifying its cholesterol content with Cyclodextrins, and correlate the mechanical properties to the cholesterol content. To discern the effects of cytoskelatal proteins, we perform the experiments with intact and disrupted F-actin.

Our results demonstrate that membrane tether stiffness increases with cholesterol depletion, while tether viscosity increases in response to cholesterol enrichment. Our data also suggest a weakened membrane-cytoskeleton adhesion upon cholesterol enrichment. Using a Maxwell body to model the tether formation process, we show that membrane cholesterol modulation is also associated with changes in the local stiffness and viscosity of a composite plasma membrane-cytoskeleton system. Disruption of F-actin affects the tether formation process, decreases the membrane-cytoskeleton adhesion, and is associated with changes in local cell stiffness and viscosity. In summary, our studies show that changes in membrane composition not only influence membrane nanomechanics, but also affect membrane-cytoskeleton adhesion and local mechanics of the composite membrane-cytoskeleton nanostructure.

COLL 661

Degradable poly(diol citrate) elastomers with tethered quaternary ammonium biocides

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The development of novel biodegradable elastomers has not only facilitated the emergence of unique medical therapies, but has also addressed concerns regarding the persistence of plastics in the environment. Unfortunately, many of these materials are prone to bacterial colonization due to the fact that their degradation products are potential nutrient sources for microbial organisms. As such, the development of degradable elastomers that possess adequate antibacterial properties is a crucial aspect for the implementation of absorbable materials in numerous applications such as packaging materials for food and medical products and use as medical implants. We report the development and evaluation of novel poly(diol citrate) elastomers with tethered quaternary ammonium biocides. The influence of elastomer structure on resulting mechanical, degradation, and biocidal properties are evaluated and discussed with respect to potential applications.

COLL 662

Influence of quaternary ammonium biocides on electrospun polymer microfiber surfaces

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Novel quaternary ammonium biocides have recently been developed that effectively surface segregate in polymeric coatings of various surface energies, maximizing antimicrobial activity. Furthermore, the electrospinning of polymers results in fibers with diameters on the scale of nanometers to microns with extremely high surface area to volume ratios. Herein, quaternary ammonium biocides were incorporated into polymer solutions and electrospun into microfibers. The combination of surface segregating biocides with high surface area to volume polymers holds potential to result in a material exhibiting enhanced biocidal behavior. Polymers investigated included poly(carbonate), poly(cellulose acetate), and Nylon 6,6. Optimization of electrospinning parameters was required for each polymer to achieve desired fiber diameter and dispersion. The effects of different concentrations of quaternary ammonium additives and multiple polymer formulations on fiber morphology were investigated by SEM. Additionally, antimicrobial activity against both gram positive and gram negative bacteria are reported.

COLL 663

Super-hydrophobic/hydrophilic switching of photocatalytic titanium dioxide coatings

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Certain forms of photoactive titanium dioxide (TiO_2) can create highly washable surfaces. The light-induced conversion of relatively hydrophobic to hydrophilic surfaces, especially in the case of TiO_2, has been attributed to an increase in surface hydroxyl groups generated during the photochemical conversion processes. A coated surface is considered wetted if a liquid spreads evenly over the surface without the formation of droplets. As the photocatalyst surface becomes more hydrophilic, water contact angles will decrease. Coating wettability can be influenced by environmental conditions, such as heat, light intensity and wavelength distribution, and relative humidity. The hydrophobic/hydrophilic switching of several commercially available and custom photocatalytic thin films were investigated by measuring the water contact angles as a function of UV irradiation time and wavelength. The experimental conditions required to achieve the superhydrophilic state for each photocatalytic coating material and the persistence of this state in the absence of light is discussed.

COLL 664

Antimicrobial Poly-N-vinyl carbazole-graphene oxide (PVK-GO) polymer nanocomposite coating on conducting substrate

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The effective dispersion of GO using a poly-N-vinyl carbazole (PVK) as dispersant was demonstrated. The use of a well dispersed PVK-GO solution resulted in the large scale fabrication of an antimicrobial PVK-GO coating on a conducting substrate via electrodeposition. The resulting film was 90 % more effective in preventing *Escherichia coli* colonization relative to the unmodified surface.

COLL 665

Antimicrobial surfaces derived by surface-grafted biocidal groups: Designs and mechanisms

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A great challenge of modern humankind is the prevention of the spread of diseases, for example the various dangerous influenza types or the most recent EHEC outbreak in Europe. Since many diseases are spread via surfaces, the development of materials that do not allow microbes to survive or at least to proliferate is in focus of material research ever since. Modifications that kill microbes on contact or render themselves antimicrobial in case of a microbial infection only are the most advanced systems. Here, designs that lead to contact-active antimicrobial surfaces by surface grafted antimicrobial polymers and biocidal groups will be presented with particular focus on self-organizing systems. Further, we suggest possible microbe-killing mechanisms of such materials based on surfaces with grafted antimicrobial polymers, such as poly(4-vinyl-*N*-methylpyridinium iodide), antimicrobial quarternary ammonium functions on inert polymeric spacers, and surfaces directly modified with such groups.

COLL 666

Antimicrobial materials for coatings and latex paints

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A novel acrylamide monomer has been prepared and copolymerized with other monomers to produce copolymers which could be rendered antimicrobial upon exposure to dilute household bleach (sodium hypochlorite). The antimicrobial copolymers included siloxanes and epoxides which could be covalently attached to surfaces containing hydroxyl groups such as cellulose and sulfonates which were water soluble and could be added to latex paints. Data will be presented showing that the copolymers exhibited excellent antimicrobial efficacies and stabilities toward hydrolyses and photodegradation. The antimicrobial copolymers show potential for use in a variety of medical applications, including surgical gowns, bed sheets, gauze bandages, and wall and floor coatings.

COLL 667

Controlling bacterial and fungal biofilms with rechargeable antimicrobial biomaterials

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Conventional biomaterials are susceptible to microbial adhesion and biofilm-formation, causing serious problems including device-related infections and hospital-acquired infections. In response to these challenges, we have developed a range of novel rechargeable antimicrobial biomaterials. The new biomaterials act as “rechargeable batteries” that bind and then slowly release various antimicrobial agents to prevent microbial colonization and biofilm formation. Extended use consumes antimicrobials and reduces biofilm-controlling activities. However, the consumed antimicrobials can be repeatedly recharged to extend antimicrobial duration for long-term use. In recharging, antimicrobials can be changed/rotated to enhance antimicrobial potency and reduce the risk of microbial resistance. At the time when the infections are cleared, the remaining antimicrobial agents in the biomaterials can be “quenched” to stop the therapy when no further drug release is need. If needed, the biomaterials can be recharged with the same or charged antimicrobial agents again to re-initiate antimicrobial release.

COLL 668

WITHDRAWN

COLL 669

Physicochemical and structural characterization of liposome-gold nanorod hybrids

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We report on the physicochemical and structural characterization of previously unreported liposome-gold nanorod (AuNR) hybrids as a promising strategy for the engineering of systems for combinatory detection, therapy and monitoring of disease. The hybrids were formed using fluorescently labelled cationic liposomes following the lipid film hydration method and sonication. AuNRs of three different lengths were allowed to self assemble with naked and PEGylated cationic liposomes. Higher colloidal stability of the liposome-AuNR hybrids was observed using particle size measurements, transmission electron microscopy (TEM) and atomic force microscopy (AFM). The incorporation of the different AuNRs in the cationic liposomes leads to enhanced absorbance intensity of the AuNRs. In order to elucidate the interaction between AuNRs and liposomes, size exclusion chromatography-based hybrid purification was performed. We also report the construction of PEGylated anionic liposome-AuNR hybrids, corroborating that the primary driving force for the acssociation between lipid bilayers and AuNRs are hydrophobic and molecular rather than electrostatic interactions.

COLL 670

Protein microspheres as suitable devices for piroxicam release

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Piroxicam is a non-steroidal anti-inflammatory drug (NSAID) and is commonly employed in the treatment of inflammatory diseases. The use of this NSAID can lead to several adverse effects, thus increasing the need of appropriate devices to reduce such undesired effects.

In this work, bovine serum albumin-piroxicam (BSA-piroxicam) and human serum albumin-piroxicam (HSA-piroxicam)-piroxicam microspheres were sonochemically prepared and characterized. The results demonstrated that the use of stabilizers led to an improvement of formulation characteristics, including smaller size, lower polydispersity index, higher entrapment efficiency and higher stability. The release kinetics of these microspheres was determined in presence of protease, indicating an anomalous drug transport mechanism (diffusion and protein degradation). These proteinaceous devices did not show cytotoxicity against human skin fibroblasts *in vitro*, for range concentrations below to 300 mg.L^{-1}, greatly supporting their potential application in the treatment of inflammatory diseases.

COLL 671

Liposomal formulations for specific drug delivery

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Liposomes have received considerable scrutiny as possible vehicles for drug delivery due to properties such as sustained release, increased drug stability, ability to overcome drug resistance and targeting of specific tissues.

In this study, we have produced several liposomal formulations prepared by thin film hydration method. The different formulations were extensively characterized and preliminary tests were performed to evaluate their potential as specific drug delivery systems. The liposomes present very small values of size and polydispersity index, as well as lower cytotoxicity, which are compatible with intended *in vivo* applications. The incorporation of imaging and targeting agents in the liposomes was performed, what improved selectivity to the system, being the liposomes specifically internalized in target cells. The encapsulation of drugs was also performed and their effect analysed in the target cells. In summary, the liposomal formulations obtained exhibit suitable characteristics to be used *in vivo* as specific drug delivery systems.

COLL 672

Controlled drug release from magneto-liposomes by pulsed magnetic fields

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Since the first synthesis of liposomes, liposomes have been seen as an efficient way to deliver drugs to a specific location in the body. Most drug delivery methods that rely upon liposomes are dependent upon the slow release of the drugs as the liposomes decay over time. While this type of delivery method is adequate for some situations, others require that the drugs be released all at once. In this research a new way for quick delivery was investigated involving magnetic nanoparticles as a “switch” to open up the liposomes on demand. The method used in this study depended upon the superparamagnetic properties of magnetic nanoparticles. Liposomes were made with the magnetic nanoparticles in their interior and then subjected to alternating magnetic fields which caused the magnetic nanoparticles to align with the field of the pulsed magnet. The efficiency of the interior nanoparticles to break the liposomes was tested by the release of fluorescent carboxyfluorescein dye. Several different types of nanoparticles were tested, but it was found that the most effective nanoparticles at breaking open the liposomes were cobalt and gold coated cobalt. While it was shown that the basic idea behind this method was an effective means for quick delivery, the experimental parameters need further adjustment to improve the amount of content released. One of the next steps to be taken will be to attach these nanoparticles in the phospholipid bilayer rather than include them in the interior of the liposomes.

COLL 673

Novel non phospholipid liposomes with high sterol content: Development and characterization

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We show that systems composed of a monoalkylated amphiphile and a sterol can form a stable liquid-ordered lamellar phase that could be extruded to form Large Unilamellar Vesicles (LUVs). The passive permeability of these LUVs was drastically limited due to the high sterol content. Specific molecular requirements must be respected to successfully form these non phospholipid liposomes. At the hydrophobic core level, the sterol chain at position C17 should not be bulky to ensure the proper tight chain packing. At the interface level, the hydration of the bilayer is essential for the liposome stability. Octadecyl methyl sulfoxide can form, with high content of cholesterol, LUVs that are stable at room temperature. This formulation, exclusively composed of neutral molecules, likely exists because of the strong H-bond capability of the sulfoxide group. These novel formulations display a great potential for applications in many areas such as drug delivery.

COLL 674

Designed a novel siRNA delivery system using the monodisperse mesoporous silica nanoparticles as nanovehicle

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In this contribution, we designed a novel siRNA delivery system combined the advantages of mesoporous silica nanoparticles (MSNs) and the RNA interference technology. The siRNA, to interference survivin gene overexpressed in numerous tumor types, was loaded into the channel of amino-modified MSNs where the siRNA can be free from enzymatic degradation, maximal adsorption capacity up to 125 μg/ml. The synthesized spherical particles with excellent monodisperse characteristic facilitated drug uptake with the optimal particles size of ca. 120 nm. The results of cellular experiments presented that the vectors with high concentration siRNA could be internalized by more than 95% Hela or HepG2 cells. MTT assay results indicated that there is little cytotoxicity by the presence of MSNs for loadings of up to 200 μg/ml. After MSNs were surface-functionalized with transferin and folic acid as cell penetrating agent, the efficiency of internalization and apoptosis of tumor cells was further improved.

COLL 675

Synthetic hollow enzyme loaded porous nanoShells (SHELS) for enzyme based therapies

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A novel therapeutic approach for enzyme based therapies that we refer to as SHELS can shield immunogenic enzymes by internally encapsulating them from immune system and other forms of degradation while maintaining the enzymes active close to ideal levels. SHELS have pores on the surface that allows enzyme substrates to easily diffuse in and products to diffuse out but prevents the larger enzymes to leak out preventing antibodies and other enzymes like proteases to penetrate and destroy the protected enzymes. SHELS surface can also be functionalized for targeting and improving circulation half-life eliminating any modification on the enzyme. Since SHELS are nanoshells, very small amount of inorganic mass is involved maximizing *in vivo* loading capacity. SHELS platform enables a variety of therapeutic approaches such as direct enzymatic depletion of tumor cell nutrients, enzymatic conversion of pro-drug to drug, and enzyme replacement therapy in addition to *in vivo* bio-sensing applications.

COLL 676

Synthesis, characterization, and in vitro toxicity of paramagnetic Au nanorods

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Coated Au nanorods are widely known for their absorption in the near infrared[1], making them excellent candidates for near infrared imaging and photo thermal therapy[2]. Furthermore, recent studies have shown that these nanomaterials are excellent candidates for Magnetic Resonance Imaging (MRI) since they can be used as T_1 contrast agents when functionalized with Gd^{3+}-containing moieties and as multimodal agents for MR-CT[3] and MR-plasmonic[4] imaging. In this context, our aim is to explore the possible incorporation of Gd^{3+} complexes to these nanosystems in order to use them as T_1 contrast agents for MRI and, in a more advanced stage, as multimodal imaging agents. Here we describe the synthesis, characterization, properties and *in vitro* toxicity of paramagnetic nanorods coated, in one step, with combinations of thiol functionalized Gd^{3+} complexes of a 1,4,7,10-tetraazacyclododecane-1,4,7-tris(acetic acid) (DO3A)-based ligand and polyethylene glycol (PEG). Preliminary results show that these paramagnetic Au nanorods are biocompatible, show T_1 contrast at low Gd^{3+} concentrations and are envisioned to become excellent candidates for multimodal purposes.

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COLL 677

Synthesis of novel platinum-based nanostructures for combinatorial drug delivery

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We report the synthesis of a phospholipid-like platinum derivative and its self-assembling into liposome-like nanostructure, named Ptsome as a novel delivery system for Pt(II)-based therapeutics. Utilizing coordination chemistry, an amphiphilic cis-Pt (II) chloride, *bis(2-stearoylhydrazinyl) platinum(II) chloride* (BSPC), is synthesized. Thus formed BSPC compound can spontaneously self-assemble into Ptsomes through a typical preparation procedure of phospholipid liposomes. The resulting Ptsomes demonstrate similar physicochemical characteristics of liposomes, including size, size distribution, morphology, and fusion activities. Cellular cytotoxicity studies show that the Ptsomes are equivalent to cisplatin in terms of effectively killing cancer cells. In addition to the formation of Ptsomes, the BSPC can also self-assemble as a monolayer shell on the surface of polymeric nanoparticles to form lipid-polymer hybrid nanoparticle, which are capable for combinatorial drug delivery. We expect that these novel Pt(II)-based nanostructures open up new opportunities in the delivery of cisplatin analogues alone or in combination with other cancer chemotherapeutics. Moreover, the concept of the synthesis and use of Ptsomes and hybrid nanoparticle system can be generalized to other types of metal ions for preparing a variety of nanostructures for different purposes.

COLL 678

How to make a half-metallic molecular wire on silicon surface?

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Based a series DFT calculations including the molecular dynamic simulation, at first time, we describe a feasible reaction path to make a robust ferromagnetic half metallic Mo-borine sandwich molecular wire on hydrogen-terminated silicon (001) surface along [100] direction. The wire is chemically bonded to the surface, therefore, it is solid enough against thermo-perturbation, meanwhile, it appears *independent* from the silicon substrate since both electrical or magnetic properties are mainly ascribed to d electrons of transition metal atoms even under an external electric field. More importantly, this surface wire exhibits multifunctional electronic and magnetic states, which allows it to work as a multistep electrical switch and multistep information storage component. These features should be meaningful in molecular electronics/spintronics, and surface science.

COLL 679

Molecular mechanisms of selective ion trapping by "striped" nanoparticles: A molecular dynamics Simulation Study

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Recent experiments have discovered that nanoparticles functionalized with alternating stripes of hexane thiols (HT) and hexane thiols terminated with ethylene glycol units (EG_n) are able to trap ions with distinct selectivity. We investigated this interesting phenomenon using molecular dynamics (MD) simulations. Our study revealed that the trapping of ions occurs at the edges of the EG_n stripes with the ethylene glycol units bending over the neighboring HT molecules and encasing/wrapping around the ions. We found that the efficiency of this trapping mechanism is highly ion-specific, and the ion selectivity is significantly affected by the sizes of the EG_n and HT stripes.

COLL 680

Soft condensed matter: A view through the density window

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Density concept has been used in the form of single particle electron density in the microscopic length scale and single particle number density in the intermediate mesoscopic length scale to obtain an appropriate picture of the equilibrium and dynamical processes in chemistry and physics. A wide class of problems involving nanomaterials, interfacial science and soft condensed matter has been addressed using the density based theoretical formalism as well as atomistic simulation in the mesoscopic regime. The basic ideas underlying the versatile uses of the concept of density in the modeling of molecules and materials, as visualized in various length scales, along with selected illustrative applications to some recent areas of research on soft matter under confinement, and chemical reactions in condensed phase, will be presented.

COLL 681

Computer simulation study of self organized nanopore formation in oxide layers on anodized metal surface

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Self organized arrays of hexagonally arranged nanopores can form readily in oxide layers on anodized metal surfaces. The origin of this phenomenon has not found a satisfactory explanation. In the present work we seek a minimal model of the cellular automata type that could account for the occurence of this phenomenon and its dependence on the experimental conditions. The main ingredients of our model are; a Laplacian field that represents an instable surface growth of the electrostatic type and surface smoothing jointly due tu interfacial tension and dissolution equilibrium at the layer surface. Our results show nanopore formation similar to certain experimental findings, However it is not as perfect as in some other experimental systems. Clearly the problem is a statistical noise introduced by our stochastic approach. We are working at present on an improved model that would reduce the noise level in the observed simulation results.

COLL 682

Nanoparticle dispersions: Experiments, mechanism, modeling

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Individual (primary) nanoparticle diameter, charge and morphology of an ensemble of these nanoparticles - either in an isolated or an aggregated form - are key parameters dictating colloidal stability and shelf-life of aqueous particulate dispersions. Our time-scale based nanoparticle formation mechanism models primary particle diameter, and interparticle potential-driven Monte Carlo simulation predicts their equilibrium state of aggregation and dispersion stability. This in conjunction with a model of cell-particle interaction explains experimental data on coated magnetite nanoparticle uptake by HepG2 cells, correctly predicting contrasting behavior of different coating agents on extent of uptake. The validated model is useful in designing synthesis conditions to achieve controlled size, shape and aggregation of primary nanoparticles, aimed towards maximum uptake of solid particles, or extending further, in elucidating diffusion and accessibility issues of guest molecules in porous nanoparticles. These aspects will be illustrated by data from our experiments on both magnetite and mesoporous silica nanoparticles.

COLL 683

Analytic theory of polymer-mediated interactions between nano-colloids in polymer melts and solutions.

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We theoretically investigate several important cases of the polymer mediated interaction between spherical colloids immersed in polymer melts and semi-dilute solutions. In the first case study, we discuss the calculation of the polymer-mediated interaction potential acting between nano-particle colloids with the many-body effects taken into account. In addition, we study the potential of the polymer-mediated interaction between nano-colloids in the presence of hard walls, which allows us to thoroughly investigate the effect of confinement on the depletion interactions. In a separate case study, we investigate the polymer mediated interaction between colloids that bear irreversibly adsorbed polymer layers. As a final stage of the reported work, we perform thorough comparison of the presented theoretical findings with the available experimental data and simulations.

COLL 684

Theory of nanocrystal size-focusing and how surfactants inhibit/enhance the effect

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We present a full analytical theory of nanocrystal "size focusing", a phenomenon in which injections of precursors at various quantities can generate monodisperse nanocrystals in solution. Nanocrystal applications in bio-imaging, sensors, and solar power all have stringent requirements on the size and polydispersity of the product nanocrystals. This investigation provides mathematical insight into how best to control the nanocrystal size distribution in a synthesis experiment. The primary results of the theory are (a) that size focusing is controlled explicitly by the rate of reaction of the precursor-to-monomer conversion, (b) that exquisite control of the size and polydispersity requires that the nucleation of nanocrystals must be separated (decoupled) from the growth process, and (c) that the presence of surfactants on the nanocrystals' surfaces will affect (i.e. either inhibit or even enhance) the maximum possible degree of size focusing. The resultant theory describes others' experimental results with qualitatively accuracy, but the real novelty of our analysis is that we recommend and inspire new methods for the synthesis of size-controlled nanocrystals, which have as yet remained unexplored. The predictions of the theory offer new avenues for experimental studies that can optimize and even help *a priori* to design new producesures for the production of monodisperse nanocrystals in solution.

COLL 685

Bending of layered silicates on the nanometer scale: Mechanism, stored energy, and curvature limits

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Bending and failure of aluminosilicate layers are common in polymer matrices although mechanical properties of curved layers and curvature limits are hardly known. We examined the mechanism of bending, the stored energy, and failure of several clay minerals. We employed molecular dynamics simulation, AFM data, and transmission electron microscopy (TEM) of montmorillonite embedded in epoxy and silk elastin polymer matrices with different weight percentage and different processing conditions. The bending energy per layer area as a function of bending radius can be converted into force constants for a given layer geometry and is similar for minerals of different cation exchange capacity (pyrophyllite, montmorillonite, mica). The bending energy increases from zero for a flat single layer to ~10 mJ/m2 at a bending radius of 20 nm and exceeds 100 mJ/m2 at a bending radius of 6 nm. The smallest observed curvature of a bent layer is 3 nm. Failure proceeds through kink and split into two straight layers of shorter length. The mechanically stored energy per unit mass in highly bent aluminosilicate layers is close to the electrical energy stored in batteries.

COLL 686

Chemical and electrical passivation of silicon surfaces through hydrosilylation and chlorination reactions

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Hydrogen-passivated Si(111) surfaces are produced through two different preparation methods: modified RCA and HF treatment. The two types of surfaces have been examined by infrared spectroscopy (IR) X-ray photoelectron spectroscopy (XPS) and charge-carrier lifetime measurements, and display different chemical and electrical properties. The HF treatment yields long charge-carrier lifetime and low surface recombination velocity, but atomically rough surface. The modified RCA method produced chemically well defined mono-hydride silicon surface with relatively poor electrical properties. The two types of surfaces produced were further subjected to modification with chlorine (PCl_5) and alkene monolayers (C_{11} and C_{18}). The chemical and electrical properties, surface structure, and chemical reactivity of the surfaces have been investigated by X-ray photoelectron spectroscopy, IR, and atomic force microscopy. The procedures for surface preparations and modifications will be discussed.

COLL 687

Micromolding surface-initiated polymerization: Coatings that replicate nature's superhydrophobic surfaces

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This presentation will introduce the use of a confined surface-initiated ring-opening metathesis polymerization (SI-ROMP) of perfluoroalkyl norbornene monomers from solid substrates to synthesize surface-bound polymer structures with tunable physical and chemical properties that accurately replicate those exhibited by Nature's engineered, microscopically rough, and highly functional surfaces. This approach not only allows replication of highly evolved and functional surface architectures but also provides versatility beyond Nature in that it introduces a wide variety of chemical compositions available in materials chemistry, including partially fluorinated polymers with ultralow critical surface tensions. Optical microscopy and scanning electron microscopy confirm growth of the polymer structures and the precise reproducibility of the microscale features exhibited by the target surface with the added freedom to expand beyond Nature's chemical building blocks. Advancing contact angle measurements show that the surface coatings exhibit superhydrophobicity and oleophobicity.

COLL 688

Autonomous nanomotor based on copper-platinum segmented nanobattery

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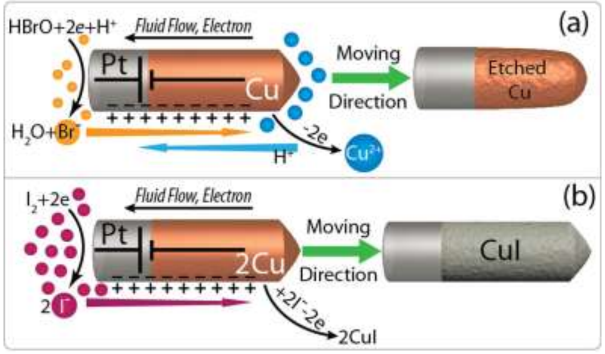
We describe an efficient, bubble-free nanoscale motor consisting of a copper-platinum (CuPt) segmented rod that operates as a nanobattery in dilute aqueous Br_2 or I_2 solutions. The motion of the rod is powered by self-electrophoresis caused by redox reactions occurring on the two different metal segments . Asymmetric ratchet-shaped pure copper nanorods were also found to rotate and tumble in aqueous Br_2 solution because of the ion gradient arising from asymmetric dissolution of copper.



COLL 689

Optical line shapes for polymethine dyes and their aggregates: Dozy-chaos theory of quantum transitions and its correlation with experiment

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Though theoretical treatment of the optical line shapes for polymethine dyes and their aggregates has been a top problem in chemistry and physics for many decades, it has not been solved conclusively to date. The author proposes a novel theory of quantum transitions on the basis of dozy chaos (see [1] and refs there) that gives insight into the nature of the optical line shapes for polymethine dyes, their dimers, H-, H*-, and J-aggregates. This theory formulates a proper definition of electron-nuclear coupling in the dynamics of the transient state, which is of paramount importance for quantum transitions in such organic systems due to their largeness. Dozy chaos is a mix of chaotic motions of the electronic charge, nuclear reorganization and electromagnetic field in the transient state. By dozy chaos the light electrons succeed in controlling the motion of extremely heavy nuclei in the transient state, making it chaotic. Dozy chaos is absent in the initial and final states, and arises in the transient state alone. Formerly in terms of the dozy-chaos theory the author clarified the nature of optical line shapes for dye monomers and J-aggregates. Now this theory is developed to involve exciton effects that are important in dimers and H-aggregates. Some of the results are in theoretical absorption line shapes fitted by the author to the basic experimental data on dye monomers, dimers, H-, H*-, and J-aggregates and also theoretical line shapes fitted to the well-known data on the monomer–dimer and monomer–J-aggregate concentration equilibriums.

[1] V.V. Egorov, J. Lumin. 131 (2011) 543.

COLL 690

Harnessing colloidal aggregation for anti-reflection coatings

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We present a controlled colloidal aggregation technique for tuning the properties of spin-processed anti-reflection coatings. In comparison to layer-by-layer methods, our technique yields a convenient one-step processing alternative for flat and moderately curved surfaces whereby both the coating thickness and refractive index can be tuned to the desired specifications. From the perspective of colloidal chemistry, this technique also offers a unique method of tracking aggregation kinetics via thickness measurements of the deposited coatings.

COLL 691

Wrinkle-assisted linear assembly of plasmonic-core/soft-shell particles: A lithography-free approach towards anisotropic nanostructures

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This contribution addresses wrinkle assisted assembly [1] of silver-poly-(N-isopropylacrylamide) core-shell particles. Anisotropic alignment is found on two length scales, macroscopically guided through the wrinkle structure and locally due to deformation of the polymer shell leading to smaller inter-core separations as compared to assembly on flat substrates without confinement. The structures were analysed by means of scanning electron microscopy. Radial distribution functions are shown, clearly highlighting the impact of confinement on nearest neighbour distances and symmetry. The observed ordering is directly compared to Monte-Carlo simulations for hard-core/soft-shell particles, showing that the observed symmetries are a consequence of the soft interaction potential and differ qualitatively from a hard-sphere situation. As a first evidence for the impact of the alignment on optical properties[2], we show UV-vis absorbance measurements revealing optical anisotropy of the generated structures due to plasmon coupling. Furthermore, the high degree of order of the assembled structures on macroscopic areas is demonstrated by laser diffraction effects.

[1] A. Schweikart, A. Fortini, A. Wittemann, M. Schmidt and A. Fery,
Soft Matter, 2010, 6, 5860-5863.

[2] N. Pazos-Perez, W. Ni, A. Schweikart, R. A. Alvarez-Puebla, A. Fery
and L. M. Liz-Marzan, Chemical Science, 2010, 1, 174-178.

COLL 692

Assembling magnetite nanoparticles to fixed photonic nanochains

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One dimensional photonic nanochains, which may be one of the smallest photonic structures, has been fabricated by a magnetic-field-assisted assembly process and a further sol-gel coating method. They have periodically arrangements of magnetite nanoparticles along their long axis and are able to strongly diffract the normally incident light. The length of chains, the spacing between magnetite nanoparticles within chains are all tunable during the fabrication but are totally fixed afterwards. Due to the magnetic cores imbedded inside them, the orientation of these nanochains can be easily manipulated by an external magnetic field. Distinct “On” and “Off” states can be established for their photonic properties. When they are aligned parallel to the viewing direction, their structural color can be observed; otherwise people can only see the native brownish color of magnetite. Their further applications as photonic inks have been demonstrated. Photonic inks based on these nanochains can be driven by magnetic stimuli and are able to show bistability, keeping their photonic properties even after the removal of magnetic fields.

COLL 693

Nanoparticle superlattice engineering with DNA

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Many researchers are interested in rationally assembling nanoparticle building blocks into periodic lattices, as such structures could, in principle, be used to create designer materials for multiple applications. In this work, we present a set of six rules to use DNA as a programmable linker to deliberately stabilize nine distinct colloidal crystal structures, with lattice parameters that are tailorable over the 25-150 nm size regime. This assembly method affords simultaneous and independent control over nanoparticle structure, crystallographic symmetry, and lattice parameters with nanometer scale precision. Additionally, we have developed a phase diagram that predicts the design parameters necessary to achieve a lattice with a given symmetry and lattice parameters *a priori*. The rules developed in this work present a major advance towards true materials by design, as they effectively separate the identity of a nanoparticle core (and thereby its physical properties) from the variables that control its assembly.

COLL 694

Self-assembly of Clathrin protein nanostructures

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Clathrin is a ~630 kDa protein that resembles a three-legged pinwheel, with each leg having a height of ~50 nm. Inside cells, clathrin self-assembles with the help of adaptor proteins to form cage-like structures that facilitate the encapsulation of extracellular material by the cell membrane and transportation into the cell cytoplasm. In vitro, clathrin can self-assemble without the need for lipid membranes or adaptor proteins to form a variety of three-dimensional shapes like tetrahedra, cubes, and spheres as well as two-dimensional sheets. The underlying mechanisms that enable clathrin to self-assemble into such a diversity of nanostructures is not well understood. Here we utilize Cryo Transmission Electron Microscopy (cryo-TEM) and Dynamic Light Scattering (DLS) to explore the influence of pH and ionic concentration on clathrin self-assembly and to discover potential new nanostructures that clathrin may be able to form.

Our results demonstrate that clathrin has different assembly properties in 100 mM MES at pH 5 versus pH 6. Within 30 minutes of inducing self assembly, large fused aggregates ~200-600 nm were found at pH 5; in contrast, in pH 6, spherical cages of diameter ~60-100 nm were observed under cryo-TEM. Interestingly, upon aging for 4 days at room temperature, the large aggregates initially observed at pH 5 remodeled to form 60-100 nm cages, while the sample assembled at pH 6 remained unchanged. This corroborates DLS data that indicate clathrin self-assembly is a function of both pH and time. The stability of clathrin cages at pH 6 and transformation/evolution of cages at pH 5 lend new insight into the role of kosmotropic and chaotropic ionic interactions in mediating protein self-assembly via electrostatic interactions. Current efforts are underway to construct a phase diagram of clathrin nanostructures and to compare our experimental results with computational predictions.

COLL 695

Directional assembly interactions in oligonucleotide-modified anisotropic gold nanostructures

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While spherical colloidal nanostructures are attractive candidates for understanding nanoscale self-organization phenomena, they often lack directional interactions analogous to those found in atomic systems due to their high symmetry. The introduction of nanoparticle shape anisotropy in colloidal crystallization assembly techniques provides the opportunity to impart directional interactions between structures by causing some orientational modes of association to be more favorable than others. Non-spherical gold nanostructures functionalized with a dense layer of duplexed oligonucleotide ligands that facilitate interparticle interactions are capable of such directional interparticle “bonds” through commensurate overlap of their flat, faceted surfaces. This preference for face-to-face orientation of neighboring nanostructures facilitates the assembly of nanoparticle superlattices whole symmetry and dimensionality depend on the shape of the nanoparticle building blocks used in their construction. Finally, some of the unique nanoparticle crystals synthesized by this methodology are shown to exhibit novel plasmonic optical properties that arise only in the ordered state.

COLL 696

Novel non-close-packed structures assembled by spherical colloids under electric field

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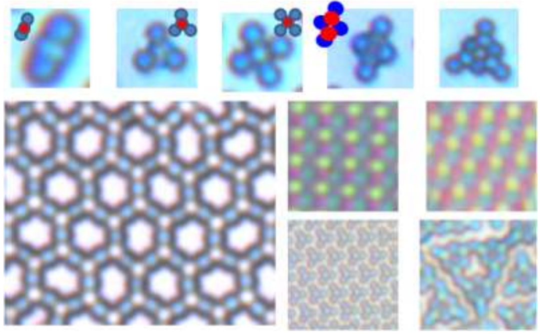
Spherical colloids with isotropic properties have been used as building blocks to assemble a variety of 2D and 3D structures in past, such as FCC, HCP, and BCT crystals. We recently, however, have observed new type of sphere-packing under the influence of electric field at the liquid-solid interface. At low concentration and low frequency of the electric field, the isotropic spheres can form a series of colloidal clusters. The plot of cluster distribution shows non-trivial peaks for trimer, tetramer, hexamer, and nanomer. At high concentration, the colloidal clusters will further assemble and connect themselves into a good variety of two-dimensional non-close-packed networks. By precisely controlling the electric field strength, frequency, volume fraction of colloids, and ionic strength, we have made diversified non-close-packed structures that have potential applications in photonic crystal, catalysis, or filtration.



COLL 697

Experimental and molecular dynamics studies of self-assembly of plasmonic nanoparticles with wormlike micelles

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Cationic surfactants such as cetyl-trimethylammonium bromide (CTAB) have the ability to self assemble with nanoparticles (NPs) to form a corona or a double-layered vesicular structure. These structures, upon further interaction with wormlike micelle (WLM) fragments, are hypothesized to form NP-micelle elastic networks. In this work, we show that self-assembly of metal NPs with WLMs in solution is a robust route for producing stable multicomponent plasmonic nanogels with remarkable color uniformity and tunable optical properties by varying size, shape and/or composition of the NPs [T. Cong *et al*., Applied Physics Letters, 99, 043112 (2011)]. The structure of the plasmonic nanogels was studied by small angle X-ray scattering and rheological experiments. Molecular Dynamics simulations suggest that vesicular NP-surfactant structures can form stable bridges with cylindrical micelles through two mechanisms, namely, end-cap opening and lateral attachment. The applications of the plasmonic nanogels to optofluidics and light trapping in photovoltaics will be discussed.

COLL 698

Thermoresponsive assembly and disassembly of charged gold nanoparticles

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Charged gold nanoparticles can be assembled into aggregated structures at low temperature, and disassembled at high temperature with addition of salt in agarose hydrogel. The reversibility and stability of the system are studied by temperature controllable UV-vis absorption spectroscopy based on the different plasmonic profiles during the transition between assembly and disassembly processes. A semi-quantitative theoretical model has been proposed based on both thermodynamic and kinetic considerations. The role of salt concentration and gold nanoparticle concentration are also investigated which qualitatively agree with the theoretic model. The effect of agarose was also studied and can be concluded that it can enhance the stability of the system at high salt concentration.

COLL 699

Click chemistry for colloidal assembly

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Previously having studied DNA ligation and hybridization as an assisting agent for directed colloidal assembly[1]; this study looks at the viability of Cu(I)-catalyzed azide alkyne cycloaddition (CuAAC) as an assisting agent. Select surface functionalizations were used to prepare alkyne functionalized glass substrates, and two distinct surface functionalizations were utilized for obtaining azide functionalized polystyrene and silica colloidal particles. Colloidal assembly was studied using sedimentation and vertical deposition methods. Sedimentation showed that CuAAC can be incorporated into a colloidal assembly process. Colloidal monolayer was obtained using vertical deposition, after unanchored layers of the colloidal crystal above the monolayer were washed off. A layer-by-layer process is proposed for fabricating chemically active colloidal crystals and structures, that are not readily made using conventional methods.

[1] M. Shyr, D. Wernette, P. Wiltzius, Y. Lu, P. V. Braun, Journal of the American Chemical Society, 130, 8234-8240 (2008).

COLL 700

Binary colloidal crystals: Directed-assembly using external magnetic fields

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Assembly of colloidal building blocks into complicated structures is of fundamental and technological importance for their applications in photonics and devices. External fields are also frequently used for directing colloids not only for studying the equilibrium behavior but also for drug delivery and cancer therapy. Here we employ precisely controlled, to a micrometer scale, external magnetic fields to direct assembly of binary colloidal systems into colloidal crystals or into interesting core-shell assemblies. It is known that non-magnetic particles dispersed in a ferrofluid can be directed by magnetic field gradients since the pioneering work of Skjeltrop (*Phys. Rev. Lett.* **51** , 2306, **1983**). Recently this principle was employed to assemble multipolar colloids and 2D crystals of colloids. We use magnetophoretic forces (magnetic forces in a field gradient) to specifically direct magnetic and non-magnetic particles into specific spots, which may find applications in photonics and devices due to functionality brought by the binary nature of the system.

COLL 701

Interfacial chemistry in graphene

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Graphene, graphene nanoribbons, and carbon nanotubes show remarkable promise for next generation electronic device applications. However, due to their higher susceptibility in responding to chemical interactions with the environment [1], understanding the interfacial characteristics is crucial for device applications. In this work, the energetics and chemical or electronic characteristics of graphene with SiO_2 and H_2O are studied using density functional theory calculations. A significant difference between interaction energies of H_2O with graphene-with-grain-boundary and H_2O with graphene-without-grain-boundary is obtained. Furthermore, in SiO_2, it is found that the energetic preference for a graphene layer to bind on specific sites on the O-terminated surface differs substantially from that on the Si-terminated surface. A density of states analysis shows that a semiconducting graphene nanoribbon deposited on SiO_2, either amorphous or crystalline, the bandgap remains unaltered by the chemical activity at the interface. [1] M. Z. Hossain, APL (2009); APL (2010); APL (2009); APL (2010).

COLL 702

Liquid adsorption behavior and surface properties of single- and multiwall carbon nanotubes

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The liquid adsorption behavior and surface properties, e.g. surface free energy and acid-base properties, of carbon nanotubes with single wall (SWCNTs) and multiwall (MWCNTs), were studied by capillary rise method. A comparison of the adsorption of water, formamide, diiodomethane and hexane showed these two types of CNTs both adsorbed the greatest diiodomethane, especially the MWCNTs. MWCNTs adsorbed the greatest non-polar liquid while SWCNTs adsorbed the greatest polar liquid. This adsorption behavior was found due to both these CNTs having the greater Lifshitz-van der Waals, LW, interactions component, because it is up to about 95% in the total surface free energy. The SWCNTs are stronger in the Lewis base while MWCNTs are stronger in the Lewis acid.

COLL 703

Understanding graphene growth on copper substrates

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The atomically thin material known as graphene has sparked a tremendous amount of interest within the scientific community because of its unique electronic and mechanical properties. To have potential for widespread use, a variety of avenues for synthesis are being explored by researchers around the world. The current work describes the synthesis and characterization of graphene grown on copper substrates. A combination of scanning tunneling and transmission electron microscopy are used to understand the fundamental aspects of growth. It is found that graphene grows on both polycrystalline and single crystal substrates without limitation by the underlying substrate. Recent work indicates that control of the nucleation at the surface will be the primary means to achieving high quality synthesis of graphene on copper. Through this understanding and development of transfer techniques, it is expected that the synthesized graphene can serve as a potential material for solving important biological problems.

COLL 704

Facile and transfer free fabrication of graphene membranes via direct growth method.

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Suspended graphenes have been attracted not only for their distinctive physicochemical properties but their various applications. Compared the usefulness of graphene membrane, however, it is not easy to produce. Most of them undergo the inaccurate transfer process, which lowers the yield, applications are also limited. Here we developed the direct growth method for the transfer free process. Firstly, 300 nm of Cu films were deposited as a catalyst on SiN substrates, which has 500 um^2 of suspended SiN membrane. After the graphene growth process, adequate regions of SiN membrane were drilled by FIB equipment, which determines the size of suspended graphene. As a final step, the Cu film was partially etched through the drilled regions by dipping the FeCl3 solutions for 10 min. As one of applications, transmission electron microscopy samples were fabricated via low temperature ion coupled plasma chemical vapor deposition (ICP-CVD) process. Through TEM characterizations, we investigate the feasibility of low temperature growth method and compare the basic properties with thermally grown one.

COLL 705

Stabilization of aqueous carbon nanotubes/graphene dispersions: insights from molecular dynamics simulations

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Preventing the agglomeration of carbon nanotubes, and that of graphene sheets in aqueous media remain some of the biggest hurdles towards the application of such interesting nanomaterials. Surfactants have been used to stabilize aqueous dispersions, achieving promising results. A detailed understanding of the molecular driving forces responsible for such important results could lead to innovative technologies. Towards achieving such detailed understanding, we conducted equilibrium MD simulations for the structure of self-assembled aggregates of SDS, SDBS, FMN, and AOL surfactants on carbon nanotubes and graphene sheets of different sizes. We quantified the effect of surface density, and that of surfactant molecular structure on the aggregates morphology. The results have been compared, favorably, to available experimental data. The structural results have been used to calculate nanotube – nanotube potential of mean forces. We will summarize here the features the surfactants should offer to secure stabilization of the dispersions.

COLL 706

Formation mechanism of graphene oxide paper

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Graphene oxide papers are fabricated by passing an aqueous solution of graphene oxide nanoparticles through a filter. While the processing is simple, the resulting material possesses hierarchical ordering with three length scales of interest. We will discuss the mechanism of nanoscale ordering of the graphene oxide sheets, and the role that pressure plays in the process. The importance of the structure and it's relationship to the resulting material properties will be elucidated.

COLL 707

Mecanochemically-controlled Incorporation of anthracene into sIlica-surfactant nanostructures

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Silica–surfactant nanostructures prepared by supramolecular templating method possess attractive features such as a well-defined and controllable pore size, large surface area, and reactive surface. In this study, incorporation of anthracene (Ant) molecules into alkylammonium-nanoporous silica composites was carried out by a mechanochemical solid-solid reaction at room temperature. Ant was successfully incorporated into the nanopores with preserving the silica nanostrucrues. The hydrophobic interactions between the alkylammonium and aromatic compounds of Ant are thought to be the driving force for the solid-state reactions. The composites showed the photoluminescence peak due to the monomeric Ant molecules, and the intensity was enhanced with increasing the milling force. Thus, it is suggested that the aggregation form amoung Ant molecules initially was dissociated and subsequently the hydrophobic interaction at the monomer state was enhanced.

COLL 708

Wetting properties and surface energy of carbon-ionomer composites

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The focus of this work is to investigate the wetting and surface energy of carbon-ionomer composites, which can be used in many applications, such as fuel cells, lithium-ion battery, water purification, and so on. Carbon-Nafion composites were fabricated by controlling the Nafion fraction from 5% to 50%. Contact angle of carbon-Nafion composites with different compositions were measured by Kruss DSA 100 surface analyzer at different temperatures (5°C to 100°C), in order to understand the composition and temperature dependence of wetting properties in carbon-Nafion system. Contact angle decreased with increasing the fraction of Nafion until 30%, and then stayed constant. There was a significant decrease of contact angle with decreasing temperature (lower than 20 ^{o}C). Surface energy was calculated by using four different theories, which are Acid base, EOS, Wu, and Fowkes. Other characterizations and modifications (profilometer, dynamic light scattering, and force balance analysis) will be included in the further investigation.

COLL 709

Carbon nanocoatings via carbonization of poly (bisphenol A carbonate)

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Poly (bisphenol A carbonate) (PC) is one of the most widely used plastic materials. Considering this widespread application its recycling might become a problematic issue. This study aimed to demonstrate that PC could be utilized as a precursor for formation of variety of ultrathin (2-100 nm) carbon coatings. Three major types of the coatings/films were prepared: *i*-partially carbonized polymer, *ii*-completely carbonized polymer and *iii*-soot-like coating.

Variations in carbonization temperature (430-700 ^{o}C) as well as an environment surrounding the polymer (nitrogen, air) result in particular coating to be produced. Their properties (optical, structural, electrical, spectral characteristics, surface roughness) were determined experimentally. It was found that obtained coatings could exhibit transformations (for example, insulator-conductor) when subjected to additional high temperature treatment.

The method to deposit the coatings on the objects of complex geometry was developed. Practical application of the coatings in reducing friction was demonstrated for glass molding process.

COLL 710

Stabilization mechanisms of multiwalled carbon nanotubes by natural organic matter

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The fate and transport of CNTs in aquatic environments is a complex function of the CNT physicochemical properties and solution chemistries. This study utilizes atomic force microscopy (AFM) to gain insight into the interactions between MWNT (bundles) and how ionic strength and adsorption of NOM to the surface of MWNTs affect these interactions.

MWNT-MWNT interaction forces are directly measured using a single-MWNT AFM probe tip in the presence and absence of natural organic matter (NOM).

Force vs. distance curves indicate extremely strong adhesion forces between the single MWNT probe and MWNT aggregates in DI water due to the MWNT-MWNT interactions arising from the p-p interaction between MWNT surfaces. In comparison, when the aqueous MWNT dispersions are stabilized by SR-NOM, the magnitude of the adhesion force is dramatically decreased. Interestingly, in the presence of SR-NOM, the MWNT force vs. distance curves followed an apparent 'slide-in' mechanism (i.e., there was no significant repulsive force at any distance) rather than the classical hard surface-AFM probe interaction.

COLL 711

Towards supramolecular manipulation of cell function

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Supramolecular chemistry provides an excellent prospect to construct dynamic biological interfaces that can be employed for supramolecular cell manipulation experiments. Knowing the limitations involved in ordering proteins at different length scales will surely hasten the development of future applications, supramolecular nanobiology being the most prominent. The construction of synthetic supramolecular assemblies of proteins provides an excellent tool to fabricate organized bioactive components in the sub-micron regime at surfaces. I will present new synthetic procedures for site-specific anchoring of proteins to surfaces and polymers aiming at more control over structure and function of the proteins. Special attention is paid to orientational and conformational aspects at the surface, and supramolecular interactions that are sensitive to remote electrochemical stimuli, using cucurbituril (CB) and cyclodextrin (CD)-modified surfaces containing embedded electrodes. Cell release was studied using cell-adhesive peptides and growth factors. Dynamic linkers were compared to nonreversible linkers providing insight in the cell-receptor signaling pathway.

COLL 712

Adsorption of proteins in polyelectrolyte brushes

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Polymer brushes are dense layers of polymer chains end-attached to an interface that stretch out into the surrounding medium. In this presentation we focus on the interaction between proteins and polyelectrolyte brushes, i.e., bovine serum albumin and a polyacrylic acid brush. It is observed that net negatively charged protein molecules adsorb into a net negatively charged polyelectrolyte brush. This can be the result of several phenomena, such as specific interactions, charge regulation, that is conversion of charge sign of the protein resulting from the high negative electric field in the polyacrylic acid brush, and/or charge anisotropy (existence of positively and negatively charged patches on the protein). We will discuss the contributions of these phenomena using mean field theory and an analytical model. Furthermore, we will treat the effect of polydispersity of the brush on adsorption and antifouling properties.

COLL 713

Modulation of α-Chymotrypsin activity through monodisperse nano-graphene oxide

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We have recently reported the usage of graphene oxide (GO) as an artificial protein receptor for α-Chymotrypsin (ChT) and discovered that it possessed properties superior to those of other artificial systems[1]. Specifically, we have reported that pristine GO demonstrates reversible inhibition of ChT enzyme. Perhaps more interestingly, it exhibited the highest inhibiting efficiency when compared to all other artificial inhibitors. Similar to many reports regarding graphene oxide however, the report utilized a polydisperse population of graphene oxide making quantitative investigations of GO size-dependent inhibition impossible. To elucidate these size dependent effects on ChT inhibition, we recently applied monodisperse nano-GO synthesized through carbon nanofibers[2]. Using the new GO system, we investigated how changes in GO size affects the inhibition constant (K_i) and loading of ChT on GO.

1. De, M.; Chou, S. S.; Dravid, V. P., Graphene Oxide as an Enzyme Inhibitor: Modulation of Activity of α-Chymotrypsin. *Journal of the American Chemical Society* **2011** .

2. Luo, J.; Cote, L. J.; Tung, V. C.; Tan, A. T. L.; Goins, P. E.; Wu, J.; Huang, J., Graphene Oxide Nanocolloids. *Journal of the American Chemical Society* **2010,** *132* (50), 17667-17669.

COLL 714

Graphene oxide based “nose” array for protein sensing

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There has been considerable interest in developing biosensors that operate using principles governing the mammalian olfactory system. Herein, we examine adaptation of nano-graphene oxide[1] (nano-GO) for this purpose. In the past year, GO became a popular platform for biosensor development (DNA, enzymes, etc). Interestingly, almost universally, these sensors utilized a specific “lock-key” approach similar to ELIZA. Because we have shown that GO is capable of selective protein binding through its complex chemical surface[2], we believe it has potential to discriminate between protein phenotypes without any need of a specific biotarget. This opens the door for the creation of “nose” biosensors that can differentiate proteins through the binding patterns of a small array of selective, but not specific, receptors. Through statistical discrimination, the binding patterns can then differentiate a larger set of analytes. This is analogous to how the brain deciphers signals from olfactory bulbs. Here, we have built a protein “nose” sensor array using nano-GO that can differentiate a diverse set of proteins. Using this approach, we were able to create a sensor array that can capably separated seven proteins down to the 10 nM concentration.

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2. De, M.; Chou, S. S.; Dravid, V. P., Graphene Oxide as an Enzyme Inhibitor: Modulation of Activity of α-Chymotrypsin. *Journal of the American Chemical Society* **2011** .

COLL 715

Antimicrobial peptides at work

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Antimicrobial peptides (AMPs) are essential tools for combating a variety of pathogens. In this study, two different AMPs (NK-2 and Ar-1-S) have been investigated by IRRAS and GIXD to get information about their secondary structure and arrangement at interfaces. The AMPs are able to distinguish mammalian from bacterial cells due to the different lipid composition, but the mechanism is not completely understood. Therefore, Langmuir monolayers of anionic and zwitterionic phospholipids have been used to model their interactions with cellular membranes. The amphiphilic AMPs adsorb at the air/buffer interface. NK-2 reorients from random coil in bulk to alpha-helix lying flat at the interface, and Ar-1-S exists in bulk mostly in beta-turn conformation whereas it exhibits beta-sheet conformation at the surface. The AMPs also insert into uncompressed phospholipid monolayers. The interaction with anionic lipids is much stronger than that with zwitterionic lipids: High maximum insertion pressure and fluidization of the aliphatic chains.

COLL 716

Investigation of protein-ligand interactions using second harmonic generation spectroscopy and imaging

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Second harmonic generation (SHG), was applied to detect protein-ligand binding events at planar supported lipid bilayer surfaces. As a proof-of-principle that SHG is suitable to detect protein-ligand binding, several biotin-bound protein complexes; avidin, neutrAvidinTM, streptavidin, anti-biotin antibody, were investigated. The equilibrium binding affinities of these biotin-protein interactions were determined, revealing the relative energetic contributions for each protein to the biotinylated lipid. The results provide important new insights into these biotin-bound protein complexes commonly used in several bio-analytical applications. We also show the sensitivity of this technique for studying other protein-ligand models such as cholera toxin binding to ganglioside GM1. These investigations demonstrate SHG can be used as an alternative and highly sensitive label-free technique to directly detect protein-ligand binding at the lipid membrane surface. Further extension of this methodology for high-throughput visual detection of protein-ligand interactions using lipid microarrays containing various ligand compositions and SHG imaging will also be discussed.

COLL 717

Surface tension measurements cannot uniquely define surface excess concentration during competitive protein adsorption

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An expressed goal of our research is to understand how bio-surfactants populate gas-liquid and solid-liquid interfaces so that we may ultimately exercise control over the molecular composition of the interface to confer the desired physiological and mechanical properties. Biological systems inherently require an understanding of competitive adsorption from high concentration solutions. Our experiments indicate that multi-species systems can exhibit competitive and cooperative surface tension change. While these observations may be explainable by competitive adsorption models derived from the Gibbs equation of state, a mechanistic understanding of this behavior cannot be verified with surface tension data alone. Furthermore, the roles of post-adsorption conformation change, aggregation, or bonding in surface tension change remain unclear. This highlights a need for a method to measure the surface excess concentration directly. We are developing confocal microscopy measurement techniques to image the protein adsorption process, and provide insight into interfacial protein behavior.

COLL 718

Effects of aggregation and protein corona on the cellular internalization of iron oxide nanoparticles

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Engineered nanoparticles are essential components in the development of nanotechnologies. For applications, particles need to be functionalized to ensure a good dispersibility. In many cases however, functionalization is not sufficient: the particles in biological fluids become either coated by a corona of serum proteins or precipitate out of the solvent. Here, we show that by changing the coating of iron oxide particles from citrate ligands to small carboxylated polymers, the colloidal stability of the dispersion is improved and the adsorption/internalization of iron towards living cells is profoundly affected. Citrate-coated particles are shown to be covered by plasmic proteins and to destabilize in physiological conditions, whereas the polymer-coated particles exhibit an outstanding dispersibility and a structure devoid of protein corona. The interactions between nanoparticles and human lymphoblastoid cells are investigated by transmission electron microscopy and flow cytometry. [1]

[1] M. Safi et al., Biomaterials 32 (2011) 9353-9363

COLL 719

Nanoparticle size and PEG grafting density control protein adsorption and cellular interactions in a physiological environment

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Understanding and controlling protein adsorption is a prerequisite to controlling the interaction of nanomaterials with physiological systems. Here, we apply shotgun mass spectrometry to systematically examine how nanoparticle size and the surface density of poly(ethylene glycol) (PEG) influences protein adsorption from serum. We find that size and PEG density determine the relative and total adsorbed abundance of over 80 different proteins. Increasing PEG density and nanoparticle size decreases total protein adsorption, but does not eliminate it. We further show that by controlling the composition of the adsorbed protein layer, nanoparticle size and PEG density determine the efficiency and mechanism of cell uptake. At low PEG densities, cell uptake is efficient and driven by adsorbed serum proteins, while at high density it is inefficient and independent of adsorbed serum proteins. The results of this study establish guidelines for the rational design of nanomaterials with controlled protein adsorption and cell uptake.

COLL 720

Dynamics and aggregation of proteins at the oil-water interface characterized by single molecule tracking

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Single molecule total internal reflectance fluorescence microscopy was used to track between 1,200 and 12,000 single protein (bovine serum albumin) objects at the silicone oil-water interface. The dynamics of isolated proteins showed showed multiple populations of proteins. The connections between surface residence time, fluorescence intensity and interfacial diffusion revealed identified these populations as monomers, dimers and trimers. At higher aqueous protein concentrations, a systematic decrease in interfacial diffusion was used to characterize the formation of an interfacial protein layer. The distribution of hydrodynamic radii (obtained from diffusion coefficients of individual protein objects) indicated that protein aggregation was the mechanism of this protein layer formation. The time scale of the decrease in interfacial diffusion showed the kinetics of this layer formation was non-linear. A kinetic population balance was used to model the non-linear kinetics of this process.

COLL 721

Electrostatic-driven assembly of uni-lamellar catanionic facetted vesicles

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Nature utilizes shape to generate function. Organelle and halophilic bacteria wall envelopes, for example, adopt various polyhedral shapes to compartmentalize matter. The origin of these shapes is unknown. A large variety of shell geometries, either fully faceted polyhedra or mixed Janus-like vesicles with faceted and curved domains that resemble cellular shells can be generated by coassembling water-insoluble anionic (–1) amphiphiles with high valence cationic (+2 and +3) amphiphiles. Electron microscopy, X-ray scattering, theory and simulations demonstrate that the resulting faceted ionic shells are crystalline, and stable at high salt concentrations. The crystallization of the co-assembled single tail amphiphiles is induced by ionic correlations, and modified by the solution pH. This work promotes the design of faceted shapes for various applications and improves our understanding of the origin of polyhedral shells in nature.

COLL 722

Comprehensive analysis of compositional interface fluctuations in planar lipid bilayer membranes

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The formation and dynamics of spatially extended compositional domains in multicomponent lipid membranes lye at the heart of many important biophysical phenomena. In this talk, we present a comprehensive analysis of line tension driven compositional interface fluctuations in planar lipid bilayer membranes. Our starting point is the advective Cahn-Hilliard equation for the local lipid composition in symmetric membranes, which explicitly incorporates both advective and diffusive lipid transport processes, and which is coupled to the continuum hydrodynamic equations governing the flow behavior of the membrane and surrounding solvent. The resulting expression incorporates the effects of diffusive and advective lipid transport processes, viscous or viscoelastic membrane properties, coupling between membrane and solvent, and fluid inertia. It is shown that previously considered scenarios naturally emerge as limiting cases of our general result. Finally, we discuss how to extend our approach to asymmetric membranes.

COLL 723

Meshless particulate model for the study of cell membrane deformations

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A novel mesoscale particulate model of a lipid membrane is developed in which the local directionality of the 2D surface is extracted from the state of aggregation of particles in a local cluster. Particles interact via (i) a pair-wise Lennard-Jones interaction, (ii) a normal, restoring force that imparts both a spontaneous curvature and bending elasticity by penalizing particle departure from the local plane, and (iii) an anisotropic Brownian motion that imparts fluidity. The anisotropic multi-body potentials are parameterized such that the simulation produces a stable, elastic 2D membrane with in-plane fluidity. The meshless elastic membrane will be integrated with a model representing embedded membrane proteins. The integrated model will be used to probe the importance of protein coat geometry and other characteristics such as signaling reaction induced charge in mediating membrane deformation – a precondition for vesicle formation and endocytosis.

COLL 724

Thin film buckling in polymer-tethered membranes

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Buckling patterns in model membranes consisting of phospholipids and lipopolymers were quantitatively investigated using epi-fluorescence microscopy and AFM. Results show that increased concentrations of lipopolymers in the membrane enhanced the formation of buckled regions in the monolayer. Similarly, increasing cholesterol concentrations in a monolayer with low lipopolymer concentration also cause formation of buckling structures. By applying mean-field calculations of polymer-tethered membranes and thin film buckling theory of an Euler column, we are able to quantitatively link buckling structures and membrane elasticity. Our results demonstrate that cholesterol and lipopolymers induce buckles due to increased biaxial stress in the membrane. Intriguingly, no additional lipid monolayer was able to form on top of the buckling regions of the polymer-tethered monolayer containing poly(2-ethyl-2oxazoline) lipopolymers, thus forming a compartmentalized polymer-tethered lipid bilayer. Our experiments demonstrate the fascinating materials properties of polymer-tethered membranes and reveal a complex interplay of their elastic, organizational, and dynamic properties.

COLL 725

Membrane scaffold DNA orgami assembly

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DNA origami is a new field in which the specificity of DNA base pairing is used to create multidimensional structures at the nanoscale. However, the field is limited by its low yield and slow assembly rate. Scaffolding is a general mechanism used in living systems to increase the local concentration and organization of various signal components. We are developing fluid self-assembled scaffolds that guide the growth of origami structures. Specifically, by anchoring several of the strands onto a two dimensional lipid membrane bilayer, the rate of assembly and the yield of the desired structure will increase. We generate a fluid lipid bilayer which is functionalized with DNA using the biotin-streptavidin system. The assembly process is monitored using fluorescence microscopy. Once optimized, it will be applied to a more commonly utilized scaffold structure. This is an important step toward building hierarchical structures that take advantage of orthogonal molecular assembly strategies.

COLL 726

Dynamic control of hybrid cell-supported lipid membrane junctions

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Cells respond to the chemical and physical properties of their environment through membrane receptors. One challenge in this area pertains to investigating receptor response to the physical properties of a signaling ligand *in situ.* Herein, we describe the development of a photoactivatable platform to dynamically control the immobilization of biomolecules to a supported lipid membrane with high spatial and temporal resolution. This system employs photocleavable DNA tethers that are easily multiplexed and labeled with ligands of interest to selectively release anchored biomolecules from a lipid membrane surface. Biotin-streptavidin anchoring chemistry is used to incorporate oligonucleotide capture strands that are functionalized with a 5'-2-nitrophenyl group into the membrane. These strands are complementary to cyclic RGD peptide conjugated oligonucleotides that engage adhesion receptors in cells, and can be released upon photo-irradiation. This presentation will describe the synthesis and properties of these model membranes and their potential use in studying dynamic cell adhesions.

COLL 727

Molecular theory of lipid bilayer structure perturbations by interacting antimicrobial peptides

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We present a molecular thermodynamic treatment of interactions between lipid bilayers and antimicrobial peptides. We formulate a global free energy model that considers the presence of individual peptides adsorbed on the surface of the bilayer, peptides inserted into the bilayer creating pore structures and peptides forming free aggregates with lipid molecules in solution. We consider the peptide-induced changes to the membrane free energy arising from hydrophobic effects, electrostatic effects, entropic effects, and chain packing effects which are dependent on the manner in which the peptide affects the membrane structure. From this free energy model we identify conditions under which surface adsorption or transmembrane pore formation would occur, the peptide to lipid ratio at which these changes are possible and the structural features of the membrane perturbation induced by the peptide.

COLL 728

Development of broad-spectrum antimicrobial latex paint surfaces employing active amphiphilic compounds

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With the increase of antibiotic-resistant microbes, the production of self-decontaminating surfaces has become an area of research that has seen a surge of interest in recent years. Such surfaces, when incorporated into commercial products such as children's toys, medical devices and hospital surfaces could reduce the number of infections caused by pathogenic microorganisms. A number of active components for self-decontaminating surfaces have been investigated, including common antibiotics, metal ions, quaternary ammonium salts (QAS), and anti-microbial peptides (AMP). A recent research focus has been development of a wide range of amphiphilic anti-microbial additives that when combined with modern low volatile organic compound (VOC), water-based paints leads to a surface concentration of the active compounds as the coating cures. Herein we report the development of antimicrobial coatings containing a variety of additives, both QAS and AMP that are active against a broad-spectrum of potentially pathogenic bacteria (1-7 log kill), as well as enveloped viruses (2-7 log kill) and fungi (1-2 log kill). Additionally, these additives were compatible with water-dispersed acrylate coatings (latex paint) which have a broad range of real world applicability, and remained active for multiple challenges and when exposed to various cleaning scenarios in which they might encounter in real world situations.

COLL 729

Multifunctional conjugated polymers for light-activated antibacterial activity with imaging capability

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The development of alternative antibacterial therapeutics is becoming urgent due to antibiotic resistance to pathogen bacteria. We have shown that an anionic water-soluble polythiophene (PTP) and a cationic porphyrin (TPPN) can form complex through electrostatic interactions, and efficient energy transfer from PTP to TPPN occurs upon the irradiation under white light (400-800 nm). The produced singlet oxygen by sensitizing oxygen molecule effectively kills the bacteria. Very recently, we have also shown that a multifunctional cationic poly(*p*-phenylene vinylene) derivative bearing polyethylene glycol (PEG) side chains can be used for selective recognition, imaging and killing of bacteria over mammalian cells. These multifunctional conjugated polymers combine recognition, imaging and killing functions into a single system to achieve the collaborative and selective antimicrobial effect. Our new strategy will exert a far-reaching impact on the future development of antimicrobial materials, exhibiting its potential applications in pathogen infections and medical implants.

COLL 730

Improved surface biocompatibility and antimicrobial properties of plasma-treated biomaterials and biomedical implants

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The surface mechanical and biological properties of biomaterials and biomedical implants can be improved by plasma-based technology. The technology takes advantage of the synergistic effects of energetic ion bombardment and plasma deposition enabling the production of a surface layer that has different properties than the bulk materials. In this way, selected biomedical and relevant surface properties can be enhanced while the favorable properties of the bulk materials such as strength can usually be preserved. In this invited talk, recent research activities pertaining to plasma surface modification and engineering of biomaterials conducted in our laboratory are described. Examples include fixation implants for complex and multiple fractures, total hip replacements, automatic scoliosis correction devices, as well as biodegradable metallic and polymeric materials.

COLL 731

Photo-induced antibacterial chemicals and materials: Chemistry and applications

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Organic photo-sensitive chemicals including certain colorants could produce reactive oxygen species such as hydroxyl radicals, superoxide, and singlet oxygen under ultraviolet or even visible light exposure. Such photo-reactions could be utilized in preparation of biologically and even chemically functional agents and polymers. We have investigated a series of anthraquinone compounds by chemically incorporating them onto different polymers or dissolving them in different solution media under UVA (365 nm) light exposure. The results indicated that the photo-active properties of the anthraquinone compounds are significantly affected by different solvents and polymer media. The photo-chemistry of the agents and the reaction mechanisms were investigated and proposed. The experimental results support the proposed reaction mechanism. Potential applications of the chemistry and these photo-active chemicals in biological protection area will be discussed. Nanofibrous membranes and materials with photo-induced antibacterial functions will be provided as an example of the applications.

COLL 732

Versatile approach for analyzing bacterial growth on solid supports

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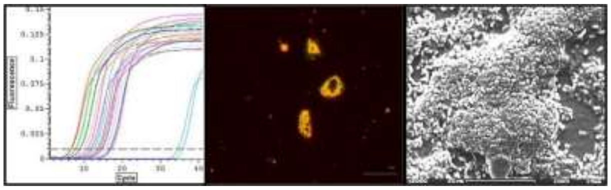
Analyzing the bacterial growth on surfaces is highly important when aiming for the design of novel materials in medicine, food technology, water purification, or for surface coatings.

The bacterial growth on surfaces is usually investigated by plating-out techniques, which are time consuming, subjective, of limited reproducibility, and do not allow the direct investigation of surfaces.

We present a new approach for analyzing microorganism growth directly on surfaces based on: real time polymerase chain reaction (RT-PCR), fluorescence staining, and control via scanning electron microscopy (SEM). Combining these techniques, one can quantify the total amount of bacteria on a surface (RT-PCR), distinguish between death and alive bacteria (fluorescence staining), and investigate the bacterial growth (SEM).

The developed approach allows analyzing flat surfaces as well as fibers or hollow fiber membranes.



The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 214653.

COLL 733

Structural aspects of layer-by-layer assembly of carboxymethyl cellulose and antimicrobial poly(4-vinyl-N-alkyl pyridinium) ultrathin films

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Multilayer films of carboxymethylcellulose (CMC) and antimicrobial poly(4-vinyl-N-alkyl pyridinium) were fabricated by layer-by-layer (LbL) self assembly. In order to investigate the effect of alkyl side chain length on the multilayer structures bromide salts of poly(4-vinylpyridine) quaternized with linear aliphatic chains of 2 (ethyl) and 5 (pentyl) carbon

atoms, coded as QPVP-C2 and QPVP-C5, respectively, were chosen. Dried multilayer films were characterized by means of ellipsometry, atomic force microscopy (AFM), contact angle measurements and sum frequency generation vibrational spectroscopy (SFG) and their antimicrobial activity against *Micrococcus luteus* was evaluated in aqueous dispersion. Exponential thickness evolution with number of layers deposited was observed for systems composed of CMC and QPVP-C2 or QPVP-C5. The presence of pentyl side chains along the polycations led to flatter and more hydrophobic multilayers in comparison to those with shorter ethyl groups. SFG showed stronger molecular orientation of pyridinium groups in systems composed of QPVP-C5. These structural features were explained with basis on the diffusion of QPVP-C5 chains into the CMC pre-adsorbed layer, which is less favored than the diffusion of QPVP-C2. The high stability of QPVP-C2/CMC and QPVP-C5/CMC multilayers at pH 2 showed that multilayers build-up is driven not only by cooperative polymer-polymer ion pair, but also by hydrophobic interaction between the alkyl side chains. The biocidal activity determination after each layer deposition as a function of time showed that already after 15 min all QPVP-C2 or QPVP-C5 terminated systems were able to kill microrganisms. However, the last deposited layers were more active than the initial layers, suggesting that QPVP-C2 or QPVP-C5 initial depositions are partially “buried” in the pre-adsorbed CMC layer.

COLL 734

Comparison of the liquid adsorption behavior and surface properties of α-, β- and γ-cyclodextrins by capillary rise method

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Through the application of capillary rise method research about the liquid adsorption behavior of α, β, γ cyclodextrin, CD, in four probe solvents, we obtained its properties such as adsorption kinetics, the adsorption contact angle, and surface free energy which including the Lewis acid-base interactions. A comparison of these three CDs found that the α- and β-CD can adsorb greater polar liquid, and the γ-CD α-CD can adsorb greater non-polar liquids. The β-CD has the greatest surface free energy than that of others while all these CDs are dominated by the Lifshitz-van der Waals interaction component because this value to be up to the total surface free energy at least 77%. Of these CDs, the γ-CD has the greatest Lewis base and polarity as compared with others.

COLL 735

Interactions between membranes and synthetic antimicrobials

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Antimicrobial peptides comprise a key component of innate immunity for a wide range of multicellular organisms. It has been shown that natural antimicrobial peptides and their analogs can permeate bacterial membranes selectively. There are a number of proposed models for this action, but the detailed molecular mechanism of the induced membrane permeation remains unclear. We investigate interactions between model bacterial membranes and a prototypical family of methacrylate-derived antimicrobials with controllable hydrophilic and hydrophobic volume fractions. Preliminary results from synchrotron small angle x-ray scattering (SAXS) and fluorescent dye leakage assays will be presented.

COLL 736

Energy harvesting with triboluminescence for damage sensors

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The triboluminescence (TL) phenomenon has generated extensive research interest over the years because of its potential application for damage detection. [1, 2] The majority of known triboluminescent materials do not emit light with sufficient intensity to allow detection with compact and inexpensive detectors. Use of these detectors is critical to minimize the overall parasitic weight of any triboluminescent damage sensor.[3]

This work describes ongoing effort to harvest light energy using optoelectronic and photovoltaic devices, which were synthesized with sol-gel chemistry method at low temperature, for a self powered intrinsic structural health monitoring (SHM) system. Most current sensor systems consist of microelectronic detectors and actuators that require external power sources. The system under development uses the triboluminescence (TL) phenomenon as the energy (light) source, thus negating the need for any external energy source. Triboluminescence is a mechano-optical phenomenon of luminescence, where light emission occurs by rubbing or fracture of the material structure. Upon impact, the onset of structural damage is indicated by light emission, the severity of damage is indicated by the overall light intensity and the location of damage is obtained by the wavelength of emitted light.

This effort will investigate the harvesting of light energy by affixing the potential TL sensor or dye sensitized solar cells (DSCs), in the form of a surface patch on all

materials, or embedded/weaved with the composite host structures, to power an intrinsic SHM system and proffer a way towards nano-optoelectronic solution.

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COLL 737

Using DNA as a multifunctional delivery vehicle

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Discrete DNA nanostructures allow for simultaneous features not possible with traditional DNA forms: encapsulation of cargo, display of multiple ligands, and resistance to enzymatic digestion. This latter property arises from steric hindrance and the rigidity of DNA at nanometer length scales. Overall, these unique features of DNA nanostructures suggested their use as a delivery platform. We will show that DNA pyramids displaying antisense motifs can specifically degrade mRNA and inhibit protein expression in vitro, and show improved cell uptake and gene silencing when compared to linear DNA. Furthermore, the activity of these pyramids can be regulated by the introduction of an appropriate complementary strand. Ongoing work involves the incorporation of environmentally-sensitive DNA motifs into these structures, to obtain DNA-based delivery vehicles that release their cargo based on physiological or pathological cues.

COLL 738

Tailored designed polysaccharide composite nanoparticles and possible applications

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Polysaccharides are widely used for the preparation of nanoparticles or nanocapsules, which are of strong interest for medical, pharmaceutical, food- and bio-technological applications.

The main limitations of polysaccharide nanoparticles are on the one hand the hydrophilicity of most polysaccharides, which for example does not allow the entrapment of active hydrophobic substances into the particle core. On the other hand, hydrophobic cellulose ester nanoparticles lack of specific surface functionalities.

Using nanoprecipitation technique, we have generated polysaccharide composite nanoparticles of different surface charge and functionality. These particles consist of a hydrophobic cellulose acetate core, and a variable functional hydrophilic polysaccharide surface. The nanoparticles were successfully loaded with hydrophobic substances, showed a very specific adsorption behavior, and were used for introducing strong antimicrobial properties to cellulosic supports.

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COLL 739

Red blood cell membrane coated polymeric nanoparticles

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We have prepared a novel erythrocyte membrane coated nanoparticle platform with tunable size and excellent stability. In this platform, biodegradable PLGA polymeric nanoparticles are covered in the phospholipid membrane bilayers derived directly from RBCs. Using an adapted mechanical extrusion method, we demonstrate the translocation of membrane lipids, surface proteins, and their functionalities from RBCs to the nanoparticles. The resulting particles have a sharp unimodal size distribution and uniform membrane coverage. In PBS, the particles remain stable for two weeks and upon injection in mice, the RBC membrane coating enables a long circulation half-life that's superior to PEG coating. The platform presents a unique and innovative approach in nanoparticle functionalization. It serves as a new model for the study of colloid-

supported membrane bilayers and offers new opportunities in stealth nanoparticle drug delivery.

COLL 740

Stimuli-responsive hollow polymer nanoparticles for use as drug-delivery vehicles

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The preparation of a biocompatible hydrogel polymer (N-isopropylacrylamide-co-acrylic acid) on dye-loaded mesoporous silica (SiO_2) nanoparticles is reliably carried out using conventional free radical polymerization. Subsequently, gold nanoparticles are physically embedded in the polymer shell layer before the removal of the SiO_2 core with diluted hydrofluoric acid which leads to the formation of uniform hollow polymer structures containing dye molecules and gold nanoparticles. The formation and properties of polymer-coated SiO_2 and hollow polymer nanoparticles is thoroughly examined by electron microscopes, X-ray photoelectron spectroscopy, and dynamic light scattering. The resulting hollow nanoparticles (~250 nm in diameter) exhibit much greater diameter changes (i.e., swelling and deswelling) than those of polymer-coated SiO_2 nanoparticles as a function of pH and/or temperature as well as light irradiation. Given their unique features including high guest molecule loading capacity, surface functional groups, homogeneity, external stimuli-responsiveness, and biocompatible nature, these hollow nanoparticles can serve as novel drug-delivery systems.

COLL 741

Engineering colloidal interfaces to improve release from and oxidative stability of encapsulated material within solid lipid nanoparticles and emulsions

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The surfactants and co-surfactants which envelop the oil fraction within solid (SLNs) and liquid (emulsions) lipid nanoparticles are available with a wide variety of physical and chemical properties. Many times, these properties are left unexplored when selecting an emulsifier for use in the food or health industries. After careful study with several biophysical characterization techniques including FRAP, fluorescence spectroscopy and anisotropy, we discovered that the molecular ordering and mobility of the interface heavily influences the resistance to oxidative degradation and the release profile of encapsulated materials from both SLNs and emulsions.

COLL 742

Effect of solvents on stabilization of micro drug particles

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Antisolvent synthesis of micron scale Griseofulvin was carried out with simultaneous suspension stabilization under low power ultrasonic agitation. The organic solvent plays an important role because the supersaturation could be varied by using different solvents and the physicochemical characteristics of the suspension are also altered, which affects stability. In this study we present the effect of solvents on particle formation, polymorphism and stability of micron scale Griseofulvin formation in aqueous media

COLL 743

Effect of addition of cell-penetrating peptides on non-viral gene delivery systems

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The effects of addition of cell-penetrating peptides (CPPs) on different non-viral gene delivery systems were studied. For example, KALA was added in Ca-P/DNA systems to form Ca-P/DNA/KALA co-precipitates. The gene delivery efficiencies of Ca-P/DNA/KALA co-precipitates in both solution based transfection and substrate-mediated transfection were studied *in vitro*. In the substrate-mediated transfection, a fast degrading cholic acid functionalized star poly($_{DL}$-lactide) was used to fabricate co-precipitates loaded films. The effect of KALA content on the gene transfections was studied. The gene expressions in both solution based transfection and substrate-mediated transfection could be significantly enhanced by the addition of KALA with a suitable amount. Due to the surface erosion mechanism of the functionalized star poly($_{DL}$-lactide), the substrate-mediated transfection system could rapidly release Ca-P/DNA/KALA to mediate efficient gene expression. During the transfection, the degradation of the polymer films could be observed and the degradation did not show any unfavorable effects on the gene expression.

COLL 744

Extended ocular drug delivery by p-HEMA hydrogels

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We explore the interaction of corticosteroid dexamethasone phosphate sodium (DXP) with surfactant laden poly-Hydroxyethyl methacrylate (pHEMA) gels, a common contact lens material as a potential ocular drug delivery mechanism. DXP is hydrophilic and

anionic with low loading capacity. Cetalkonium chloride (CAC) is cationic and thus loading the pHEMA gels with CAC significantly increased the binding of DXP due to ionic interactions with surfactant. The increased binding leads to reduced effective diffusivity, which is critical in the potential application of the gels as contact lens matrices. Effect of time scale of drug partitioning with surfactant aggregates was observed for thinner gels and subsequently, a more complex model has been constructed to include binding kinetics. We also show that CAC laden pHEMA gels do not release CAC when soaked in phosphate buffered saline (PBS), which again is important to minimize the potential ocular toxicity due to surfactant release in the tear film.

COLL 745

Thermosensitive liposome stabilization with nanoparticle bilayer incorporation for controlled drug delivery

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The high *in vivo* stability of long-circulating liposomes leads to slow drug release that compromises drug bioavailability and efficacy. Lysolipids have been incorporated into liposomes to design temperature-sensitive systems known as low temperature sensitive liposomes (LTSL). These exhibit reduced phase transition temperature that allows for rapid drug release under hyperthermia conditions. Here, we report the engineering of hybrid vesicular systems between LTSL and metallic nanoparticles embedded within the lipid bilayer as a promising strategy to gain more control of drug release capabilities on external stimulus. Gold and superparamagnetic iron oxide nanoparticles were successfully incorporated into the LTSL. The incorporation of the metallic nanoparticles within the lipid bilayer was optimized using three techniques: lipid film hydration, reverse phase evaporation and lipid film-reverse phase evaporation methods. Doxorubicin was able to be encapsulated at high efficiencies in the liposome-nanoparticle hybrids and release profiles were compared at 37°C and 42°C. The incorporation of nanoparticles within the lipid bilayer interfered with the drug release properties of LTSL and offered higher stability at 37°C without affecting release at 42°C.

COLL 746

Nanoscale origami using surface forces

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Surface forces scale favorably at small size scales and can be used to curve or fold up thin films. In this talk, I will discuss strategies to fold up nanostructures composed of metallic and dielectric composition, including those patterned with e-beam and nanoimprint lithography. This work has resulted in the creation of precisely patterned polyhedral and curved nanoparticles and nanostructures. I will also discuss early results on the use of surface forces to deform graphene sheets.

COLL 747

Forces between hydrophobic solids in aqueous salt solution

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We show that that the force between high contact-angle solids in concentrated salt solution (1 M KCl) agrees very well with the van der Waals forces calculated from Lifshitz theory for separations greater than 5 nm. The hydrophobic solids are octadecyltrichlorosilane-coated glass, with an advancing contact angle of 108°. Thus, in 1 M salt solution, it is unnecessary to invoke the presence of an additional “hydrophobic force” at separations greater than 5 nm. Through measurement in salt solution, we avoid the necessity of accounting for large electrostatic forces that frequently occur in pure water and may obscure resolution of other forces.

COLL 748

Tunable interaction potential between colloids in an AC magnetic field

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Paramagnetic particles assemble into chain-like structures under the application of an external magnetic field. For a rotating magnetic field, a rotational torue is imposed causing the chains follow the field until the drag forces cause the chain to asynchronously rotate with the applied magnetic field. There exists a critical frequency where this rotational torque averages out to zero, leaving only an attractive interaction potential between the particles. This interactional potentail can be used from 2kT to 50kT by simply changing the magnitude of the external field. Here will discuss the colloidal phases that are formed by modifying this pair potential.

COLL 749

Magneto-optical study of solvation force between colloidal silica particles

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Understanding interactions between colloids is of both fundamental and practical interests. The widely used DLVO theory failed in explaining the superior stability of silica colloids under conditions of high ionic strength. The most plausible explanation attributes the stability to solvation force, the formation of a thin rigid layer of solvent molecules in the vicinity of silica surface through hydrogen bonding. To confirm this theory, we exploit a magneto-optical strategy to study the effects of different solvents on solvation force between superparamagnetic $Fe_3O_4@SiO_2$ core-shell colloids based on the Bragg diffraction of the magnetically induced particle chains. By selectively screening the electrostatic force, we are able to measure the thickness of solvation layer and identify a correlation between the hydrogen bonding ability of the solvents and the thickness of solvation layer, which is consistent with the hydrogen-bonding origin of solvation force.

COLL 750

Effect of field heterogeneity on electrical destabilization of thin liquid films

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Electrical destabilization and drainage of thin liquid film have been numerically studied assuming long-wave asymptotic analysis of the governing equations. Morphological evolution of the film interface is captured for different configurations of applied field to identify the effect of field heterogeneity on the film drainage time and submicrometer-scale surface pattern formation. Influence of substrate heterogeneity combined with heterogeneous electric field has also been demonstrated. Results indicate that faster film drainage can be achieved by the introduction of any heterogeneity when compared to that of the homogeneous field. For rapid de-emulsification studies, this work initiates the exciting possibilities of harnessing the applied field heterogeneity and optimizing its configuration according to the emulsion properties. This developed methodology can contribute in the design of an *efficient* electrostatic coalescer that requires a fundamental understanding of the thin film drainage, the effects of electrode design, and the electric field configuration.

COLL 751

Dependence of pollen adhesion to surfaces on pollen structure and pollenkitt

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Pollens display a remarkable range of ornamentations consisting of combinations of spines and grooves composed of sporopollenin, a crosslinked organic material rich in fatty acids. In addition, some species of pollen have a viscous coating known as pollenkitt, which appears to be related to dispersion mechanisms, e.g., insect versus

wind-pollenation. It is not clear, however, how the structural features and pollenkitt contribute quantitatively to pollen adhesion to surfaces. This question has significance not only in plant biology, but also in epidemiology of asthma and allergies, and utilization of pollen as biotemplates for advanced materials. We report here the measurement of the effect of pollenkitt and geometry on adhesion of pollen from 5 plant species on 5 model surfaces. For pollen grains with intact pollenkitt, the adhesion forces varied with hydrophilicity of the counter surface, and both hydrogen bonding and van der Waals forces contributed to adhesion. In contrast, the interaction of pollen grains without pollenkitt was independent of counter surface type and was due primarily to van der Waals forces. Pollens exhibiting a nano-sized reticulate (grooved) structure (olive, poplar) had lower adhesion than those with echinate (spiked) structures (ragweed, dandelion, sunflower). In addition, increasing spike size and aspect ratio led to an increase in adhesion (from low to high: ragweed, dandelion, sunflower), which could be explained by increased contact area of the larger spikes.

COLL 752

Direct characterization of ligand nanoparticle interaction: A combined experimental and theoretical investigation

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Understanding the interaction of nanoparticle surface with functional groups from different organic ligands such as carboxylic acids is challenging because of the inherent challenges associated with the characterization of highly dynamic and reactive nature of nanoparticles. The present study is an attempt to understand the direct interaction of ceria nanoparticles surface with carboxylic acid at the molecular level by combining various spectroscopic techniques with theoretical calculations. In-situ XPS carried out by freezing the nanoparticle solution at liquid nitrogen temperature show that the Ce atoms exist predominantly as Ce^{4+} and the oxygen atoms from carboxylic acids were bound to the ceria surface in a bidentate conformation. The SFG-VS spectra from functionalized nanoparticle surface show no signature of C=O confirming the bidentate bonding of the carboxylic acid group. Findings from these characterizations combined with DFT calculations of carboxylic acid molecules adsorbed on oxygen deficient and stoichiometric ceria surface will be discussed.

COLL 753

Two-step yielding in dilute colloidal gels

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Colloidal gels are versatile materials used in a wide range of technologies, and are often subject to transient, nonlinear deformations during either processing or final consumer use. In this study, the rheology and microstructural evolution of dilute, depletion-induced colloidal gels undergoing shear-induced yielding (and ultimately flow) are investigated using quantitative time-resolved confocal microscopy and rheometry to probe the complex interplay between the thermodynamic and hydrodynamic interparticle interactions and globally applied stresses. We report that dilute gels yield via a two-step process that is qualitatively similar to dense, weakly attractive glasses, but through necessarily distinct mechanisms. The implications of this behavior include a remarkable effective “strengthening” at large strains that increases the dilute gel's resistance to subsequent shear deformation.

COLL 754

Shear induced aggregation in acrylic latex

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Particle aggregation depends on the shear rate and the attractive forces between colloidal particles. The aggregation of colloidal particles takes place on collisions between particles, which are influenced by hydrodynamic forces and inter particle forces. If interparticle forces are purely attractive, an applied shear stress may break down aggregates and fluidize the material. Colloidal particles are usually stabilized by electrostatic forces with little tendency to aggregate and only high shear rates promote aggregation in the presence of electrostatic forces. Smoluchowski equation with shear has been used as an approach that permits one to calculate the kinetics through a potential barrier under shear at arbitrary colloid concentrations

Our concentrated acrylic latex was found to behave as elastic solids at low shear rates and required a finite stress to flow. In dynamic deformation, elastic modulus showed a plateau at low shearing frequency. Effect of shear rate on shear stress and of shearing frequency on elastic modulus are analyzed in terms of aggregation of particles.

COLL 755

Self-assembly of colloidal sulfur particles on hydrophilic surface

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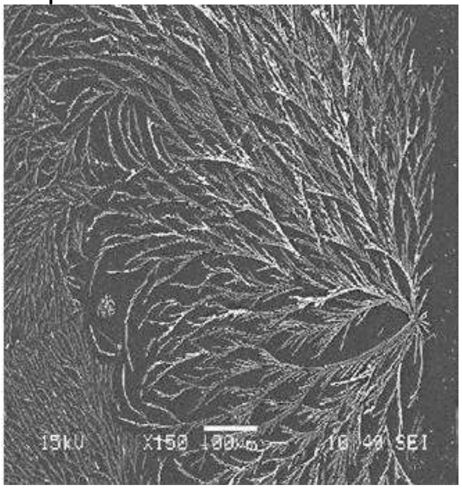
Evaporation of sessile droplets containing colloidal particles induces outward flow within the drop, which produces the well-known "coffee-ring" effect or a dense ring-like deposition along the perimeter. In this work, the formation of self-assembled structure during drying of microliter drops on the glass surface containing colloidal sulfur particles (synthesized in situ by the reaction of oxalic acid and sodium thiosulphate) is

investigated experimentally with help of optical microscopy. Our results show that the particles are self-assembled into a tree-like structure after the evaporation of liquid drops



. The structure formation is mainly influenced by evaporative flux inside the liquid drop, capillary and van der Waals attractive forces between the particles. Different parameters such as particle size, particle concentration, acid to thiosulphate ratio, drop volume, addition of surfactants strongly influences the structure formation.

COLL 756

Self-organization and directed assembly of elastomeric magnetopolymer composites

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Magneto-polymeric materials are polymer composites that respond to magnetic fields, forming well-defined sub-micron rods and other structures. Both magnetic gradients (self-organization) and magnetic templating substrates (directed assembly) can provide routes to well-organized, highly controlled materials with structure dimension and periodicity on the sub-micron scale. We have developed novel curable silicone-based nanocomposites which spontaneously form into oriented arrays of self-organized rod structures with nano- to microscale dimensions upon the application of externally imposed magnetic fields. The resulting structures and spacing are dependent on the applied field, the makeup of the composite, and the confinement of the organized structures. These materials have potential application as components within micro- and nano-devices, which will be discussed.

COLL 757

Stamping oriented molecular monolayers using liquid crystal inks

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While microcontact printing enables the creation of features with well-defined positional order, it is limited in the degree to which orientational order of deposited objects can be controlled. We describe the use of liquid crystal solvents as 'structured inks' for such purposes. Using stamps with patterned anchoring, it is shown how a single stamp can dictate both positional and orientational order in an organic monolayer, providing a simple means to deposit molecules at specific surface locations with specific orientations.

COLL 758

WITHDRAWN

COLL 759

Modeling arginine monolayers at the aqueous Au(111) interface: Impact on nanoparticle assembly in solution

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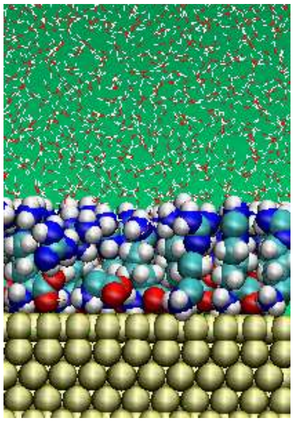
Directed assembly of nanoparticles is currently thought possible via non-covalent surface functionalisation of the nanoparticles with biomolecular ligands. Recent experimental evidence suggests that ligand exchange of citrate-capped gold nanoparticles by the amino-acid arginine can yield linear nanoparticle assemblies. Current hypotheses for this assembly process would benefit from insights gained from molecular simulation. Here we model adsorbed arginine films on the Au(111) surface under aqueous conditions using atomistic molecular dynamics, modelling the aqueous gold-molecule interface with a polarizable force-field. We have determined the optimal surface coverage and orientation of arginine molecules within the monolayer, both of which should have a substantial impact on the assembly behaviour of these systems.



COLL 760

Molecular dynamics simulations of nanoparticle self assembly at ionic liquid-based interfaces

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Nanoparticle self assembly at liquid-liquid interfaces is an important process in forming nanostructured devices and Pickering emulsions. Ionic liquids, with their unique composition, present a new kind of liquid-liquid interface which is not yet well understood. We have studied the self-assembly of hydrophobic nanoparticles at ionic liquid (IL)-water and IL-oil (hexane) interfaces using molecular dynamics (MD) simulations. For the 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6])/water system, the nanoparticles rapidly approached the IL-water interface and equilibrated more into the IL phase although they were initially in the water phase. In contrast, when the nanoparticles were dispersed in the hexane phase, they slowly approached the IL-hexane interface but remained primarily in the hexane phase. Particle-IL interactions depended significantly on particle charge and interface type (water or oil). Potential of mean force (PMF) calculations supported the observations from the equilibrium studies and correlated reasonably well with continuum models for nanoparticle desorption from the liquid-liquid interface.

COLL 761

Nanopatterned surfaces for the templated assembly of nanostructures: From DNA-origami to quantum dot self-assembly

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The controlled self-assembly of nanostrucutres on surfaces with nanometer resolution is of great interest in the fields of nanoscience and nanotechnology.

Here we describe different strategies to control the immobilization of nanostructures on lithographically defined, biochemically functionalized metal nanopatterns.

Using electron-beam and nanoimprint lithography we fabricated sub-10nm metal dots arranged in multiple configurations.

DNA nanostrucutres (such as DNA-origami) have been assembled with high precision via hybridization in situ on properly funnctioanlized nanodots. The DNA-origami employed functioned as a model-system for the self-assembly of nanorods on metal-nanodot pairs: we characterized the self-assembly via fluorescence microscopy and Atomic Force Microscopy.

Similarly, we have developed a platform for the self-assembly of Quantum Dots (QDs) on nanopatterned surfaces. . The method here presented yields control at the single dot level to achieve predominantly single particle structures consisting of a QD coupled to a metal nanoparticle (MNP).

The high density and resolution achievable with our platform/s can find general application for the self-aasembly of other nanocrystals, and nano-moieties

COLL 762

New class of self-assembled monolayers (SAMs) based on dithiophosphinic acids (DTPAs) with functionalized tail groups

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We present the formation of new self-assembled monolayers (SAMs) on gold that feature nanoscale control of the SAM composition as well as the structure normal to the substrate. Our studies use dithiophosphinic acids (RR'P(S)SH), which spontaneously form SAMs by chelating to the gold surface. The use of different R and R' groups yield to unsymmetrical DTPAs, which form SAMs with a 50:50 mixture of the two groups. Characterization methods of the DTPA SAMs are made by using x-ray photoelectron spectroscopy (XPS) reflection-absorption infrared spectroscopy (RAIRS), contact angle measurements and electrochemical impedance spectroscopy (EIS). We will discuss potential uses for these new SAMs.

COLL 763

Reversible photoinduced twisting of metal-coated molecular crystal microribbons

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Molecular crystal microribbons formed by 9-anthracenecarboxylic acid (9AC) show reversible twisting by irradiating and turning-off 440nm light, which originates from a reversible [4+4] photodimerization. For applications of these microribbons, for example as photomechanical actuators, ways to connect molecular crystals to external objects need to be developed without sacrificing the reversible photomechanical properties of these molecular crystals. A simple strategy for this purpose is to coat thin gold layer on the surface of the molecular crystal and use this gold layer as an interface for attaching external molecules. Molecular crystals are formed by slowly evaporating a solvent (ethyl acetate) of 1.9 mg/ml solution on a clean water surface in a Petri dish. These microribbons are collected on an Anodisc filter and dried under vacuum. A gold layer of 10 nm thickness was deposited using e-beam evaporation, and the supporting Anodisc filter was dissolved in a 50% phosphoric acid solution. With a gold layer on the surface, the 9AC molecular crystals maintain their reversible twisting behavior. It is expected that external molecules with thiol groups can be immobilized onto the surface of these gold-coated microribbons and provide them with various functionalities. The coating of the microribbons with a magnetic metal like Ni will also be described, so that the ribbons can be moved using an external magnetic field.

COLL 764

Sub-100 nm controlled patterning of functionalized gold nanorods on polymer-derived surface patterns

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Directed and Self assembly concepts provide intriguing avenues to fabricate translationally-ordered nanoparticles arrangements, but lack the robustness to deliver complex spatial organization that is comparable to traditional lithographic concepts. The crucial challenge is to determine how to best synergize the salient features of assembly and lithography to provide ordered arrays, across macroscopic length scales so as to enable mass production of functional devices. Here, the assembly of gold nanorods (AuNR) (width ~15-30 nm, aspect ratio ~2-6, nanomolar aqueous dispersion) onto sub-100 nm polymer derived surface patterns (PDSP) is discussed. Using a site-specific functionalization chemistry to tune the surface property of the AuNR, CTAB-free-PEG-AuNR, PEG-mercaptosulfonate (PEG-MS-AuNR) and MS-AuNR afford adsorption

contrast to various hydrophilic and hydrophobic polymer regions. This preferential interaction enables selective AuNR adsorption and thus replication of the underlying PS-P2VP down to 25 nm line widths. In contrast to prior studies on spherical nanoparticles, the NR organization and orientation on the chemical contrast pattern strongly depend on both size and pitch of the pattern, the size and aspect ratio of AuNR, the surface functionalities as well as electrolyte content. For example, with the P2VP pattern width 100 nm, 50 nm and 25 nm, MS-AuNR (aspect ratio 2.5) will assemble perpendicular, tilted or parallel to the P2VP pattern axis respectively. Similarly, helical structures are obtained from anisotropic interaction and the confinement effect. Large-scale organization of such patterns provide novel anisotropic optical properties arising from hybridized plasmon modes associated with the engineered coupling of the AuNR plasmon resonances.