

## Electron Hopping Dynamics in Au<sub>38</sub> Nanoparticle Langmuir Monolayers at the Air/Water Interface

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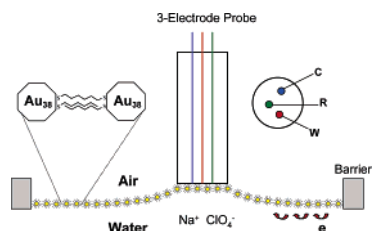
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Gold nanoparticles containing a few tens of atoms have been the focus of recent investigations because of their novel electronic and optical properties.<sup>1</sup> They appear to represent the bulk-to-molecule transition region where electronic band energetics yield to quantum confinement effects and discrete electronic states emerge. The electrochemical and optical properties of these metal quantum dots have been described.<sup>1</sup> A natural extension of these studies is the exploration of the collective properties of assembled arrays of these nanoparticles since practical electronic devices may in fact depend on average properties of their constituents. Although the electron-transfer (ET) dynamics has been extensively studied in three-dimensional network<sup>2</sup> and polyether melt<sup>3</sup> nanoparticle assemblies, the unified picture of the ET dynamics–structure relation remains incomplete. This is largely due to their structural ambiguity and disordering effects.<sup>2d</sup> We report here the first quantitative voltammetry at the air/water interface that delineates the distance-dependent electron hopping (self-exchange) dynamics in well-defined Langmuir monolayers of a metal quantum dot.

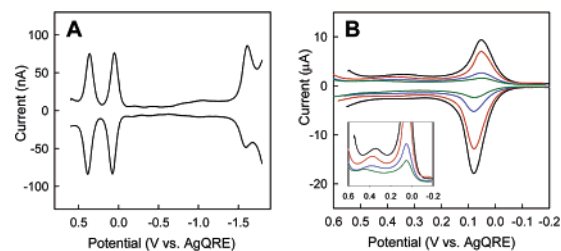
Our approach is to fabricate a monolayer using (a) a nanoparticle that exhibits well-defined single-electron charging peaks in voltammetry<sup>1,2a</sup> with which the electron hopping rate can be estimated and (b) well-defined ligand spacers that can link nanoparticles and reinforce the monolayer stability. Chen<sup>4</sup> has demonstrated that (b) is possible, although we introduce here more structurally compatible linking ligands, namely alkanedithiols (C<sub>n</sub>DT = HS(CH<sub>2</sub>)<sub>n</sub>SH; *n* = 5, 6, 8, and 9), with the protecting ligand. The added dithiols appeared not only to link nanoparticles to enhance the monolayer stability but also to fill up the free space between cores, preventing spontaneous aggregation and thus rendering the interparticle distance more controllable by the mechanical compression barriers. The nanoparticle used in this work has a composition of Au<sub>38</sub>(SC6)<sub>24</sub> where the protecting ligand SC6 = hexanethiolate and TEM core diameter = 11 ± 2 Å and was synthesized by using a modified Brust method<sup>5</sup> and solvent fractionated to reduce size dispersity.

To probe the electron hopping dynamics, we have extended the horizontal touch voltammetry (HTV) technique pioneered by Fujihira and Araki<sup>6</sup> and further developed by Majda and co-workers<sup>7</sup> using line electrodes. Scheme 1 illustrates the HTV experiment of

### Scheme 1



a Au<sub>38</sub> nanoparticle Langmuir monolayer at the air/water interface using a three-electrode probe<sup>8</sup> (the subphase contains 0.1 M NaClO<sub>4</sub>

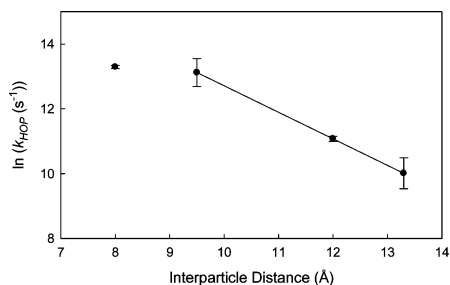


**Figure 1.** (A) Square wave voltammetry (SWV) of 0.4 mM Au<sub>38</sub>(SC6)<sub>24</sub> in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> at 0.2 mm-radius Pt working electrode and (B) SWVs of Au<sub>38</sub>(SC6)<sub>24</sub> monolayers fabricated with various lengths of dithiols: C5DT (black), C6DT (red), C8DT (blue), and C9DT (green), in contact with a 3-electrode probe,<sup>8</sup> at 60 mV/s, 25 mV pulse. Inset: close-up of cathodic scans.

for voltammetric measurements). Experimental details of the HTV and monolayer formation are described in Supporting Information.

The surface pressure versus area ( $\pi$ -A) isotherms (Supporting Information) before and after the introduction of dithiol are similar, except for the shift in area accounting for the added dithiol. This may indicate that added dithiol linkers participate in the nanoparticle networking without disrupting the monolayer integrity, presumably through ligand interdigitation<sup>2b</sup> and/or surface place–exchange reaction.<sup>2a</sup> TEM images (Supporting Information) show relatively uniform distribution of nanoparticles in the monolayers, and the average interparticle distance is consistent with the distance experimentally controlled by the barriers.

Figure 1 shows the square wave voltammetry (SWV) of Au<sub>38</sub> nanoparticle solution (A) and monolayers (B) formed with various lengths of dithiols: C5DT, C6DT, C8DT, and C9DT and the corresponding interparticle distances of 8.0, 9.5, 12.0, and 13.3 Å, respectively.<sup>9</sup> The solution voltammetry exhibits the characteristics of Au<sub>38</sub> nanoparticles;<sup>1d</sup> the current peaks lying at the formal potentials of the nanoparticle charge state couples are unevenly spaced, reflecting the discretization and spacing of electronic levels of Au<sub>38</sub> core. Voltammograms of Au<sub>38</sub> monolayers also display a well-defined reversible peak assigned to the Au<sub>38</sub><sup>+0</sup> couple. Close-up of the voltammograms (Figure 1B inset) reveals that there is another peak at ~0.35 V that can be assigned to the Au<sub>38</sub><sup>2+/+</sup> couple and the peak spacing between Au<sub>38</sub><sup>+0</sup> and Au<sub>38</sub><sup>2+/+</sup> couples is comparable with that of solution voltammetry. The peak current of the Au<sub>38</sub><sup>2+/+</sup> reaction is, however, substantially smaller than that of the Au<sub>38</sub><sup>+0</sup> reaction; for solution, the currents associated with these two reactions are comparable (compare panels A and B of Figure 1). This difference can be attributed to a relative amount of charge-compensating counterions available for Au<sub>38</sub><sup>+0</sup> and Au<sub>38</sub><sup>2+/+</sup> reactions, as has been observed for sequential reductions of a surface-confined fullerene monolayer.<sup>10</sup> The current for the second oxidation (Au<sub>38</sub><sup>2+/+</sup>) reaction is substantially reduced because the available counterions (ClO<sub>4</sub><sup>-</sup>) are significantly reduced upon the first oxidation (Au<sub>38</sub><sup>+0</sup>) reaction (and the incorporation of counterions); only the portions of the monolayer that can incorporate



**Figure 2.** Dependence of  $\ln(k_{\text{HOP}})$  on the experimentally controlled interparticle distance in  $\text{Au}_{38}$  monolayers. Line: linear fit for interparticle distance = 9.5–13.3 Å.

additional counterions will be electroactive. The reason for limiting counterion incorporation for the second oxidation is unclear at this time. It may be caused by the limited free volume available for the incorporation of counterions in the monolayer and/or directly under the monolayer. The first oxidation appears, however, to be fully supported; indeed, the first oxidation current was very reproducible<sup>11</sup> and increased significantly with decreasing the interparticle distance. Further, the width of the peak at half-height is  $\sim 90$  mV, consistent with that predicted for one-electron change.<sup>12</sup> We note that this HTV experiment is fundamentally different from that reported by Chen et al.<sup>13</sup> in which no supporting electrolyte was used for voltammetry.

The Figure 1B voltammetry opens the way to estimate the rate of electron hopping between the  $\text{Au}_{38}$  cores and to correlate it with the monolayer structural parameters. The electron hopping process is a diffusion-like phenomenon, and the peak current relates with the apparent diffusion coefficient ( $D_{\text{APP}}$ ) by the Osteryoung equation.<sup>14</sup> The peak current associated with oxidation of  $\text{Au}_{38}^0$  to  $\text{Au}_{38}^+$  is remarkably dependent on the interparticle distance; the resulting  $D_{\text{APP}}$  increases from  $3.3 \times 10^{-10}$  to  $5.4 \times 10^{-9}$   $\text{cm}^2/\text{s}$  by ca. 16-fold with decreasing the distance from 13.3 to 8.0 Å.  $D_{\text{APP}}$  can be expressed as a summation of a physical diffusion coefficient ( $D_{\text{PHYS}}$ ) with an electron (hopping) diffusion coefficient ( $D_{\text{E}}$ ).<sup>7c</sup> To calculate the first-order electron hopping rate constant ( $k_{\text{HOP}}$ )<sup>7a,c</sup> from  $D_{\text{E}}$ , we make the assumption that  $D_{\text{APP}} \gg D_{\text{PHYS}}$  as has been done before for nanoparticles in network polymer films<sup>2a</sup> and for polyether redox melts,<sup>3</sup>

$$D_{\text{APP}} = D_{\text{PHYS}} + D_{\text{E}} \approx D_{\text{E}} = k_{\text{HOP}}\delta^2/4 \quad (1)$$

in which  $\delta$  is the equilibrium center–center  $\text{Au}_{38}$  core separation. The resulting rate constant in Figure 2 exponentially increases from  $2.2 \times 10^4$  to  $5.0 \times 10^5$   $\text{s}^{-1}$  by ca. 23-fold as the distance decreases from 13.3 to 9.5 Å. The slope of the linear fit, a measure of the tunneling decay constant, is  $0.82 \text{ \AA}^{-1}$ . These results compare very well with those<sup>15</sup> obtained from alkanethiol monolayers on Au electrodes in which the electron tunneling pathway was precisely controlled by the monolayer length, demonstrating that the present approach provides a powerful way to study the ET dynamics–structure relation.

In Figure 2, the apparent flattening in  $k_{\text{HOP}}$  at 8.0 Å may reflect the competing nature of tunneling pathways. The protecting ligands, the linkers, or both, presumably serve as tunneling bridges in the ET. While the average interparticle distance is effectively controlled by the barriers as well as the dithiol length in longer dithiol-based

monolayers, in the C5DT-based monolayer the effective tunneling pathway appears to be limited by the minimum distance of the interdigitated protecting ligands. TEM results (Supporting Information) indeed support this; the average interparticle distance (9.2 Å) is considerably longer than the experimentally controlled distance (8.0 Å),<sup>16</sup> yielding a smaller  $k_{\text{HOP}}$  as in Figure 2.

In summary, these are the first results demonstrating that the ET dynamics can be quantified by in situ voltammetry of nanoparticle monolayers whose structure is precisely controlled by the Langmuir technique and well-defined linkers. The improved understanding of correlation between ET dynamics and assembly structure may prove useful in designing and developing nanoparticle-based devices.

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**Supporting Information Available:** HTV experiment, Langmuir isotherms, and TEM data for  $\text{Au}_{38}$  nanoparticle monolayers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- This may imply that the monolayer is locally collapsed.

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