Electrochemical Studies of Langmuir–Blodgett Thin Films of Electroactive Nanoparticles

Shaowei Chen†

Department of Chemistry, Southern Illinois University, Carbondale, Illinois 62901-4409

Received May 10, 2001. In Final Form: July 18, 2001

Thin films (monolayers and multilayers) of ω-ferrocenated gold nanoparticles were fabricated by using the Langmuir–Blodgett technique. The transfer of nanoparticle layers onto a solid substrate surface was quite efficient for the first few layers, exhibiting a proportional increase of optical absorption in the UV–vis range. The interfacial dynamics of the nanoparticle monolayers was studied by using electrochemical methods where the surface reorganization was ascribed to the particle molecular mobility due to relatively weak interparticle interactions. With depositions of more nanoparticle layers, the particle thin films became less conductive, resulting in the anodic shift of the ferrocene formal potential. Because of the compact characteristics of the nanoparticle thin films, not all ferrocene sites were active and accessible, and the corresponding voltammetric currents varied only slightly with more particle layers.

Introduction

The versatile LB technique should be able to be extended to electroactive nanoparticles as well; however, this subject has not received extensive attention so far. The major motivation comes from the more complicated chemical functionalization of the nanoparticle assemblies. For instance, ferrocene has been used quite extensively as a model system in the investigation of interfacial electron-transfer kinetics. One of the typical approaches is based on immobilizing the ferrocene moieties onto electrode surfaces through an aliphatic chain where the separation of reaction products and the detection of electron-media-

1 E-mail: schen@chem.siu.edu.

1 See all the review articles in the February 16, 1996 and November 24, 2000 issues of Science.


to their two-dimensional counterparts, the ferrocene moieties are “concentrated” on the nanoscale particle surface. Previous electrochemical studies of ferrocenecentered nanoparticles in solutions have shown that the particle-bound ferrocene moieties undergo (independent) successive 1-e redox reactions due to the rapid spinning of the nanoparticles in solutions.

However, when the particles are immobilized onto a substrate surface, due to the three-dimensional (3D) nature of the particle core, the associated interfacial electron transfer between the ferrocene moieties and the electrode might be complicated by the interactions with electrolyte ions (charge compensation, for instance) as well as double-layer effects. The spatial distribution of the ferrocene moieties on particle surface is anticipated to lead to the variation of the energetic states, demonstrated in different redox (over)potentials. In addition, in multilayer thin films, the electrochemical responses of the electroactive moieties buried within the thin films might be further complicated by ion penetration/compensation as well as charge propagation. Thus, in this report, we describe a series of electrochemical studies of Langmuir thin films of ferrocenecentered gold nanoparticles, where effects of the particle film thickness on the ferrocene electrochemistry will be investigated. In particular, the electroactive ferrocene moieties will serve as the molecular probe to electrochemically examine the interfacial dynamics of the MPC surface thin films.

**Experimental Section**

**Materials Preparation.** All chemicals and solvents (Fisher/ACROS) were used as received except for potassium nitrate (KNO₃) which was recrystallized twice prior to use. Water was supplied with a Barnstead Nanopure water system (18.3 MΩ). Gold nanoparticles (diameter ~2 nm, characterized by transmission electron microscopic measurements) protected with a monolayer of n-octanethiolates (C₈Au MPCs) were synthesized by following a literature route. Multiple copies of 8-mercaptotoclyferrocene (HSC₈Fc) were incorporated into the particle protecting monolayer by using ligand place-exchange reactions with the resulting nanoparticles denoted C₈FcAu. The final surface concentration was found to be approximately 5%, corresponding to an average of 4.6 Fc moieties per particle as characterized by proton nuclear magnetic resonance (¹H NMR) measurements. Gold thin films were prepared by vapor-depositing ca. 200 nm of gold onto cleaned microscope glass slides.

**Fabrications of Particle Surface Layers.** The particle surface layered structures were constructed by using the Langmuir—Blodgett technique with a NIMA 611D LB trough. A particle solution of 1.75 mg/mL (ca. 23 μM) was prepared by dissolving the particles in hexane, typically 50–70 μL of which was spread onto the water surface with a Hamilton microliter syringe. At least 20 min was allowed for solvent evaporation before the first compression isotherm was acquired. The time interval between consecutive compression cycles was also kept at least 20 min. The compressing rate was 20 cm²/min, where the steep rising slope suggests an increase drastically, where the steep rising slope suggests the rigidity of the particle close-packed thin films. By protection monolayer by using ligand place-exchange reactions with the resulting nanoparticles denoted C₈FcAu. The final surface concentration was found to be approximately 5%, corresponding to an average of 4.6 Fc moieties per particle as characterized by proton nuclear magnetic resonance (¹H NMR) measurements. Gold thin films were prepared by vapor-depositing ca. 200 nm of gold onto cleaned microscope glass slides.

**Results and Discussion**

We begin with an investigation of the phase behaviors of the particles on the water surface, followed by optical and electrochemical studies of the particle assemblies deposited by using the Langmuir—Blodgett technique. Effects of the thickness of particle layers will be investigated. The interfacial dynamics of the MPC thin films deposited onto electrode surfaces will also be discussed.

**Langmuir Thin Films.** Figure 1 shows a representative surface pressure (π)—area (A) isotherm of the above C₈FcAu nanoparticles on a water surface, which is quite similar to those observed with simple alkanethiolate-protected gold nanoparticles. One can see that, at surface area greater than 12 nm²/MPC, the surface pressure is virtually zero, indicating a two-dimensional gaseous phase of the particles on the water surface. However, at area smaller than 12 nm²/MPC, the surface pressure starts to increase drastically, where the steep rising slope suggests the rigid nature of the particle close-packed thin films. By assuming a hexagonal distribution of the particles in the thin films (Figure 1, inset), this takeoff area (12 nm²/MPC) corresponds to a center-to-center distance of about 3.72 nm. As the fully extended chain length of an octanethiolate is 1.01 nm (calculated by Hyperchem), this distance is somewhat smaller than the nanoparticle molecular diameter (core + two monolayer ligands),

![Graph](image)

**Figure 1.** Langmuir isotherm of C₈FcAu particles on water surface. 70 μL of 1.75 mg/mL particle solution was spread onto the water surface. Compression rate 20 cm²/min. Dash lines depict the deposition pressure and surface area. Inset shows a schematic of the structure of the nanoparticle assemblies on the water surface.

Concentrated particle solutions prepared in benzene-d₆, where the absence of sharp peaks indicated the samples were spectroscopically clean (of free ligands). In addition, the peak areas of the alkyl and ferrocenyl moieties were used to calculate the surface concentration of ferrocenecentered ligands after exchange reactions. UV–vis spectroscopy was performed with an ATI Unicam (UV4) UV–vis spectrometer with a resolution of 2 nm. A blank glass slide was used as the reference.

**Electrochemical Measurements.** Electrochemical measurements were carried out with a BAS 1008/W electrochemical workstation. The gold thin films (with deposited particle layers) were used as the working electrode, a Ag/AgCl (3 M NaCl, from BAS) as the reference, and a Pt coil as the counter electrode. The electrolyte solution (0.1 M KNO₃) was deaerated for at least 20 min with a water-saturated N₂ stream and blanketed with a N₂ atmosphere during the entire experimental process.

**Spectroscopic Measurements.** ¹H NMR spectroscopy was carried out with a Varian 300 VX NMR spectrometer with a sample probe to electrochemically examine the interfacial dynamics of the MPC surface thin films.
indicating the initiation of ligand intercalation at this surface area, leading to the observed sharp increase in surface pressure with further compression.

A second transition starts at 10.5 nm²/MPC, with a somewhat smaller rising slope. This might be ascribed to the further ligand intercalation between neighboring particles leading to the formation of solidlike dose-packed MPC thin films on the water surface. In fact, on the water surface, brown MPC thin films are very visible.

The particle monolayers were then deposited onto a glass slide using the Langmuir-Blodgett (LB) technique (vertical deposition) at 8 mN/m with a lifting speed of 1 mm/min. Figure 2A shows the optical responses of the resulting particle LB assemblies. While the surface plasmon band of nanosized gold particles is not very well-defined here, partly due to the small particle core size (ca. 2 nm in diameter), the absorption profiles do exhibit a Mie character, where the absorption intensity decreases exponentially with decreasing photon energy. In addition, the absorption intensity at 520 nm (the surface plasmon band of nanosized gold particles) shows an exponential decrease with a peak splitting of only 20 mV, suggesting a very facile electron-transfer reaction. These peaks are ascribed to the oxidation/reduction of the particle-bound ferrocene moieties, where the peak currents are found to increase linearly with potential sweep rate (Figure 4), consistent with a surface-confined system. From the slope (Figure 4B), one can estimate the effective surface coverage of ferrocene moieties as \( \Gamma_{\text{Fc}} = 3.87 \times 10^{-13} \) molecules/cm²; hence, the MPC surface coverage (\( \Gamma_{\text{MPC}} \)) is 8.41 \times 10^{-12} particles/cm², corresponding to an effective particle area of 11.9 nm², somewhat larger than the original MPC area during LB deposition (10.7 nm², Figure 1). This might be accounted for by at least two possibilities; e.g., MPC molecular area expanded due to interfacial dynamics (relaxation), and/or part of the MPC-supported ferrocene moieties were not accessible and active (vide infra).

Interfacial Dynamics. As the MPC molecules in these LB thin films are not chemically cross-linked to each other, the particles might exhibit some degree of mobility when deposited onto the substrate surface, though not as free as in solution. This could lead to particle reorganization (i.e., annealing) and be monitored by electrochemical measurements using the electroactive ferrocene moieties as the molecular probes. Figure 3 shows the cyclic voltammogram of a C8FcAu particle monolayer (B) freshly deposited onto a gold thin film electrode in 0.10 M KNO₃. One can see that compared to that at the same bare electrode (A) the charging current within the potential range of 0 to +0.5 V is suppressed substantially, indicating the coating of organically functionalized gold MPCs onto the electrode surface. In addition, a pair of voltammetric peaks are observed at +0.36 V with a peak splitting of only 20 mV, suggesting a very facile electron-transfer reaction. These peaks are ascribed to the oxidation/reduction of the particle-bound ferrocene moieties, where the peak currents are found to increase linearly with potential sweep rate (Figure 4), consistent with a surface-confined system. From the slope (Figure 4B), one can estimate the effective surface coverage of ferrocene moieties as \( \Gamma_{\text{Fc}} = 3.87 \times 10^{-13} \) molecules/cm²; hence, the MPC surface coverage (\( \Gamma_{\text{MPC}} \)) is 8.41 \times 10^{-12} particles/cm², corresponding to an effective particle area of 11.9 nm², somewhat larger than the original MPC area during LB deposition (10.7 nm², Figure 1). This might be accounted for by at least two possibilities; e.g., MPC molecular area expanded due to interfacial dynamics (relaxation), and/or part of the MPC-supported ferrocene moieties were not accessible and active (vide infra).

Additionally, this ferrocene surface concentration corresponds to 20% of the approximate maximum coverage of \( \omega \)-mercaptoalkyl ferrocene derivatives self-assembled onto flat gold surfaces. The appearance of a single pair of voltammetric waves for the ferrocene sites in the LB monolayers suggests a similarity of the energetic states of these surface electroactive groups. In our earlier (unpublished) studies where a compact monolayer of \( \omega \)-ferrocenated particles was formed by chemisorptive linkages to the electrode surface (particles were first rendered surface active with peripheral thiol groups by

surface coverage. There appear to be at least two mixed monolayers of phenomena were also reported with two-dimensional systems. Despite the fact that the particle layers were interactions by thiols on gold in the self-assembled particles and the electrode surface mainly involved weak interactions between the particles and between the degree of conformational mobility, in part, because the deposited particle molecules might still possess some possibilities to account for the discrepancy observed here. First, the interfacial charging current (within 0 to +0.3 V) actually decreases upon the aging of the monolayer, suggesting some surface rearrangement of the deposited particle molecules. This is akin to potential-induced annealing. The driving force of these particle rearrangements seems likely to originate from the bulky ferrocene sites, which, when oxidized (to positively charged ferrocenium), became energetically less favorable to stay in a hydrophobic environment and hence less likely to have an interpenetration conformation with the monolayer ligands of neighboring particles. This deintercalation leads to the more spread-out of MPC molecules and enhances hydrophobic interactions between the surface particle molecules, consequently decreasing the double-layer charging current (by reducing the electrode surface defect sites, for instance). This is also consistent with the above observation of expanded MPC molecular areas.

Second, the voltammetric peaks of the ferrocene groups became much broader and the formal potential shifted anodically (E°' = +0.40 V). Considering the suppression of the double-layer current envelope discussed above, it is rather unlikely that the decrease in ferrocene faradaic current is due to particle loss from the electrode surface. Additionally, due to the hydrophobic nature of the nanoparticles, it is energetically unfavorable that the particles would desorb from the electrode surface into the aqueous solution. Also, the peak potential splitting appears to be virtually unchanged, suggesting a thermodynamic rather than a kinetic effect. In earlier studies involving self-assembled monolayers of ferrocene-terminated alkanethiols and n-alkanethiol derivatives at relatively high ferrocene surface coverage.10,11 There appear to be at least two possibilities to account for the discrepancy observed here. First, it might be attributed to the fact that the LB-deposited particle molecules might still possess some degree of conformational mobility, in part, because the interactions between the particles and the electrode surface mainly involved weak van der Waals forces, as compared to the chemisorptive interactions by thiols on gold in the self-assembled systems.10,11 Despite the fact that the particle layers were deposited at relatively high surface pressures (e.g., 8 mN/m), not all particles appeared to be in the crystalline configuration, i.e., intercalated to each other, due to particle size dispersity.7a Thus, in this case, part of the particle assemblies might be free to rotate on the electrode surface (though unlikely to desorb from the electrode surface), which might then help initiate the interfacial dynamic transition of the MPC monolayers, rendering the ferrocene sites accessible to the electrode electron. A second possibility is that the initial LB thin film might possess some defects which facilitate ion transport for charge compensation during the electrode oxidation/reduction of the ferrocene groups (more discussion below).

The dynamic characters of the electrode-supported particle assemblies were further observed voltammetrically. Figure 3C shows the cyclic voltammogram of the above same particle monolayer assemblies after ca. 20 min of potential sweeps. Compared to that observed with a freshly deposited MPC monolayer (B), there are two aspects that warrant attention here. First, the interfacial charging current (within 0 to +0.3 V) actually decreases upon the aging of the monolayer, suggesting some surface rearrangement of the deposited particle molecules. This is akin to potential-induced annealing. The driving force of these particle rearrangements seems likely to originate from the bulky ferrocene sites, which, when oxidized (to positively charged ferrocenium), became energetically less favorable to stay in a hydrophobic environment and hence less likely to have an interpenetration conformation with the monolayer ligands of neighboring particles. This deintercalation leads to the more spread-out of MPC molecules and enhances hydrophobic interactions between the surface particle molecules, consequently decreasing the double-layer charging current (by reducing the electrode surface defect sites, for instance). This is also consistent with the above observation of expanded MPC molecular areas.

Figure 4. (A) Cyclic voltammograms of the freshly deposited C8F4Au MPC monolayer (as in Figure 3B) in 0.10 M KNO₃ at various potential sweep rates. (B) Variation of the voltammetric peak currents with potential scan rate. Line is the linear regression.

Incorporating multiple copies of alkanedithiols into the particle protecting monolayer through exchange reactions, the resulting electrochemical measurements revealed two pairs of voltammetric waves which were ascribed to the variation of ferrocene energetic states due to spatial distribution on the particle surface. Similar phenomena were also reported with two-dimensional mixed monolayers of n-ferrocenated alkanethiols and n-alkanethiol derivatives at relatively high ferrocene surface coverage.10,11 There appear to be at least two possibilities to account for the discrepancy observed here. First, it might be attributed to the fact that the LB-deposited particle molecules might still possess some degree of conformational mobility, in part, because the interactions between the particles and the electrode surface mainly involved weak van der Waals forces. As compared to the chemisorptive interactions by thiols on gold in the self-assembled systems.10,11 Despite the fact that the particle layers were deposited at relatively high surface pressures (e.g., 8 mN/m), not all particles appeared to be in the crystalline configuration, i.e., intercalated to each other, due to particle size dispersity. Thus, in this case, part of the particle assemblies might be free to rotate on the electrode surface (though unlikely to desorb from the electrode surface), which might then help initiate the interfacial dynamic transition of the MPC monolayers, rendering the ferrocene sites accessible to the electrode electron. A second possibility is that the initial LB thin film might possess some defects which facilitate ion transport for charge compensation during the electrode oxidation/reduction of the ferrocene groups (more discussion below).

The dynamic characters of the electrode-supported particle assemblies were further observed voltammetrically. Figure 3C shows the cyclic voltammogram of the above same particle monolayer assemblies after ca. 20 min of potential sweeps. Compared to that observed with a freshly deposited MPC monolayer (B), there are two aspects that warrant attention here. First, the interfacial charging current (within 0 to +0.3 V) actually decreases upon the aging of the monolayer, suggesting some surface rearrangement of the deposited particle molecules. This is akin to potential-induced annealing. The driving force of these particle rearrangements seems likely to originate from the bulky ferrocene sites, which, when oxidized (to positively charged ferrocenium), became energetically less favorable to stay in a hydrophobic environment and hence less likely to have an interpenetration conformation with the monolayer ligands of neighboring particles. This deintercalation leads to the more spread-out of MPC molecules and enhances hydrophobic interactions between the surface particle molecules, consequently decreasing the double-layer charging current (by reducing the electrode surface defect sites, for instance). This is also consistent with the above observation of expanded MPC molecular areas.

Second, the voltammetric peaks of the ferrocene groups became much broader and the formal potential shifted anodically (E°' = +0.40 V). Considering the suppression of the double-layer current envelope discussed above, it is rather unlikely that the decrease in ferrocene faradaic current is due to particle loss from the electrode surface. Additionally, due to the hydrophobic nature of the nanoparticles, it is energetically unfavorable that the particles would desorb from the electrode surface into the aqueous solution. Also, the peak potential splitting appears to be virtually unchanged, suggesting a thermodynamic rather than a kinetic effect. In earlier studies involving self-assembled monolayers of ferrocene-terminated alkanethiols and n-alkanethiol derivatives at relatively high ferrocene surface coverage.10,11 There appear to be at least two possibilities to account for the discrepancy observed here. First, it might be attributed to the fact that the LB-deposited particle molecules might still possess some degree of conformational mobility, in part, because the interactions between the particles and the electrode surface mainly involved weak van der Waals forces. As compared to the chemisorptive interactions by thiols on gold in the self-assembled systems.10,11 Despite the fact that the particle layers were deposited at relatively high surface pressures (e.g., 8 mN/m), not all particles appeared to be in the crystalline configuration, i.e., intercalated to each other, due to particle size dispersity. Thus, in this case, part of the particle assemblies might be free to rotate on the electrode surface (though unlikely to desorb from the electrode surface), which might then help initiate the interfacial dynamic transition of the MPC monolayers, rendering the ferrocene sites accessible to the electrode electron. A second possibility is that the initial LB thin film might possess some defects which facilitate ion transport for charge compensation during the electrode oxidation/reduction of the ferrocene groups (more discussion below).

The dynamic characters of the electrode-supported particle assemblies were further observed voltammetrically. Figure 3C shows the cyclic voltammogram of the above same particle monolayer assemblies after ca. 20 min of potential sweeps. Compared to that observed with a freshly deposited MPC monolayer (B), there are two aspects that warrant attention here. First, the interfacial charging current (within 0 to +0.3 V) actually decreases upon the aging of the monolayer, suggesting some surface rearrangement of the deposited particle molecules. This is akin to potential-induced annealing. The driving force of these particle rearrangements seems likely to originate from the bulky ferrocene sites, which, when oxidized (to positively charged ferrocenium), became energetically less favorable to stay in a hydrophobic environment and hence less likely to have an interpenetration conformation with the monolayer ligands of neighboring particles. This deintercalation leads to the more spread-out of MPC molecules and enhances hydrophobic interactions between the surface particle molecules, consequently decreasing the double-layer charging current (by reducing the electrode surface defect sites, for instance). This is also consistent with the above observation of expanded MPC molecular areas.

Second, the voltammetric peaks of the ferrocene groups became much broader and the formal potential shifted anodically (E°' = +0.40 V). Considering the suppression of the double-layer current envelope discussed above, it is rather unlikely that the decrease in ferrocene faradaic current is due to particle loss from the electrode surface. Additionally, due to the hydrophobic nature of the nanoparticles, it is energetically unfavorable that the particles would desorb from the electrode surface into the aqueous solution. Also, the peak potential splitting appears to be virtually unchanged, suggesting a thermodynamic rather than a kinetic effect. In earlier studies involving self-assembled monolayers of ferrocene-terminated alkanethiols and n-alkanethiol derivatives with coadsorbed electroinactive n-functionalized n-alkanethiol derivatives,10,11 it was found that, in aqueous electrolyte solutions, the formal potential of the ferrocene moiety also shifted anodically when the n-terminal groups of the coadsorbates became less polar. This observation was interpreted on the basis of the combined effects of local ion solvation and double-layer potential distribution.10,11,13 These effects might also account for the present observations with the LB particle layers where the enhanced hydrophobic interaction resulting from the structural rearrangements leads to more difficult penetration for electrolyte ion for charge compensation. The broad voltammetric peak widths might reflect the wide spatial distribution of ferrocene sites on the electrode surface due to the three-dimensional nature of the nanoparticle cores, suggesting that after the surface structural reorganization the particles became less mobile.

Similar dynamic reorganizations were also observed with multilayer structures (not shown); however, the ferrocene voltammetric currents decreased to a much less extent with more MPC layers. This might be understood in terms of the decrease in MPC molecular mobility,
This is drastically smaller than the theoretical 1.59:1.52 with the subscripts referring to the number of surface-confined systems, the slopes (vide ante). However, surprisingly, the voltammetric currents (Figures 5 and 6) are proportional with the number of MPC layers, which is rather counterintuitive. While the ferrocene faradaic currents increase linearly with potential sweep rates with varied layers of C8FcAu MPCs freshly deposited onto a gold thin film electrode. First, one can see that the double-layer charging current within the potential range of 0 to +0.5 V decreases with the deposition of additional MPC layers, consistent with the presence of more organically functionalized MPC molecules onto the electrode surface (vide ante). However, surprisingly, the voltammetric current due to the ferrocene moieties does not increase proportionally with the number of MPC layers, which is rather counterintuitive. While the ferrocene faradaic currents increase linearly with potential sweep rates with varied layers of C8FcAu MPCs (Figure 6), again, consistent with surface-confined systems, the slopes (S) normalized to that with an MPC monolayer (Figure 4) are S₁:S₂:S₃:S₄ = 1.187:1.59:1.52 with the subscripts referring to the number of MPC layers. This is drastically smaller than the theoretical value of S₁:S₂:S₃:S₄ = 1:2:3:4, which is anticipated from the aforementioned optical measurements (Figure 2) by assuming that all ferrocene sites are active and accessible. This is in great contrast to colloidal multilayers fabricated by alternating-dipping self-assembling method with electroactive species incorporated in between the particle layers, where the voltammetric currents due to the faradaic processes increase linearly with the number of particle layers, indicating that all sites are accessible in the electron-transfer reactions and the porous nature of the resulting colloidal thin films. The discrepancy observed here suggests that in the LB thin films of nanoparticles, due to ligand intercalation, some ferrocene sites are buried within a hydrophobic environment which creates a large energetic barrier for charge transfer as well as charge compensation. In other words, the film behaves less conductive with more MPC layers, resulting in the decrease of accessible ferrocene sites and hence smaller voltammetric currents (Figures 5 and 6). This might also account, at least in part, for the anodic shift of the formal potential of the ferrocene moieties with more MPC layers (Figure 5, inset), where an overpotential of 15 mV is found with each additional layer of MPC molecules.

It should be noted that, of these active ferrocene sites, their peak splittings remain very small (~40 mV), again indicating that the effect of the local environmental variation is reflected thermodynamically rather than kinetically, as mentioned earlier.

**Concluding Remarks**

Using the electroactive ferrocene moieties as the molecular probes, electrochemical investigations were carried out to investigate the interfacial dynamics of nanoparticle Langmuir–Blodgett thin film. The deposition of nanoparticle molecules onto the substrate surface was quite successful only in the first few layers as characterized by optical absorption measurements. It was found that in the nanoparticle monolayers the molecular mobility due to relatively weak interparticle interactions led to the potential-induced reorganization of the particle molecules, reflected in a decrease in the electrode double-layer charging current and the surprising suppression of the faradaic currents of the ferrocene moieties. With the deposition of additional nanoparticle layers, the particle thin films became less conductive, leading to the anodic shift of the ferrocene formal potential as well as the drastic decrease in ferrocene faradaic currents.

**Acknowledgment.** The author gratefully acknowledges the following agencies for their generous financial support: the National Science Foundation (CAREER Award), the Office of Naval Research, the Petroleum Research Fund, administered by the American Chemical Society, the Illinois Department of Commerce and Community Affairs, and SIU Materials Technology Center. S.C. is a Cottrell Scholar of Research Corporation.

**Supporting Information Available:** Differential pulse voltammogram (DPV) of four LB layers of ferrocnated gold nanoparticles in 0.10 M KNO₃. This material is available free of charge via the Internet at http://pubs.acs.org.

LA0107042

(19) In the case of four layers of gold nanoclusters, the ferrocene peak potential was determined by differential pulse voltammetry (DPV). Please see the Supporting Information for details. Also, in a dropcast thick film (~um) of the same ω-ferrocenated nanoparticles, the formal potential of the ferrocene moieties was found at an even more positive position, ~0.45 V.