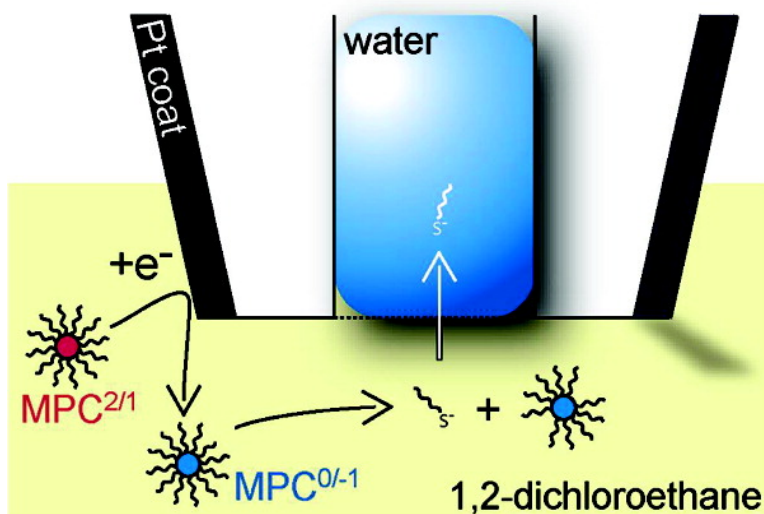Communication

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Reductive Desorption of Thiolate from Monolayer Protected Gold Clusters

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Thiol-protected gold nanoparticles, so-called *monolayer protected clusters* (MPCs), are unique in that they can be repeatedly isolated and dispersed without irreversible aggregation.[1] This extraordinary stability is due to the strength of the gold−thiol bond.[2] From extensive research on 2D self-assembled thiol monolayers on Au (SAMs), the gold−sulfur bond is broken only under extreme oxidative conditions, at high temperatures, or by electrochemical reduction.[2] MPCs are essentially 3D SAMs[3] and have been termed *freely diffusing nanoelectrodes*.[1b] The size of the MPC "electrochemical potential window" (the range of core charges where the MPC is neither decomposing nor reacting with the solvent/base electrolyte) has not been addressed to date. Here we use a novel approach based on the electrified liquid−liquid (L−L) interface as a detector to probe the reactivity of the MPC "electrode" as a function of the charge stored on the metal core. The first report of reductive desorption of thiolate attached to the Au_{147} MPCs is presented.

Hexanethiol capped Au (C6S-Au) particles were prepared as previously described ($r = 0.81$ nm, Au_{147}).[1a,4] The equilibrium or rest potential, E_{eq}, is a measure of the charge stored in the metal core.[1b] As-prepared MPCs tend to have a negative core charge; in this case, E_{eq} ca. -0.14 V vs NHE, ($MPC^{0/-1}$).[4c,5] MPCs were oxidized by bulk electrolysis to vary the core charge ($E_{eq} = 0.29$ and 0.79 V vs NHE giving $MPC^{2/1}$ and $MPC^{4/3}$, respectively).[5] The electrified water/1,2-dichloroethane (w/DCE) interface supported at the tip of a micropipet was used as a novel probe of MPC reactivity with solvent, base electrolyte, and oxygen.[6,7] Cyclic voltammograms (CVs) recorded at the w/DCE detector interface in the presence of dispersed MPCs are given in Figure 1.

It was noted that CVs recorded in the presence of as-prepared MPCs in the DCE phase *always* gave a positive current offset throughout the $\Delta_o^w\phi$ window (blue line in Figure 1). As this steady-state response is characteristic of mass transfer limitation to a disk-shaped micro interface, the current is limited by diffusion of a DCE phase anion to the interface. Offset current was not removed after exhaustive cleaning of multiple preparations and was characteristic of reduced MPCs. For a given $MPC^{0/-1}$ preparation, the current offset was proportional to the concentration. Identical CVs were obtained in the absence of oxygen, ruling out heterogeneous electron transfer with aqueous phase molecular oxygen. Measurements were repeated with isolated as-prepared Au_{38}[4c] and offset current was not observed. Thus, the small subpopulation of Au_{38} typically present in Au_{147} preparations is not the source of the offset.

The offset was *only* removed by increasing the core charge (all other experimental conditions were identical). In Figure 1, it can be seen that the response in the presence of $MPC^{2/1}$ was identical to the response observed in the absence of MPCs. From this simple measurement, we have a clear indication that a very hydrophilic anionic species ($\Delta_o^w\phi_{A^-}^0 < -200$ mV) is present in the organic

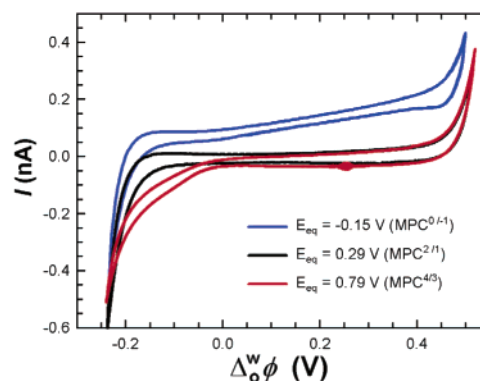**Figure 1.** CVs recorded at the w/DCE interface supported at the tip of a 25 μm diameter pipet in the absence (black line) and presence of MPCs dispersed in the DCE phase of varying core charge.[7] The base electrolyte response in the absence of added MPCs was identical to that in the presence $MPC^{2/1}$. Concentrations of $MPC^{0/-1}$, $MPC^{2/1}$, and $MPC^{4/3}$ were 95, 160, and 105 μM, respectively. Scan rate = 25 mV s^{-1}. $\Delta_o^w\phi$ is the Galvani potential difference between the phases defined as $\phi^w - \phi^o$. $MPC^{z/z\pm1}$ signifies the presence of both MPC^z and $MPC^{z\pm1}$ at this E_{eq}.

phase with the reduced MPCs that transfers to the aqueous phase throughout the $\Delta_o^w\phi$ window.[6d]

The reductive desorption of thiolate at 2D Au SAMs has been the subject of numerous reports and has been shown to be a 1e$^-$ transfer reaction (AuSR + 1e$^-$ → Au(0) + RS$^-$).[8] Here it is proposed that comparable reductive desorption of thiolate from the MPC occurs when the core is reduced. The desorbed hydrophilic thiolate is detected at the L−L interface where the offset current corresponds to the diffusion-limited transfer of the anion from the DCE phase to the aqueous phase.[8e] The equilibrium between bound and free thiolate when the core is negatively charged is perturbed by thiolate transfer (product removal), increasing the driving force for desorption. Washing the MPC solution repeatedly with water reduced the offset but never completely removed it. In separate measurements where the aqueous and DCE phases were contacted over a period of months, there was no evidence of an interfacial film, transfer of Au_{147} to the aqueous phase, or precipitation in DCE. Therefore, not all thiolates are removed from the cluster at this core charge. It has been proposed that desorption of thiolate from the defect sites (edges) on the Au crystal lattice is more facile than at terrace sites.[5b,c,9a] We propose that the response at the L−L detector interface corresponds to thiolate desorbed from defect sites with the stability of thiolate on the terraces preventing aggregation.

The L−L CV response obtained for $MPC^{4/3}$ is also given in Figure 1 (red line). A negative wave is apparent at $\Delta_o^w\phi < 0$, the height of which was proportional to the $MPC^{4/3}$ concentration. The sigmoidal wave shape is consistent with an interfacial reaction where the current is limited by MPC mass transfer to the w/DCE interface.[6c,d] Interfacial oxidation of water by $MPC^{4/3}$ is unlikely based on previous reports where scanning electrochemical micros-
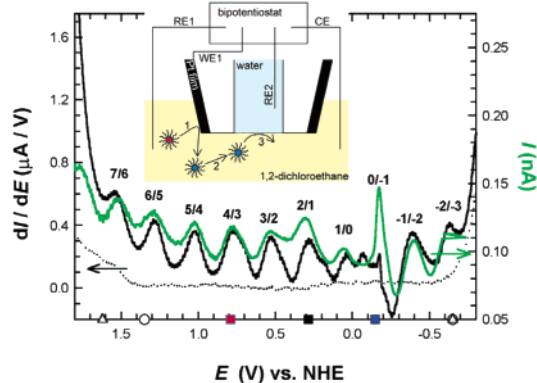
Figure 2. Derivative of the CV response obtained at the Pt coat electrode in the absence (- - -) and presence of 380 μM as-prepared MPC$^{0/-1}$ (black —) compared with the response obtained at a 25 μm diameter Pt electrode (180 μM) (green —). The equilibrium potentials of the MPCs used in Figure 1 are denoted by the squares ($\square$) and the coat electrode bias used in Figure 3a and 3b are designated by ($\triangle$) and ($\bigcirc$), respectively. A schematic of the Pt coat-pipet experimental arrangement is given in the inset.

copy was used to probe MPC reactivity at the w/DCE interface as a function of core charge.[9b] Oxidative desorption of thiolate at 2D Au SAMs has been previously reported[8d,9c−e] and it has been noted that thiol place exchange reactions at MPCs are facilitated by a positive core charge due to the desorption of Au(I)SR species.[5b,c] Oxidative desorption has been noted to be a multisptep process involving cleavage of the Au−S bond and subsequent oxidation of the alkylsulfur to sulfate species.[9c−e] The sign of the pipet current here is inconsistent with the transfer of an anionic sulfate and the wave is ascribed to the transfer of cationic Au(I)SR desorbed from the positively charged core.[5b,c] The absence of a peak in the reverse scan indicates that the transfer is irreversible.[6d]

As a further verification, the Pt coat−micropipet supported L−L interface was used to vary the core charge in situ as illustrated schematically in the inset of Figure 2a.[6b,c] This technique essentially involves MPC oxidization/reduction at the Pt coat electrolyte solution interface while concurrently recording CVs at the L−L interface. With this arrangement, the Pt coat electrode functions as a generator electrode and the electrified w/DCE interface is the collector "electrode".

An example of the derivative of the CV response obtained at the Pt coat is given in Figure 2b showing a series of regularly spaced current peaks characteristic of single electron charging of the metal core.[1c] It is comparable to the microelectrode differential pulse voltammogram (DPV) given in the same figure. The sharp spike in the DPV and dI/dE plots is in the same potential region as E_{eq} for MPC$^{0/-1}$ and is characteristic for the deposition/stripping of an electroactive film.[4c] Its appearance was dependent only on MPC concentration and not on the base electrolyte or its concentration. Core charge dependent thiolate desorption/adsorption is most likely responsible for this deposition/stripping behavior. Examples of the CV response at the detector w/DCE interface as a function of coat bias are given in Figure 3. For the oxidized MPC$^{2/1}$ (Figure 3a) with an unbiased Pt coat electrode, the pipet CV response is comparable to the base electrolyte response. Biasing the generator Pt electrode at reducing potentials induced a positive current offset response, while conversely the application of oxidation potentials does not induce offset but results in the development of a negative wave at $\Delta_o^w\phi < 0$. This measurement was then repeated with the reduced MPC$^{0/-1}$ (Figure 3b), and the same trend in the pipet CV response was noted for oxidizing and reducing Pt electrode bias.
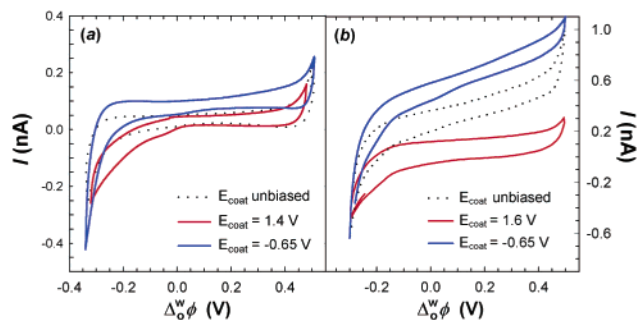

Figure 3. Pipet CV response for (a) bulk oxidized MPC$^{2/1}$ (80 μM) and (b) as- prepared MPC$^{0/-1}$ (380 μM) at various Pt coat electrode bias. Scan rate 100 mV s^{-1}.[7]

In contrast in the absence of dispersed MPCs, the pipet response was invariant with Pt coat bias (Supporting Information). These in situ measurements provide additional proof that the species detected at the L−L interface are determined *solely* by the MPC core charge. The core charges between the limits of thiolate and Au(I)SR desorptions constitute the bounds of MPC electrochemical window. The 1 V potential range of stability is comparable to that reported for 2D alkanethiolates on Au.[8a−e,9c−e]

Supporting Information Available: Additional experimental details and CVs recorded in the absence of MPCs at the coat-pipet w/DCE interface. This material is available free of charge via the Internet at http://pubs.acs.org.

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