

pH-Gated Single-Electron Tunneling in Chemically Modified Gold Nanoclusters

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The correlated transfer of electrons one-by-one in metallic islands occurs when the energy e^2/C_T (e is electron charge, C_T is total island capacitance) required to charge the island by a single electron is large relative to that supplied by thermal energy (kT).¹ Although single-electron tunneling (SET) has been investigated intensely since the early 1960s, the relatively large size of devices prepared photolithographically has demanded extremely low temperatures (typically subkelvin) to observe SET behavior.² Recent methods for synthesizing ligand-stabilized metal (Au, Ag, Pt)³ and semiconductor (CdS, CdSe) nanoclusters with diameters of <10 nm have enabled electronic characterization of tunnel junctions with capacitances of $<10^{-18}$ F; indeed, SET has now been observed in several nanoscopic systems at room temperature.⁵ These experiments have renewed enthusiasm regarding the use of single-electron devices as data storage elements in which bits of information are represented by single electrons.

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A significant challenge to incorporating single-electron devices into nanoscale electronic circuitry is the sensitivity of SET currents to impurities which may reside on or near the nanoparticle.¹ Impurities introduce shifts in SET current–voltage (i – V) curves, making it unlikely that any two SET devices will be electronically equivalent. One proposed method for overcoming a current shift is to use a gate electrode to “reset” the device. Our group has been considering the possibility of employing particle capping ligands as “chemical gates” to manipulate SET currents.^{1c} Developing a basic understanding of how capping ligand chemistry affects nanocluster electronic function is of vital importance in implementing this idea.

We communicate here the i – V characteristics of ligand-stabilized Au nanoclusters in aqueous solutions. Two different capping ligands were investigated, octanethiol (C_8 -Au; 5 nm diameter) and galvinoxol (Gal-Au; 3 nm diameter), a ligand with $pK_a \sim 12$ when bound to Au nanoclusters.⁶ When individual nanoclusters were probed electronically with the STM, clear i – V steps (Coulomb staircase) were observed for C_8 -Au in H_2O (pH 5 and 12) and Gal-Au in H_2O (pHs 5, 8, 10, and 12). Because there is no chemical difference in C_8 -Au at the two pH values tested, we expected, and observed experimentally, little change in i – V behavior as a function of pH. Galvinoxol, however, is converted to the galvinoxide anion as pH is increased. Thus changes in i – V behavior were expected for Gal-Au in response to deprotonation, even though only approximately 10 galvinoxide anions are generated on the cluster surface at pH 12.

A collection of i – V curves for Gal-Au and C_8 -Au in H_2O is shown in Figure 1.⁶ Several clear current steps and voltage plateaus are apparent in these data, indicative of SET in individual nanoclusters. Current–voltage curves recorded for a single cluster at different tip heights revealed clear Coulomb gaps and currents which increased exponentially with decreasing tip–particle distance (see Supporting Information), consistent with previous measurements in ultrahigh vacuum.^{5e,8} Comparing the pH data for C_8 -Au, little difference is observed in the positions and magnitudes of the staircase voltage plateaus.⁷ Voltage plateau widths (ΔV) were 59 ± 7.8 mV and 63 ± 4.6 mV at pHs 5 and

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(6) Galvinoxol was used as a pH-active probe because it has been characterized previously in a variety of solvent systems as the free ligand and in monolayer films on Au substrates: (a) Shultz, D. A.; Tew, G. J. *Org. Chem.* **1994**, 59, 6159. (b) Shultz, D. A.; Zhao, Q. *Tetrahedron Lett.* **1996**, 37, 8837. (c) Sagara, T.; Midorikawa, T.; Shultz, D. A.; Zhao, Q. *Langmuir*, submitted for publication. (d) Bock, H.; John, A.; Havlas, Z.; Bats, J. W. *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 416. pK_a 's for galvinoxol have been determined for the free molecule in aqueous solution ($pK_a = 12$) and for Gal-Au in CH_3CH_2OH ($pK_a = 12.5$). We are unable to determine the pK_a for Gal-Au in H_2O due to poor solubility. Gal-Au and C_8 -Au were synthesized using procedures developed by Schiffrin and co-workers. Galvinoxol coverage (~ 15 galvinoxols/Au nanoparticle) was estimated on the basis of geometry and a galvinoxol-terminated thiol footprint of 1 nm^2 determined electrochemically on planar Au.^{6a–d} Nanoparticles were cast on octanethiol-coated Au substrates by placing a drop of a dilute solution (toluene, Aldrich Chemicals) containing the desired nanocluster onto the slide followed by slow evaporation. Scanning tunneling spectroscopy (STS) was performed with a Digital Instruments (DI) Nanoscope III Scanning probe. Pt/Ir tips were purchased from DI and coated with polyethylene. The tip was then reexposed as described by Fan and Bard (ref 9). Leakage currents were < 1 pA. The pH 5 solution was Millipore (18 M Ω) H_2O . The pH 8, 10, and 12 solutions were ~ 5.6 mM in K_2HPO_4 (Fisher) and were 20 mM ionic strength. \pm values indicate standard deviations calculated from data acquired on at five different C_8 -Au nanoparticles. We estimate a tip–particle separation distance of 1 nm at the bias voltage where current steps are observed (150 mV, 1.5 nA). Approach curves display an exponential increase in current as the tip approaches the nanoparticle, an observation consistent with previous results of Andres and co-workers (see ref 5e and the Supporting Information).

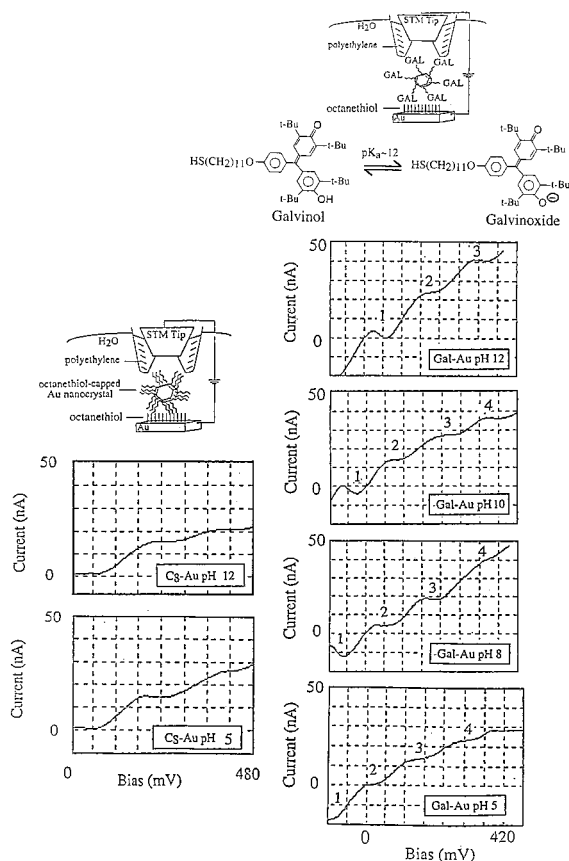


Figure 1. Current–voltage curves for C_8 -Au (left) and Gal-Au (right) in H_2O as a function of pH (adjusted with phosphate buffer, see ref 6). The numbers 1–4 in the Gal-Au data identify voltage plateaus. Cartoons of the experimental arrangements for measuring i – V curves of individual nanoclusters in solution are shown at the top of each data column. The insulated STM tip, ligand-capped Au nanocluster, and octanethiol-coated planar Au substrate are shown. Lengths and shapes are not to scale.

12, respectively.⁶ ΔV can be used to estimate cluster capacitance using $\Delta V = e/C$,^{1,2,5,8} giving capacitances of ca. 2.7 ± 0.30 aF/cluster and 2.5 ± 0.10 aF/cluster (0.05 aF/nm²). These values are similar to calculations based on geometry and to values obtained by Murray in bulk C_8 -Au nanocluster electrochemical experiments (0.04 aF/nm²)⁸ and Porter for C_8 monolayers on planar Au surfaces (0.02 aF/nm²).⁹

In contrast to C_8 -Au, a number of differences are apparent in i – V curves of Gal-Au recorded at pHs 5, 8, 10, and 12 (Figure 1). First, a subtle shift (ca. 30 mV) in the entire staircase to positive bias potentials is noticeable from pH 5 to pH 8. The shift is even more prevalent in i – V curves obtained at pHs 10 and 12 (from ca. 60 to 120 mV).¹⁰ Second, ΔV decreases in magnitude from 74 ± 7.8 mV at pH 5 to 64 ± 4.0 mV and 48 ± 5.6 mV at pHs 8 and 12, respectively. Third, slight peaks are evident in the i – V curves at pHs 8, 10, and 12 which are absent in the data acquired at pH 5.¹¹ Importantly, the peaks appear superimposed on plateaus (i.e., a peak appears at periods in bias potential where a step should occur).

The chemically induced changes in SET staircases presented above may be rationalized by considering the effects of charge

(7) The positions of the voltage plateaus varied by <20 mV in curves acquired on five different C_8 -Au clusters, a variation likely attributed to cluster size dispersity.

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(10) Within a single experimental run, the positions of the voltage plateaus varied by <10 mV in curves acquired on four different Gal-Au clusters.

(11) Current peaks were not used in calculations of cluster capacitance.

and/or structural changes¹² which occur to the galvinoxide monolayer upon deprotonation. At pH 5 galvinoxide is in a protonated neutral form. Coulomb staircases of Gal-Au at pH 5 are therefore typically symmetrical, with the first step centered near 0 V (the Coulomb gap, see Supporting Information). As the pH is increased galvinoxide is converted to galvinoxide anion. The increased negative charge on the nanocluster has two consequences. First, the total capacitance of the cluster increases. Based on ΔV , an increase in nanocluster capacitance from 2.2 ± 0.24 aF/cluster (0.06 aF/nm²) at pH 5 to 2.5 ± 0.14 aF/cluster (0.09 aF/nm²) and 3.3 ± 0.31 aF/cluster (0.12 aF/nm²) at pHs 8 and 12, respectively, was calculated. Similar behavior has been observed previously by Murray and co-workers in electrochemical experiments conducted on millimolar solutions of ferrocene-capped Au nanoclusters. In their studies, a ca. 7-fold increase in cluster capacitance was observed when ~ 30 ferrocenes bound to the particle surface were oxidized.¹³ The second consequence of forming the galvinoxide anion is to increase negative charge on the nanocluster surface. In solid-state SET devices negative charge located near the metal island, either from an impurity or via application of a gate electrode bias, causes the Coulomb staircase to shift to positive bias potentials.¹ The shift to positive bias in the Gal-Au system is qualitatively in accord with solid-state measurements. The fact that potential shifts and capacitance changes are only observed for Gal-Au, and not C_8 -Au, and for Gal-Au at three different pHs of identical ionic strength supports the notion of pH-gated SET.

Finally, the observation of a peak (negative differential resistance, NDR) at a bias potential where a voltage plateau is expected is an unusual feature of these i – V curves. In fact, to date, we have observed NDR at various bias potentials in i – V curves for C_8 -Au (typically at much more negative bias, ca. -0.5 V) and Gal-Au nanoclusters, but only in the presence of phosphate buffer. Although further investigation is required, there is precedent for NDR in SET curves of metal nanoparticles. For example, Radojkovic and co-workers observed peaks superimposed on voltage plateaus at high positive bias potentials in i – V curves of Au particles on Si substrates.¹⁴ These were attributed to charge leakage from the particle to the immediate surroundings, likely to interfacial states at the Si surface. Although a charge trapping mechanism involving freely diffusing phosphate ions in solution seems unlikely, these results further illustrate the effects of surrounding medium chemistry on SET phenomenon. We are currently exploring a range of electrolytes of varying electron accepting/donating abilities to elucidate the role of solvent composition on SET in Au nanoclusters.

The above experiments have demonstrated for the first time that SET behavior is accessible on single Au nanocrystals in high dielectric fluid environments. Moreover, this study has shown that SET is dependent on capping-ligand chemistry and solution composition. The ability to probe SET events in situ may prove useful in chemical signal transduction where SET currents in these chemically modified “nanoelectrodes” should be sensitive to single redox or analyte binding events.

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Supporting Information Available: Wide potential bias window for C_8 -Au, conductance plot, current–voltage curves, and scanning tunneling microscope images for C_8 -Au and Gal-Au (4 pages, print/PDF). See any current masthead page for ordering and Web access instructions.

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