Electrochemical Observation of a Metal/Insulator Transition by Scanning Electrochemical Microscopy

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We report the novel use of the scanning electrochemical microscope (SECM) to follow the compression of a monolayer of monodisperse silver thiol-capped nanoparticles on a Langmuir trough. SECM allowed the direct electrochemical visualization of the lateral connectivity of the particles in the film at the air/water interface through monitoring the transition from negative feedback (insulating substrate) to positive feedback (conducting substrate) at the Pt SECM tip, with ferrocene methanol (FcMeOH) as the redox mediator, as the interparticle separation decreased by compressing the film. The transition from an insulating to conductive behavior with compression could thus be followed.

Recently, it has been demonstrated that it is possible to reversibly tune a monolayer of silver thiol-capped nanoparticles,[1,2] so-called monolayer protected clusters (MPCs)[3] or quantum dots (QDs),[4] through the insulator−metal (I−M) transition using Langmuir techniques. This paper reports the novel use of the scanning electrochemical microscope (SECM)[5,6] to follow this transition. SECM enables direct electrochemical visualization of the lateral connectivity of a film of MPCs at the air/water interface through monitoring the transition from negative feedback (insulating substrate) to positive feedback (conducting substrate) at an SECM tip as the interparticle separation is decreased by compressing the film.

Currently, there is considerable interest in the electronic properties of surfactant stabilized metallic nanoparticles.[3,4,7] Assemblies of such MPCs are believed to have the potential to form the structural elements for electronic nanodevices, due to the sub-attofarad capacitance and the resulting single electron charging characteristics.[4,7,8] Murray and co-workers have established that dissolved gold MPCs demonstrate quantized double layer charging and that the term *diffusing nanoelectrodes* is readily applicable to monodisperse preparations.[3,9,10] By electronically contacting metal MPCs via redox-active molecules, Schiffrin's group has recently constructed a nanoscale electronic switch.[8,11,12] Also, much work is devoted to understanding the factors influencing the spontaneous self-organization of MPCs to form ordered nanocrystal superlattices with the ultimate goal of tuning the electronic properties of the resulting array.[13−22]

The use of Langmuir techniques to control the lateral separation of 2D arrays of thiol capped metallic particles was initially proposed by both the Murray[23] and Heath[24] groups for gold and silver QDs, respectively. Heath and co-workers successfully demonstrated that it is possible to vary the interparticle separation of a nanocrystal assembly on a Langmuir trough by changing the surface pressure.[24] A Mott−Hubbard insulator−metal transition, where the Coulombic gap closes at a critical distance between the particles, was observed by

spectroscopic and impedance methods.[1,25,26] Toward the same end, Murray and co-workers studied the lateral connectivity of gold QD films, that is the propagation of electrons between the individual QDs, as a function of compression using line electrodes.[23] However, in this case, no increase in conductivity was noted at the highest film compression, indicating that the particles remained insulated from each other. This lack of finding metallic behavior in this experiment may be due to polydispersity[27] of the particles and the sensitivity of the techniques used to follow the transition.

SECM is a very effective means of probing the conductivity of a substrate and offers a very convenient means of unequivocally determining insulating or metallic behavior. When the tip, immersed in a solution containing an electroactive mediator, approaches an insulator, the current decreases with tip/substrate distance, *d* (called negative feedback). When it approaches a conductor under the same conditions, the current increases with decreasing *d* (positive feedback).[5,6] In this study, a "submarine" SECM tip combined with Langmuir techniques[28,29] was used as a novel electrochemical means to follow the I−M transition.

Hexanthiol protected silver nanoparticles were prepared and size-selected as previously described.[25,30] Briefly, a two-phase reduction method[31] was employed whereby aqueous Ag^+ was phase transferred to chloroform using tetraoctlyammonium bromide as the phase transfer agent. A measured amount of dodecanethiol was subsequently added under stirring to the chloroform phase followed by the rapid addition of freshly prepared aqueous $NaBH_4$ under vigorous stirring. The reaction was allowed to proceed for 3 h after which the phases were separated and the choroform phase was filtered (0.22 µm Teflon filter) to remove bulk silver. The resulting dodecanethiol capped Ag particles were size selected using chloroform/methanol as the solvent/nonsolvent pair. After isolation of various size fractions, the long-chain thiol was place-exchanged with the shorter hexanethiol (C6). The resulting C6 capped particles were isolated by precipitation, filtered, and washed with copious amounts of methanol. A powder of the desired particles was then sonicated briefly in acetone and filtered to remove any residual organic material.[30] Particle size was determined using

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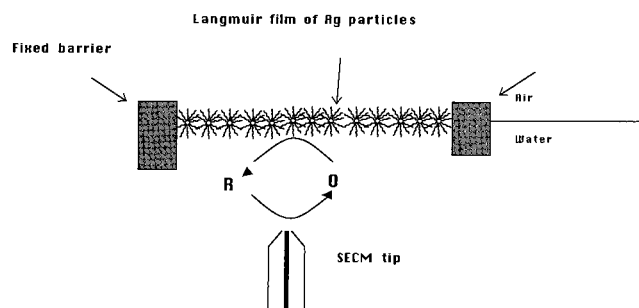
Figure 1. Schematic representation illustrating positive feedback at an inverted SECM tip on compressing a Langmuir film of Ag MPCs through the I−M transition at the air/water interface (not to scale)
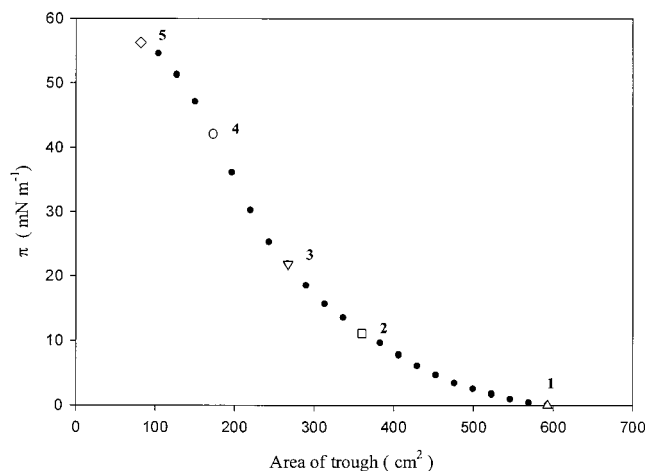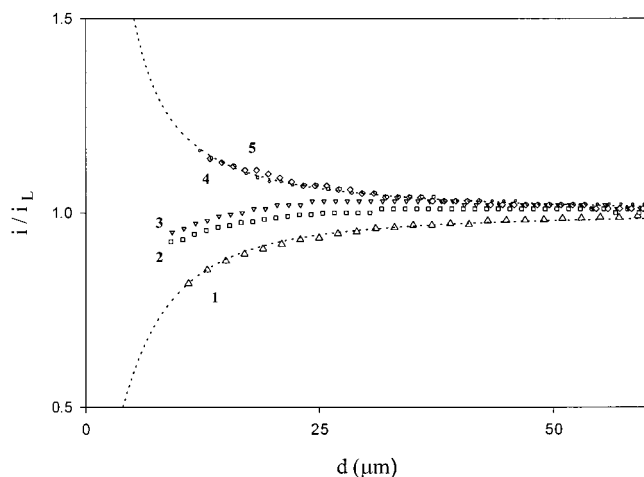

Figure 2. Surface pressure−trough area (π−A) isotherm for a film of Ag MPCs at the air/water interface. Symbols (1−5) refer to the surface pressures where approach curves were obtained.

Figure 3. SECM approach curves to the MPC film at various compressions (1−5 as in Figure 2): (1) open barrier position − 0 mN m^{-1}, (2) 11 mN m^{-1}, (3) 22 mN m^{-1}, (4) 42mN m^{-1}, and (5) 56 mN m^{-1} (closed barrier position). Dotted lines represent the theoretical approach curves to an insulator (lower) and a conductor (upper).

TEM ($d = 4 \pm 0.2$ nm) and the formation of a superlattice on the TEM grid was taken as an indication of reasonable monodispersity ($<10\%$)[15,24] (see Supporting Information). A chloroform solution of particles was spread at the air/water interface in a Lauda film balance (Brinkmann, Westbury, NY) at room temperature. Initially, the resulting film was composed of voids and islands but formed a homogeneous film with time as previously reported.[1,32] As the particles are not thermodynamically stable, particles were spread at the air/water interface immediately after preparation.[24] An insulating to conducting transition was not observed for polydisperse or aged (1 day) preparations.

 A schematic of the experimental setup is given in Figure 1. An inverted SECM tip,[28] attached to the z-direction piezo of the SECM instrument (CHI 900, CH Instruments, Austin, TX), was submerged in the well of the Langmuir trough. The subphase consisted of the base electrolyte NaCl (50 mM) with ferrocene methanol (FcMeOH) (0.25 mM) as the redox mediator. The tip was biased at the potential for the oxidation of FcMeOH and current-distance curves (i−d or approach curves), where the tip current is recorded as a function of distance between the tip and the air/water interface, were obtained in feedback mode at various film compressions.[28] The tip response was less susceptible to convective effects in the presence of the MPC film at the interface, perhaps because it damps surface waves and decreases sensitivity to air motion.

 The surface pressure-trough area isotherm and approach curves are given in Figures 2 and 3, respectively. The π−A isotherm is similar to that reported previously,[25] and the isotherm was reproducible upon several release−compression cycles. At open barrier position (zero surface pressure), negative feedback

to the MPC film was observed indicating that, as expected, the film is insulating. This fitted well to the following analytical expression describing feedback to an insulator for a tip with an RG = 5 (ratio of the overall tip diameter to that of the microdisk electrode):[33] $i/i_L = 1/[k_1 + (k_2/L) + k_3\exp(k_4/L)]$, where i an i_L are the tip current at a given tip−substrate distance, d, and in the bulk, respectively, k_1, k_2, k_3, and k_4 are constants which depend on tip RG, and L is the dimensionless tip−substrate distance. For more details, see ref 33 and references therein. As the movable barrier was closed, the surface pressure increased and approach curves were recorded at various surface pressures. At higher surface pressures (11 and 22 mN m^{-1}), less negative feedback was noted at the tip, signaling some reduction of the ferricenium cation at the film. This reduction at the portion of the film immediately above the tip occurs with oxidation of ferrocene species at other places on the film (as seen with metal surfaces). Upon further compression (42 mN m^{-1}), positive feedback was obtained, and this remained constant for a further increase in surface pressure (56 mN m^{-1}). This was in good agreement with the following analytical expression describing feedback[33] to a conductor for an RG = 5; $i/i_L = k_1 + (k_2/L) + k_3\exp(k_4/L)$, where the symbols are as given previously. Reopening the barrier to lower surface pressures resulted in the observation of negative feedback once more, confirming the reversibility of the transition. This transition from negative to positive feedback is consistent with previous reports of I−M transitions.[1,2,25] At open barrier position, the film is an insulator due to the presence of a Coulombic gap, which arises from the charging energy of the lattice sites,[32] and negative feedback is obtained. As the barrier is closed, the interparticle separation decreases resulting in a decrease in the gap until at high compressions, the gap closes giving a metallic film.[1] That is, interparticle electron transfer is too slow in the expanded film to allow effective delocalization of charge with reduction at the tip position and oxidation at more distant points on the film. With increasing pressure and decreasing interparticle distance, the electron-transfer rate increases until diffusion-controlled reduction of the ferrocenium, signaling metallic behavior, is observed. As the SECM tip approaches the metallic film, FcMeOH oxidized at the tip is reduced at the film resulting in an increase in current, i.e., positive feedback is observed.

In contrast to reports from Heath's group where the observed I−M transition was sharp, our SECM results indicate a gradual transition from the insulating to the conducting state. This may be due to the role of disorder in our film or possible kinetic effects. Disorder in the film would affect the packing density and smear out the transition.[2,34,35] The feedback response may also be dependent on the heterogeneous electron-transfer kinetics at the film/electrolyte interface. The current response depends on the rate of the reaction $Fc^+ + e^- \rightarrow Fc$ on the monolayer above the tip, the rate of the reaction $Fc - e^- \rightarrow Fc^+$ at other points on the film away from the tip, and the rate of electron transfer within the film between these points. The dependence on surface pressure suggests the latter process is rate limiting. Thus, the feedback response in the intermediate region shows incomplete turnover of tip-generated Fc^+ at the thin film. Similar SECM feedback responses have been noted for heterogeneous electron transfer at liquid−liquid,[36−38] and polymer−solution interfaces.[39] More detailed studies of the overall kinetics of the process, e.g., varying the concentration of the redox mediator,[38] are needed to obtain a more definitive description.

We have demonstrated that a "submarine" SECM tip combined with Langmuir techniques is a promising means of following the lateral connectivity of nanocrystal arrays (super-lattices). Further study will concentrate on understanding the role of the metal core and the length of the thiol cap on the observed I−M transition. In addition, SECM may enable investigation of the heterogeneous electron-transfer kinetics at the MPC film/solution interface.

Supporting Information Available: TEM image of hexanethiol capped Ag particles. This material is available free of charge via the Internet at http://www.pubs.acs.org/.

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