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Quantized Double Layer Charging of Nanoparticle Films Assembled Using Carboxylate/(Cu^{2+} or Zn^{2+})/Carboxylate Bridges

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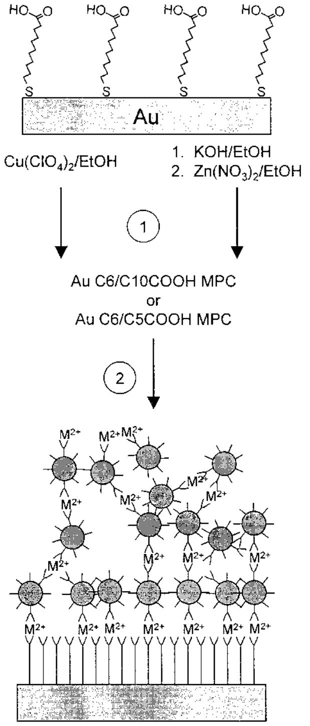
Controlled self-assembly of nanoparticles into nanoscale superstructures is an important objective.[1] Reports[2] of attachments of nanoparticle monolayers and multilayers to self-assembled monolayer (SAM) and polymer substrates have included dithiol and analogous linkers[2a−c] and polyelectrolytes,[2d] and a few examples of monolayer-protected clusters (MPCs) based on sol−gel chemistry[2e] and place-exchange reactions.[2f]

Monolayer or multilayer nanoparticle films based on ligand/metal ion/ligand linkers have not been previously described. This paper describes films of 1.6 nm diameter monolayer-protected Au clusters (MPCs), with mixed hexanethiolate/mercaptohexanoic acid (C6/C5COOH) or hexanethiolate/mercaptoundecanoic acid monolayers (C6/C10COOH),[3] that exhibit well-defined, concerted, single-electron charging of their double layers. The MPCs are attached in a two-step dip and rinse cycle (Scheme 1) to COOH-functionalized Au (and glass) substrates by carboxylate/(Zn^{2+} or Cu^{2+})/carboxylate bridges. The cycle can be repeated to attach further MPCs as desired. Depending on the concentration and soaking times of the metal ion and MPCs, multilayers can become surface-attached even in a single dip cycle.

Figure 1 shows cyclic (CV) and differential pulse (DPV) voltammetry of a submonolayer MPC film prepared in a single dip cycle using Zn^{2+}. The CV peak currents vary linearly with potential scan rate (not shown), as expected for surface-localized electrochemistry. The current peaks are interpreted as concerted, single-electron, double-layer charging of the individual MPCs immobilized in the film, analogous to previous observations for diffusing[4] MPCs, and with much better resolution than that seen[2f] for earlier immobilized MPCs. The double-layer charging occurs in single-electron steps because the MPCs have tiny individual capacitances, C_{CLU}. The slope of a plot[4b] of formal potentials from Figure 1B vs the core charge state of the cluster gives C_{CLU} = 0.62 aF/MPC, which is similar to the 0.59 aF/MPC found[4d] for solutions of the same mixed monolayer MPCs. The similarity shows that the ionic space charge formed around the MPCs upon core charging seems not appreciably affected by the metalated, immobilized environment.

Scheme 1



The quantity of immobilized MPCs can be estimated from the Figure 1A CV peak area (*) as ∼4×10^{-12} mol MPC/cm^2. Models of an MPC monolayer give (9−16) × 10^{-12} mol/cm^2, depending on assumptions about MPC chain extension. The film in Figure 1A,B thus has a fractional monolayer coverage.

Parts A and B of Figure 1 exhibit peak potential separations (ΔE_{PEAK} = 60 mV for CV and 130 mV for DPV) that are much larger than seen before[2f,4] for MPC capacitance charging. Electron tunneling between the MPC cores and the electrode in Figure 1A,B may involve a distance (a −SC10COOZnOOCC10S− bridge) that is significantly longer than any previous MPC double-layer charging architecture. We have evidence (see Supporting Information) that the observed ΔE_{PEAK} separation is plausibly interpreted as kinetic control of MPC double-layer charging.

UV−vis spectroscopy was used to monitor multilayer MPC film formation (Figure 2A). The initial spectrum (−) shows a monolayer of heavily acid-loaded C6/C5COOH (∼30/23) MPCs attached by thiolate place-exchange to a mercaptan-functionalized glass slide.[5] The second spectrum (···) is after the monolayer's immersion in first Cu^{2+} for 2 min and then in a solution of more lightly acid-loaded C6/C10COOH (∼46/7) MPCs until the absorbance became almost constant (30 min), indicating that film growth had stopped. The attachment cycle was repeated three more times (Figure 2A, three upper curves) on the same slide; the spectra shown are again for absorbance reaching a maximum.

The absorbance changes in Figure 2A are much larger than those expected for layer-by-layer film growth. The absorbance for the first layer of MPCs is $A_{300} \approx 0.03$, but subsequent dip cycles resulted in 10 to 20-fold larger absorbance increases. If all the COOH groups of the initial MPC monolayer (23/MPC) were coordinated with Cu^{2+}, then there was enough surface Cu^{2+}

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[1] Schmid, G. *J. Chem. Soc., Dalton Trans.* **1998**, 1077. (b) Ref. S-1.

[2] Grabar, K. C.; Smith, P. C.; Musick, M. D.; Davis, J. A.; Walter, D. G.; Jackson, M. A.; Guthrie, A. P.; Natan, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 1148. (b) Bethell, D.; Brust, M.; Schiffrin, D. J.; Kiely, C. *J. Electroanal. Chem.* **1996**, *409*, 137. (c) Blonder, R.; Sheeney, L.; Willner, I. *Chem. Commun.* **1998**, 1393. (d) Liu, Y.; Wang, Y.; Claus, R. O. *Chem. Phys. Lett.* **1998**, *298*, 315. (e) Yonezawa, T.; Matsune, H.; Kunitake, T. *Chem. Mater.* **1999**, *11*, 33. (f) Chen, S. *J. Phys. Chem. B* **2000,** *104*, 663. (g) Reference S-2.

[3] Mixed monolayer $Au_{140}[S(CH_2)_5CH_3]_{53-x}[S(CH_2)_nCOOH]_x$ MPCs (x = 5−18, n = 5 or 10) were synthesized according to Brust[3b] and Hostetler place-exchange[3c] reactions. (b) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whymnan, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801. (c) Hostetler, M. J.; Templeton, A. C.; Murray, R. W. *Langmuir* **1999**, *15*, 3782. (d) The MUA monolayer was formed from a 2−5 mM EtOH solution and was deprotonated with KOH/EtOH to aid Zn^{2+}-carboxylate complex formation. MPC solutions were EtOH or 1:1 EtOH:CH_2Cl_2 and all dipping steps were followed by a solvent rinse.

[4] Chen, S.; Ingram, R. S.; Hostetler, M. J.; Pietron, J. J.; Murray, R. W.; Schaaff, T. G.; Khoury, J. T.; Alvarez, M. M.; Whetten, R. L. *Science* **1998**, *280*, 2098. (b) Chen, S.; Murray, R. W.; Feldberg, S. W. *J. Phys. Chem. B* **1998**, *102*, 9898. (c) Hicks, J. F.; Templeton, A. C.; Chen, S.; Sheran, K. M.; Jasti, R.; Murray, R. W. *Anal. Chem.* **1999**, *71*, 3703. (d) Ailette Aquilla, M.S. Thesis, University of North Carolina, 1999.

[5] A layer of C6/C5COOH MPCs (∼30/23) was place-exchanged[3c] onto a mercaptan-functionalized glass slide.[5b] (b) Goss, C. A.; Charych, D. H.; Majda, M. *Anal. Chem.* **1991**, *63*, 85.

10.1021/ja0006696 CCC: $19.00

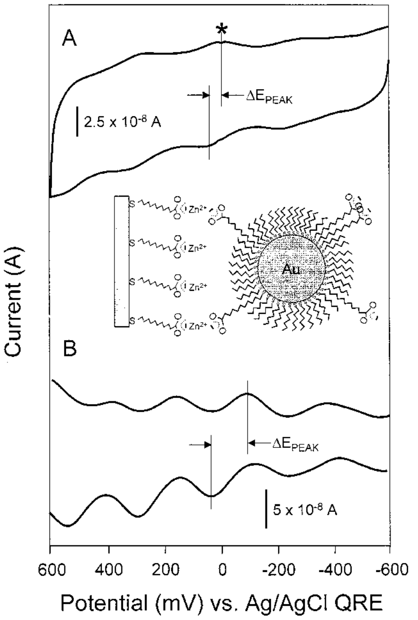

Figure 1. (A) Cyclic and (B) differential pulse voltammetry of Au C6/C10COOH MPCs (~48/5) attached with one dipping cycle to a Au (0.02 cm^2)/MUA substrate as illustrated. DC potential scan rate 50 mV/s, 0.1M Bu_4NPF_6/CH_2Cl_2.

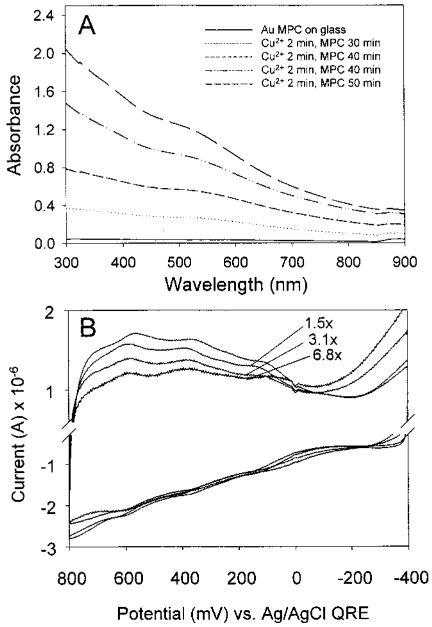

Figure 2. (A) UV−vis spectroscopy and (B) CV of the formation of Au C6/C10COOH MPC (~46/7) multilayers using Cu^{2+} linkers, on glass and Au, respectively. In (B), lower to upper curve, 5 min. Cu^{2+} exposures followed by 20, 50, 40, 30 min. MPC exposures; current scales of earlier film-forming cycles expanded for comparison. Voltammetry conditions as in Figure 1 except 100 mV/s.

to potentially bind 23 more MPC monolayers (assuming 1 Cu^{2+}/MPC) when exposed to the MPC solution. The excess surface-coordinated Cu^{2+} must migrate out toward the MPC solution to promote multilayer growth. While the data suggest that this must occur, the detailed mechanism of Cu^{2+} migration and multilayer growth is not understood.

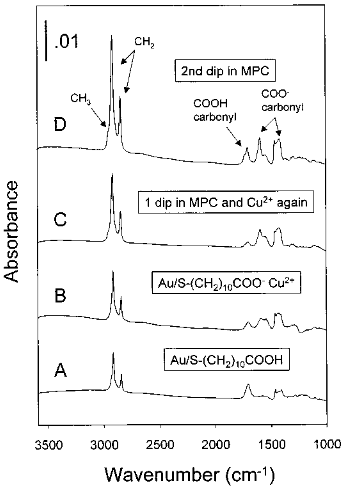

Figure 3. FTIR-ERS spectra showing attachment of Au C6/C5COOH MPCs (~35/18) to a Au/MUA surface using Cu^{2+} linkers; soaking steps indicated in the figure.

MPC double-layer charging currents in CVs of C6/C10COOH MPC multilayers similarly formed on an Au electrode (Figure 2B) increase by increments (bottom to top) very similar to the absorbance increases seen in Figure 2A. The current scales have been chosen to show that, while the currents needed to charge the thicker films of MPCs increase, only a portion of the film (presumably that nearest the electrode) displays a resolved single-electron pattern.

The surfaces in Figure 2A and 2B were dark purplish films. Exposure of similarily prepared surfaces to dilute acetic acid restores the background CV and UV−vis spectrum, showing that the MPC multilayer film formation is entirely reversible.

FTIR-external reflectance spectroscopy of MPC film formation with C6/C5COOH MPCs and Cu^{2+}-bridging ions is shown in Figure 3. The initial carboxylic acid C=O stretch (1713 cm^{-1}) decreases by ~58% and a carboxylate C=O appears[6] (1595, 1551 cm^{-1}, split assym.; 1428 cm^{-1}, sym.) in panels A and B, respectively. Panel C results from successive sequential exposures to MPC and Cu^{2+} solutions; the bands for carboxylate and methylene stretches (2920, 2850 cm^{-1} assym., sym.)[7] are enhanced and a shoulder at 2960 cm^{-1} representing the hexanethiolate methyl stretch appears.[7] Subsequent exposure to an MPC (and not Cu^{2+}) solution restores a prominent carboxylic acid C=O stretch from the MPCs added to the film that have not become carboxylated (panel D). These data confirm that MPC multilayers can be formed and that the attachment occurs via a carboxylate/(Cu^{2+} or Zn^{2+})/carboxylate linkage.

The above experiments demonstrate a controllable and reversible assembly of monolayer and multilayer MPC films by a simple procedure that should be applicable to any COOH-terminated nanoparticle and surface. The voltammetric behavior of monolayer and multilayer capacitance charging is reminiscent of that of monolayer and multilayer chemically modified electrodes,[8] and evidence that the same principles apply is sought in further work.

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Supporting Information Available: Literature references supplementary to refs 1 and 2 and discussion of electron transfer to the Au MPC core (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[6] (a) Evans, S. D.; Ulman, A.; Goppert-Beraducci, K. E.; Gerenser, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 5866. (b) Kepley, L. J.; Crooks, R. M.; Ricco, A. J. *Anal. Chem.* **1992**, *64*, 3191.

[7] Hostetler, M. J.; Stokes, J. J.; Murray, R. W. *Langmuir* **1996**, *12*, 3604.

[8] Murray, R. W., Ed.; *Molecular Design of Electrode Surfaces*; Wiley: New York, 1992.