

## Lateral Quantized Charge Transfer Across Nanoparticle Monolayers at the Air/Water Interface

Yiyun Yang, Solulit Pradhan, and Shaowei Chen\*

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

Received July 31, 2003; E-mail: schen@chem.siu.edu

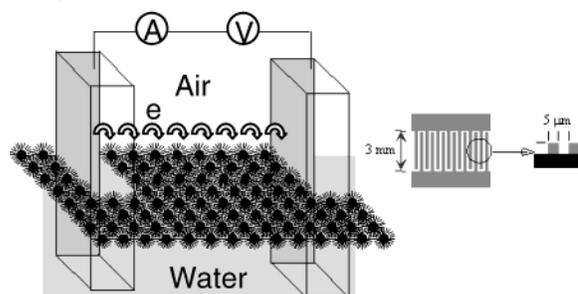
Quantized capacitance charging of nanosized particle molecules represents a new electrochemical charge-transfer phenomenon, as is elegantly exemplified by monolayer-protected gold nanoparticles.<sup>1</sup> The fundamental chemistry behind these discrete charging/discharging processes is attributable to the attofarad scale molecular capacitance of these nanoentities, which renders the energetic barrier ( $e^2/2C$ ) for single electron transfer larger than that of thermal kinetic energy ( $k_B T$ ). Previous research has been focused on nanoparticles in solutions<sup>1</sup> or surface assemblies,<sup>2</sup> where multiple well-defined voltammetric peaks were observed. From the peak potential spacing, the nanoparticle molecular capacitance can be estimated. More interestingly, in aqueous solutions, these charge-transfer processes can be sensitively rectified by hydrophobic electrolyte ions,<sup>2b-e</sup> which is ascribed to the manipulation of the electrode double-layer capacitance by the ion-pair formation between nanoparticles and electrolyte ions.

By contrast, in solid-state electrochemistry, quantized charging features have not been observed. For instance, in dropcast ( $\mu\text{m}$ ) thick films of gold nanoparticles,<sup>3,4</sup> typically only ohmic current-potential ( $I-V$ ) responses are observed. This is interpreted on the basis of the structural inhomogeneity in the particle thick films where effective electron-transfer pathways might be facilitated by film defects. Recently, using the Langmuir technique,<sup>5</sup> we measured the electronic conductivity of monodisperse nanoparticle monolayers directly at the air/water interface with a vertically aligned interdigitated arrays (IDA) electrode and observed drastic differences in terms of the  $I-V$  profiles. For short-chain protecting layers, the particle ensembles exhibited linear (ohmic)  $I-V$  responses, whereas with longer chainlengths, rectified features were observed, as a result of the manipulation of interparticle electronic coupling.

In this Communication, we report a novel finding of quantized charge transfer with nanoparticle monolayers at the air/water interface. Here, the particles, hexanethiolate-protected gold nanoclusters (C6Au), were synthesized by using the Brust protocol<sup>6</sup> and fractionated to reduce size dispersity.<sup>7</sup> From transmission electron microscopic measurements, the average particle core size is estimated to be ca. 2 nm with 30% dispersity.

The experimental setup (Scheme 1) was the same as that described previously.<sup>5,8</sup> In a typical experiment, 200  $\mu\text{L}$  of a C6Au particle solution (1 mg/mL in  $\text{CHCl}_3$ ) was spread dropwise onto the water surface of a Langmuir-Blodgett trough (NIMA 611D; subphase resistance  $> 18 \text{ M}\Omega$ , provided by a Nanopure water system). At least 20 min was allowed for solvent evaporation prior to the first compression and between compression cycles. Compression speed was set at 10  $\text{cm}^2/\text{min}$ . Prior to this, a gold IDA electrode (25 pairs of gold fingers of 3  $\text{mm} \times 5 \mu\text{m} \times 5 \mu\text{m}$ , from ABTECH) was coated with a self-assembled monolayer of *n*-butanethiol (to render the electrode surface hydrophobic) and aligned perpendicularly at the air/water interface. The two lead contacts were connected to an EG&G PARC 283 potentiostat, and the current-potential responses at varied surface pressures were collected using commercial softwares from EG&G (PowerCV and PowerPulse). It

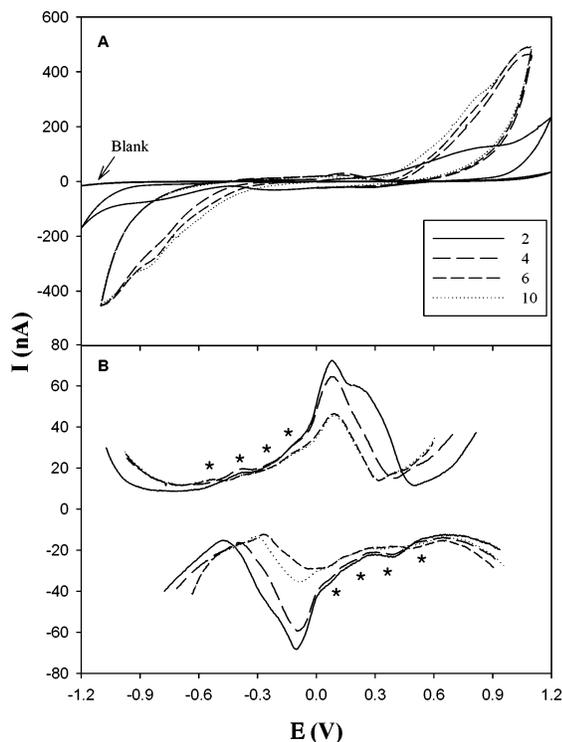
Scheme 1



should be noted that, in this procedure, the electronic conductivity of the nanoparticle monolayers was probed in situ at the air/water interface, in contrast to other reports using nanoparticle thin films deposited onto an electrode surface (by the Langmuir-Blodgett method, for instance) where the measurements were complicated by the mechanical instability of the thin films.<sup>9</sup> In addition, this setup is different from that used by Majda et al.<sup>10</sup> where they used a microband electrode and only observed negligible electronic conductivity of the particle monolayers (they also used a 50 mM  $\text{HClO}_4$  subphase in contrast to the pure water used here).

Figure 1 shows the cyclic (A, CVs) and differential pulse (B, DPVs) voltammograms of a C6Au nanoparticle monolayer at the air/water interface at varied surface pressures (and hence interparticle spacings). The Langmuir isotherm is included in the Supporting Information. The surface pressures shown here correspond to an edge-to-edge interparticle separation from 1.6 nm at 2 mN/m to 1.3 nm at 10 mN/m with varied degrees of ligand intercalation. From the CVs (A), one can see first that the voltammetric currents are all much larger than that in the absence of the particle monolayer ("blank" curve). Second, at potentials near the zero volt position, there is a rather flat current gap, whereas at more negative and positive potentials, currents start to increase quite drastically. This nonlinear current-potential feature is analogous to that of a Coulomb blockade.<sup>5</sup> In other words, the nanoparticle ensemble exhibits semiconductor-like electronic conductivity properties. More importantly, with increasing surface pressures (and decreasing interparticle spacing), the central gap starts to shrink and the voltammetric currents at the extreme potentials increase concurrently. Previously, with semiconductor nanoparticles,<sup>8</sup> we observed similar behaviors where the current gap shrank with increasing surface pressure. It was interpreted on the basis of enhanced interparticle electronic coupling which led to the decrease of particle effective band gap energy.

Using differential pulse voltammetry (DPV, B), we took a more careful look at this central gap and discovered that the voltammetric currents actually arose from the nanoparticle quantized charge transfer. Several rather visible voltammetric waves start to emerge within the potential range between  $-0.7$  and  $+0.7$  V (indicated by asterisks), and the peaks are quite evenly separated with a spacing of about 150 mV. These are ascribed to the quantized charging of



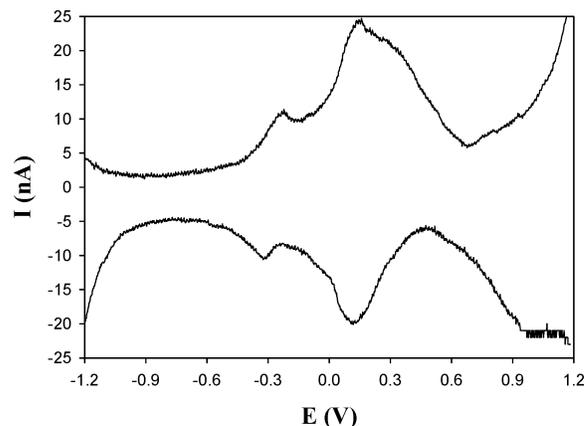
**Figure 1.** (A) Cyclic and (B) differential pulse voltammograms of a AuC6 nanoparticle monolayer at the air/water interface at varied surface pressures (shown as the legend in mN/m). Particle concentration 1 mg/mL in  $\text{CHCl}_3$ ; volume spread 200  $\mu\text{L}$ . Scan rate in (A) 50 mV/s, and in (B) 20 mV/s, pulse 50 mV. Asterisks indicate the charging peak positions.

the nanoparticle ensembles that are trapped between the IDA fingers. It should be noted that this is the first observation of single electron transfer with nanoparticle organized assemblies in the solid state under ambient conditions. Furthermore, the potential spacing is very comparable to that observed<sup>2b-c</sup> with electrode-supported nanoparticle monolayers in aqueous electrolyte solutions. By contrast, in solutions, the same batch of C6Au particles exhibits a series of voltammetric charging peaks with a peak spacing of about 270 mV (Supporting Information). Again, this can be attributed to the ligand intercalation and electronic coupling between the particle cores and hence an increase of the effective molecular capacitance per particle. The quantized charging feature is much better defined when more monodisperse particles are used as shown in Figure 2 where the potential spacing is ca. 420 mV for decanethiolate-protected gold (C10Au) nanoparticles of similar core size.

One should note that the voltammetric currents are a result of charge propagation from one electrode to the other, most probably, by a hopping mechanism (Scheme 1).<sup>3</sup> The fact that discrete charge transfer can be observed indicates that the particle patches between the IDA electrodes exhibit semiconductor-like electronic conductivity. In addition, the electronic coupling between neighboring nanoparticles should be relatively weak within the present experimental context and consequently the particles behave individually. Previous work<sup>5</sup> has shown that with strong coupling the conductivity profile exhibited a linear (ohmic) character, and the transition from linear to nonlinear charge transfer was found to coincide with a protecting chainlength of hexanethiolate (C6).

At very negative and positive potentials, the much larger current scales are a consequence of electrode polarization and accelerated charge transfer.

It has been observed previously<sup>11,12</sup> that the nanoparticle monolayers at the air/water interface undergo a metal-to-insulator transition upon mechanical compression. The present study demonstrates



**Figure 2.** DPV of a C10Au nanoparticle monolayer at the air/water interface at 13 mN/m. About 5% of the C10 ligands are terminated with an aminoxy moiety. Core size dispersity ca. 5%. Other conditions are the same as those in Figure 1B.

that with proper control of the particle structure, lateral single electron transfer can also be achieved with these nanoparticle assemblies. This may pave the way toward the development of nanoscale electronic devices based on nanoparticle organized structures.<sup>13</sup>

**Acknowledgment.** This work was supported in part by an NSF CAREER AWARD (CHE-0092760), the ACS – Petroleum Research Fund, and the SIU Materials Technology Center. S.C. is a Cottrell Scholar of Research Corporation.

**Supporting Information Available:** C6Au particle Langmuir isotherm and solution voltammograms (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (a) Ingram, R. S.; Hostetler, M. J.; Murray, R. W.; Schaaff, T. G.; Khoury, J.; Whetten, R. L.; Bigioni, T. P.; Guthrie, D. K.; First, P. N. *J. Am. Chem. Soc.* **1997**, *119*, 9279. (b) 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. (c) Hicks, J. F.; Templeton, A. C.; Chen, S.; Sheran, K. M.; Jasti, R.; Murray, R. W.; Debord, J.; Schaaff, T. G.; Whetten, R. L. *Anal. Chem.* **1999**, *71*, 3703.
- (a) Chen, S. *J. Phys. Chem. B* **2000**, *104*, 663. (b) Chen, S.; Pei, R. *J. Am. Chem. Soc.* **2001**, *123*, 10607. (c) Chen, S.; Pei, R.; Zhao, T.; Dyer, D. J. *J. Phys. Chem. B* **2002**, *106*, 1903. (d) Chen, S.; Deng, F. *Proc. SPIE* **2002**, *4807*, 93. (e) Chen, S.; Deng, F. *Langmuir* **2002**, *18*, 8942. (f) Zamborini, F. P.; Hicks, J. F.; Murray, R. W. *J. Am. Chem. Soc.* **2000**, *122*, 4515.
- (a) Wuelfing, W. P.; Murray, R. W. *J. Phys. Chem. B* **2002**, *106*, 3139. (b) Wuelfing, W. P.; Green, S. J.; Pietron, J. J.; Cliffel, D. E.; Murray, R. W. *J. Am. Chem. Soc.* **2000**, *122*, 11465.
- (a) Evans, S. D.; Johnson, S. R.; Cheng, Y. L.; Shen, T. *J. Mater. Chem.* **2000**, *10*, 183. (b) Doty, R. C.; Yu, H.; Shih, C. K.; Korgel, B. A. *J. Phys. Chem. B* **2001**, *105*, 8291. (c) Snow, A. W.; Wohltjen, H. *Chem. Mater.* **1998**, *10*, 947. (d) Clarke, L.; Wybourne, M. N.; Brown, L. O.; Hutchison, J. E.; Yan, M.; Cai, S. X.; Keana, J. F. W. *Semicond. Sci. Technol.* **1998**, *13*, A111.
- Chen, S. *Anal. Chim. Acta* **2003**, *496*, 29.
- Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801.
- Schaaff, T. G.; Shafiqullin, M. N.; Khoury, J. T.; Vezmar, I.; Whetten, R. L.; Cullen, W. G.; First, P. N. *J. Phys. Chem. B* **1997**, *101*, 7885.
- Greene, I. A.; Wu, F.; Zhang, J. Z.; Chen, S. *J. Phys. Chem. B* **2003**, *107*, 5733.
- Chen, S. *Langmuir* **2001**, *17*, 6664.
- Lee, W.-Y.; Hostetler, M. J.; Murray, R. W.; Majda, M. *Isr. J. Chem.* **1997**, *37*, 213.
- Markovich, G.; Collier, C. P.; Henrichs, S. E.; Remacle, F.; Levine, R. D.; Heath, J. R. *Acc. Chem. Res.* **1999**, *32*, 415.
- Quinn, B. M.; Prieto, I.; Haram, S. K.; Bard, A. J. *J. Phys. Chem. B* **2001**, *105*, 7474.
- Zhang, J. Z.; Wang, Z. L.; Liu, J.; Chen, S.; Liu, G.-Y. *Self-Assembled Nanostructures*; Kluwer: New York, 2002.

JA037675X