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Nanoparticle Assemblies: "Rectified" Quantized Charging in Aqueous Media

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Research efforts in organized assemblies of nanosized particle materials have been intensified lately, in part, due to their application potentialities as the building blocks for electronic nanodevices/nanocircuits.[1−9] Among these, monolayer-protected nanoclusters (MPCs)[10] have attracted particular attention thanks to the (sub)attofarad molecular-capacitor characteristics. Under ambient conditions, solutions and surface ensembles of monodisperse MPCs exhibit quantized charging to their double layers, showing analogous features to the classical Coulomb staircase.[9,11] Previous studies have also shown that these unique electron-transfer phenomena are sensitive to the particle dimensions, where a transition to molecular redox behaviors can be observed with decreasing particle sizes.[11] However, it has to be noted that these earlier *electrochemical* studies of MPC quantized charging are primarily confined to organic media,[9,11] whereas none has been reported in *aqueous* environments. Thus, several questions arise immediately: What role do solvents play in these novel interfacial electron-transfer processes? Is it possible to observe these in aqueous media and how?

In an attempt to answer some of these questions and to have a better understanding of the electron-transfer chemistry involved in these artificial molecules, we employed self-assembling[9] to construct MPC surface-organized layers and used them to investigate the effect of solvent media on the electrochemical quantized charging events. The protocol for the MPC self-assembling has been described previously (Scheme 1).[9] Briefly, alkanethiolate-protected MPCs are dissolved in hexane, and several copies of alkanedithiols are incorporated into the MPC-protecting monolayers by surface exchange reactions, rendering the resulting MPCs surface-active with free peripheral thiol groups. Excessive alkanedithiols and displaced alkanethiolates are then removed by repeated liquid-extraction using a methanol−hexane system. The particles are kept in the solution during the entire procedure (to prevent interparticle cross-linking) and they can then anchor onto a gold electrode surface, forming long-range ordered surface assemblies. Here we take 1-hexanethiolate-protected gold (C6Au) particles and 1,6-hexanedithiols (C6(SH)2) as the illustrating example. The particles had been partially fractionated[10] to narrow the size dispersity, with average core size of $\sim$2 nm and $\sim$91 C6 ligands per particle. On the basis of the initial feed ratios of C6Au and C6(SH)2, approximately 10 dithiol ligands were exchanged into the MPC-protecting monolayers. Typical incubation time for the self-assembling of MPC molecules onto a cleaned gold electrode was about 24 h, and the electrode was then rinsed thoroughly with copious hexane to remove loosely bound MPCs and dried gently in a N_2 stream before being transferred to an electrolyte solution for electrochemical measurements.

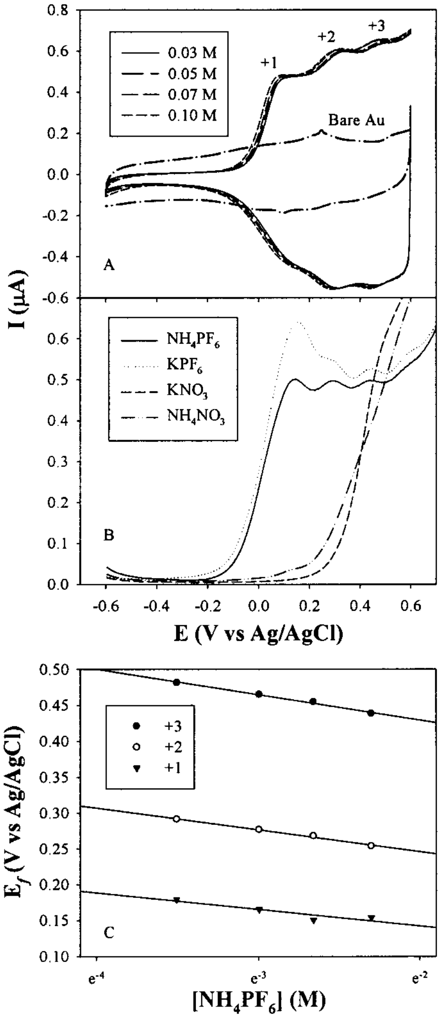

Figure 1. (A) CVs of a C6Au MPC-modified Au electrode in aqueous NH_4PF_6 solutions of various concentrations. Also shown is the CV of the same bare electrode in 0.1 M NH_4PF_6. Electrode area 1.1 mm^2. Sweep rate 100 mV/s. (B) DPVs of the same MPC-modified electrode in various electrolyte solutions (0.1 M). Pulse amplitude 50 mV, dc ramp 4 mV/s. (C) Variation of the formal potentials with the concentration of NH_4PF_6. Lines are linear regressions. $+1$, $+2$, and $+3$ refer to the three voltammetric peaks observed in (A), respectively.

Figure 1A shows the cyclic voltammograms (CVs) of a gold electrode with a self-assembled monolayer of C6Au MPCs linked by C6(SH)2, as described above, in aqueous NH_4PF_6 solutions of various concentrations. Also shown is the CV for the same bare electrode in 0.1 M NH_4PF_6. There are various features that warrant attention here. (i) Multiple well-defined voltammetric peaks can be found in the positive potential regime (0 to $+0.6$ V), which are attributed to the quantized charging to the surface-bound MPC molecules, and the peak currents increase linearly

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(1) Markovich, G.; Collier, C. P.; Henrichs, S. E.; Remacle, F.; Levine, R. D.; Heath, J. R. *Acc. Chem. Res.* **1999**, *32*, 415.

(2) Freeman, R. G.; Grabar, K. C.; Allison, K. J.; Bright, R. M.; Davis, J. A.; Guthrie, A. P.; Hommer, M. B.; Jackson, M. A.; Smith, P. C.; Walter, D. G.; Natan, M. J. *Science* **1995**, *267*, 1629.

(3) Schmid, G.; Bäumle, M.; Geerkens, M.; Heim, I.; Osemann, C.; Sawitowski, T. *Chem. Soc. Rev.* **1999**, *28*, 179.

(4) Andres, R. P.; Bein, T.; Dorogi, M.; Feng, S.; Henderson, J. I.; Kubiak, C. P.; Mahoney, W.; Osifchin, R. G.; Reinfenberger, R. *Science* **1996**, *272*, 1323.

(5) Kiely, C. J.; Fink, J.; Brust, M.; Bethell, D.; Schiffrin, D. J. *Nature* **1998**, *396*, 222.

(6) Yin, J. S.; Wang, Z. L. *Adv. Mater.* **1999**, *11*, 469.

(7) Fendler, J. H. *Chem. Mater.* **1996**, *8*, 1616.

(8) Brousseau, L. C., III; Zhao, Q.; Shultz, D. A.; Feldheim, D. L. *J. Am. Chem. Soc.* **1998**, *120*, 7645.

(9) Chen, S. *J. Phys. Chem. B* **2000**, *104*, 663.

(10) (a) Whetten, R. L.; Shafigullin, M. N.; Khoury, J. T.; Schaaff, T. G.; Vezmar, I.; Alvarez, M. M.; Wilkinson, A. *Acc. Chem. Res.* **1999**, *32*, 397. (b) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. *ibid.* **2000**, *33*, 27.

(11) Chen, S.; Ingram, R. S.; Hostetler, M. J.; Pietron, J. J.; Murray, R. W.; Schaaff, T. G.; Khoury, J. T.; Alvrez, M. M.; Whetten, R. L. *Science* **1998**, *280*, 2098.

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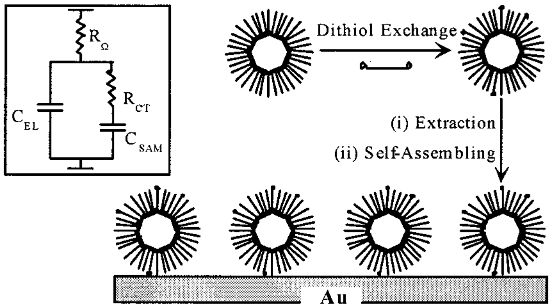
Scheme 1. Self-assembling of Monolayer-protected Nanoparticles; Inset Shows the Randles Equivalent Circuit[13]



with sweep rates (not shown), in consistence with surface-confined systems, as observed previously.[9] To the best of our knowledge, this is the first report of *electrochemical* quantized charging of MPC molecules in *aqueous* solutions. (ii) No voltammetric peaks are recognizable in the negative potential regime, demonstrating, in essence, a minimum-capacitance region from 0 to -0.6 V. (iii) Compared to the voltammetric current measured with the same bare electrode, the interfacial charging current at the MPC-modified electrode was somewhat depressed in the negative potential regime whereas in the positive region, increased rather markedly. These observations are akin to a current rectifier where the current flow is regulated by the applied potentials. In the present system, at negative potentials, the circuit is open where the surface-adsorbed MPC molecules act as an insulating assembly, whereas at positive potentials, the circuit is closed, and therefore current flow is allowed.

These are in sharp contrast with the responses in organic media.[9] For instance, in our previous study[9] with the same MPC monolayer system but in organic media (e.g., CH_2Cl_2) with 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as the supporting electrolyte, multiple well-defined quantized charging peaks were observed within a wide potential range of -1.4 to $+0.8$ V, and the charging peaks were distributed rather symmetrically around the potential of zero charge (PZC, ~ -0.22 V), indicating that both positive and negative valence states of the surface-bound MPCs could be manipulated in ease by electrode potentials. In addition, the *effective* MPC capacitance evaluated from the potential spacing between neighboring charging peaks, $C_{MPC} = e/\Delta V$, also shows a quite significant difference in these two solutions: in CH_2Cl_2, 0.75 aF,[9] and in water (in the present case), 1.05 aF.

The present observations also show dramatic deviations from those of "classical" Coulomb staircase charging based on scanning tunneling microscopy (STM)[1,4,8,10] involving only a single particle. In the STM experiments, the discrete charging features are very well-defined at both negative and positive biases in either vacuum or solutions (aqueous or organic). It has to be noted that the electrochemical responses in (low-dielectric) organic solutions are rather analogous to the STM measurements.[9,11]

It is highly unlikely that the disappearance of the negative charging waves in aqueous phase is due to the solvent-induced variation of the particle electronic energy structure (e.g., the development of a HOMO−LUMO gap).[11] Instead, it is most probably attributed to the capacitive nature of the MPC discrete electron-transfer chemistry which is quite different from the conventional Faradaic processes where similar responses are observed in both organic and aqueous media, such as the ferrocene electrochemistry.[12] This could be understood, at least in part, by the interfacial structure of the MPC surface assemblies. As described earlier,[9] in (low-dielectric) organic media, $C_{EL} < C_{SAM}$ (per unit surface area),[13] thus the overall interfacial capacitance is mainly governed by C_{SAM} and hence quantized charging observations; whereas in aqueous solutions, typically $C_{EL} > C_{SAM}$, thus the charging current is mainly due to the featureless classical charging to the electrode double layers. When the interparticle voids were filled with low-dielectric molecules (e.g., by a second deposition of alkanethiols) such that $C_{EL} < C_{SAM}$, and aqueous-phase quantized charging could then be achieved.[9]

In the present case the discrete charging features are quite visible even without the treatment of a second deposition. However, one should note that the electrolytes used are different: in our previous study,[9] KNO_3 was used whereas in the present study, NH_4PF_6. It has been found[14] that, due to their (relatively) hydrophobic nature, PF_6^- ions might expulse water molecules from the electrode interface by binding to the cationic moieties of the surface-immobilized molecules, leading to the variation of the voltammetric responses. Thus, it is most likely that it is this ion binding and water expulsion property that accounts for the discrepancy of the voltammetric responses of the MPC surface assemblies. This is evidenced by the voltammetric measurements of the charging responses in various electrolytes shown in Figure 1B, where one can see that the well-defined charging features are observed only in the presence of PF_6^- ions, virtually independent of the cations (K^+ or NH_4^+).

At positive potentials, the binding of PF_6^- anions to the MPC interface is favored, where the appearance of discrete electron-transfer processes of the surface-immobilized MPC molecules implies that C_{EL} is sufficiently depressed so that the main contribution to the interfacial charging is from C_{SAM}; whereas at negative potentials, the binding of anionic PF_6^- is disfavored, thus $C_{EL} > C_{SAM}$ and only featureless charging to the electrode double layer. In essence, the anionic PF_6^- serves as the chemical triggers for the single-electron rectifiers.

It has been found that the binding of electrolyte ions to an electroactive species leads to the shifting of the formal potentials with the electrolyte concentrations,[14]

$$E_f = E^{\circ\prime} + (RT/n_aF)\ln(K_2/K_1) - [(p-q)RT/n_aF]\ln[PF_6^-]$$

where E_f is the measured formal potential, $E^{\circ\prime}$ the formal potential in the absence of ion binding, n_a the effective number of electron transfer, K_1 and q (K_2 and p) are the equilibrium constant and the number of PF_6^- ions bound to the reduced (oxidized) forms of the MPC molecules, respectively, and other parameters have their usual significance. Figure 1C shows the variation of the formal potentials of the three charging peaks observed in (A).[15] One can see that all shift cathodically with increasing PF_6^- concentration, and the slopes from linear regressions are 23, 30, and 35 mV for the first, second and third charging peaks, respectively, effectively indicating a 1:1 ratio of the number of PF_6- ions and the MPC charge states ($n_a = 1$). It is also anticipated that the binding of anionic PF_6^- to surface MPCs increases the *effective* dielectric of the MPC protecting monolayers, leading to the larger value of the MPC capacitance (vide ante).

This study demonstrates that simple ion-binding can be utilized as the molecular triggers for the rectification of single-electron transistors. More detailed studies are desired to further investigate this ion-binding chemistry, and the effect on MPC electron-transfer kinetics.[9]

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(12) For instance: (a) Chidsey, C. E. D.; Bertozzi, C. R.; Putvinski, T M.; Mujsce, A. M. *J. Am. Chem. Soc.* **1990**, *112*, 4301. (b) Rowe, G. K.; Creager, S. E. *Langmuir* **1991**, *7*, 2307.

(13) In Scheme 1 inset, C_{EL} and C_{SAM} denote the interfacial capacitance from the interparticle voids and the adsorbed MPCs, respectively; and R_{CT} reflects the corresponding charge-transfer resistance.

(14) Sagara, T.; Maeda, H.; Yuan, Y.; Nakashima, N. *Langmuir* **1999**, *15*, 3823.

(15) Similar responses were also observed in 0.1 M solutions of a mixture of KNO_3 and NH_4PF_6 with various molar ratios.