J. Am. Chem. Soc. **1997**, *119*, 9279−9280

9279

Communications to the Editor

28 kDa Alkanethiolate-Protected Au Clusters Give Analogous Solution Electrochemistry and STM Coulomb Staircases

Roychelle S. Ingram,[†] Michael J. Hostetler,[†]
Royce W. Murray,*,[†] T. Gregory Schaaff,[‡]
Joseph T. Khoury,[‡] Robert L. Whetten,*,[‡] Terry P. Bigioni,[‡]
Daniel K. Guthrie,[‡] and Phillip N. First*,[‡]

Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27599-3290
Schools of Physics and Chemistry, Georgia Institute of
Technology, Atlanta, Georgia

Received July 11, 1997

We report here the electron transfer (*et*) behavior (Figure 1) of highly purified, 28 kDa core mass, hexanethiolate-protected gold cluster molecules[1−3] and the remarkable correspondence between tip-based tunneling spectroscopy of a *single* Au cluster molecule physisorbed on a metal surface[4] and cyclic and differential pulse voltammetry of *ensembles* of the same clusters at a metal/solution interface. This study establishes new ground in three ways: (1) the samples studied are "monodisperse" in core size and structure; thus the observed *et* properties can be assigned to a specific number and arrangement of gold atoms; (2) the *et* comparison of single molecules to a thermodynamically relevant ensemble of the same molecules demonstrates correspondence of results across these vastly different regimes; and (3) the voltammetry provides the first example of a solution-phase coulomb staircase of an ensemble of nanoparticles.

Alkanethiolate monolayer protected Au clusters (MPCs)[1] are air-stable, nonaqueous soluble, and separable according to core size, properties arising in large part from the dense ligand monolayer. The thin monolayer dielectric skin surrounding the Au core also influences its ability to store electronic charge (i.e., its capacitance). The 28 kDa cluster samples used here are obtained by organic solvent-phase reduction[1,3] of gold and have been purified of other core sizes by recrystallization, as demonstrated by mass spectrometry, X-ray diffraction, and other methods.[3] Compositional and structural evidence are consistent with a highly stable quasi-crystalline Au_{146} core (1.64 nm diameter) of truncated-decahedral morphology, stabilized by a ligand shell of *ca.* 56 hexanethiolate groups.[3c] Details of sample preparation are given in Supporting Information.

The inset of Figure 1A schematically represents the tunneling experiment, in which an STM tip addresses individual cluster molecules adsorbed on a gold-on-mica substrate under ultrahigh vacuum at 83 K. The experimental I−V curve observed for a *single* cluster (Figure 1A) is a reversible, highly repeatable
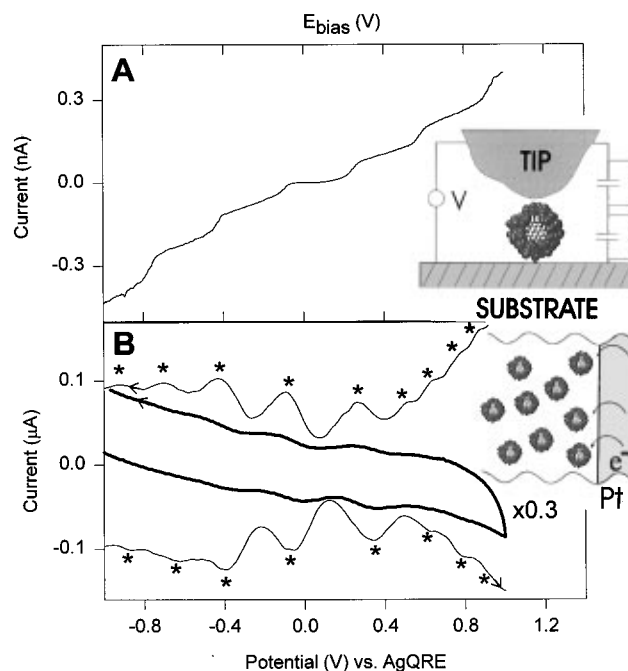
Figure 1. Panel A: Au STM tip addressing a single cluster adsorbed on an Au-on-mica substrate (inset) and Coulomb staircase I−V curve at 83 K; potential is tip-substrate bias; equivalent circuit of the double tunnel junction gives capacitances $C_{upper} = 0.59$ aF and $C_{lower} = 0.48$ aF. Panel B: voltammetry (CV —, 100 mV/s; DPV ▬, ★ are current peaks, 20 mV/s, 25 mV pulse, top and bottom are negative and positive scans, respectively) of a 0.1 mM 28kDa cluster solution in 2:1 toluene:acetonitrile/0.05 M Hx_4NClO_4 at a 7.9×10^{-3} cm^2 Pt electrode, 298 K, Ag wire pseudoreference electrode.

"Coulomb staircase" with six charging steps regularly spaced at 0.34 V increments between ±1 V bias. Each "step" in the staircase occurs at a particular bias voltage where it is energetically possible for an additional electron to reside on the cluster, and the current is very sensitive to the charge on this "middle electrode". The constant spacing between the staircase steps in Figure 1A is consistent with the semiclassical theory[5] of a double-tunnel junction, which only considers coulombic interactions and predicts a constant spacing ($\Delta V = e/C$) between each staircase step, where *e* is the electron charge and *C* the combined capacitances of the tip/monolayer/Au-core and Au-core/monolayer/substrate junctions. Based on the equivalent circuit in Figure 1A, inset, the determined capacitances of the two junctions are 0.59 and 0.48 aF, respectively.

The Au cores of MPCs also exhibit capacitive charging when dissolved in solutions, as first detected[2] in rotated disk voltammetry of solutions of octanethiolate Au MPCs (2.2 nm core size, 25% of the ligands functionalized with ω-ferrocenyl). In addition to the ferrocene oxidation wave, transport-controlled sloping current baselines, evident in both pre- and post-ferrocene wave potential regions, were ascribed to the capacitive (double layer) charging of clusters as they are transported to and equilibrate their core potentials with the electrode interface. These currents gave[2b] an *average* capacitance of reduced cluster of 0.56 ± 0.06 aF/cluster, independent of the number of ferrocenes present.

Irrespective of differences in core size and alkanethiolate chain length, the above tunneling (Figure 1A) and electrochemi-

† University of North Carolina.
‡ Georgia Institute of Technology.
(1) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801.
(2) (a) Hostetler, M. J.; Green, S. J.; Stokes, J. J; Murray, R. W. *J. Am. Chem. Soc.* **1996**, *118*, 4212. (b) Green, S. J.; Stokes, J. J.; Hostetler, M. J.; Pietron, J. J.; Murray, R. W. *J. Phys. Chem. B* **1997**, *101*, 2663.
(3) (a) Whetten, R. L.; Khoury, J. T.; Alvarez, M. M.; Murthy, S.; Vezmar, I.; Wang, Z. L.; Stephens, P. W.; Cleveland, C. L.; Luedtke, W. D.; Landman, U. *Adv. Mater.* **1996**, *8*, 428. (b) Schaaff, T. G.; Shafigullin, M. N.; Khoury, J. T.; Vezmar, I.; Whetten, R. L.; Cullen, W. G.; First, P. N. *J. Phys. Chem.,* in press. (c) Cleveland, C. L.; Landman, U.; Shafigullin, M. N.; Stephens, P. W.; Whetten, R. L. *Z. Phys. D*, **1997**, *40*, 503.
(4) (a) Andres, R. P.; Bein, T.; Dorogi, M.; Feng, S.; Henderson, J. I.; Kubiak, C. P.; Mahoney, W.; Osifchin, R. G.; Reifenberger, R. *Science* **1996**, *272*, 1323. (b) Gerritsen, J. W.; Shafranjuk, S. E.; Boon, E. J. G.; Schmid, G.; Vankempen, H. *Europhys. Lett.* **1996**, *33*, 279.

(5) (a) Hanna, A. E.; Tinkham, M. *Phys. Rev. B,* **1991**, *44*, 5919. (b) Amman, M.; Wilkins, R.; Ben-Jacob, E.; Maer, P. D.; Jaklevic, R. C. *Phys. Rev. B* **1991**, *43*, 1146.

cal[2] capacitances are remarkably similar. Correlation of solution electrochemistry of metal clusters with bulk metal/vacuum interface behavior has precedent[6] for (much smaller) Pt-carbonyl clusters. These points opened the question of *detecting discrete charging events in solution electrochemistry experiments*, since the estimated coulomb energies ($E_C = e^2/2C$) greatly exceed the ambient thermal energy. The absence of previous[2] detectable discrete charging is attributable to the core size dispersity in the samples used.

Cyclic (CV) and differential pulse (DPV) voltammetries of a 28 kDa hexanethiolate cluster solution are illustrated in Figure 1B. The CV shows several current peaks, the cathodic/anodic ΔE_{PEAK} potential separations are due at least in part to the large iR_{UNC} in the mixed solvent. More significant is the obvious presence of *multiple* CV and DPV waves; the DPV experiment, which is superior for resolving small current features, reveals as many as nine current peaks (above background). Indeed, the DPV voltammogram qualitatively mirrors the STM I−V curve in Figure 1A; both represent cluster charging responses but are obtained in very different ways.

In the Figure 1B voltammetry, a huge number of cluster molecules in the 0.1 mM solution lie at any instant very near the electrode (*ca.* 2×10^{11} /cm^2 within 3 nm), but are not in continuous contact with one another (av center−center spacing ≈ 26 nm). Thus, by rough analogy with the STM experiment, electrochemical charging can be viewed as a huge number of separately coexisting, electrolyte solution/cluster/Pt electrode junctions. If clusters arriving at such junctions are uniformly charged initially, then their charging by successive *et* steps requires excursions of e/C in the Pt electrode potential. In this picture, electrochemical charging is an *ensemble coulomb staircase*, which will be cleanly observed when all of the clusters exhibit the same capacitance (*C*).

The 0.40 V separation between adjacent current peaks near 0 V in Figure 1B corresponds to 0.40 aF/cluster (based on a *ca.* 9 nm^2 core surface area, this is 0.04 aF/nm^2). Considering their geometrical differences, the capacitance results from the STM and electrochemical experiments are reasonably close to one another and, once normalized for cluster area, to the

previous[2b] result and to an octanethiolate monolayer on a flat Au(111) surface.[7] The electrochemical staircase diverges from the STM result, however, in that the observed ΔV decreases from 0.4 V near the center of the DPV voltammogram (roughly near PZC[8]) to ca. 0.2 V on the extreme wings. This may be due to the presence of electrolyte or to a change in cluster capacitance but requires further study.

The above analysis, based on a double layer capacitance model, must break down at a sufficiently small cluster core, for which electrochemistry will take on a chemical redox character. Photoelectron spectroscopy of mass-selected Au_N clusters[9] suggests that bulklike properties become dominant on the *ca.* 0.1 eV scale for $N > 40$ atoms. Indeed, the multiple voltammetric waves observed in preliminary DPV experiments on other, similarly prepared, cluster core sizes[3c] are core size-dependent, and that of the smallest (Au_{38}), which is in the same size range as Pt-carbonyl clusters (Pt_N, $N = 19, 24, 38$)[6] and C_{76} fullerenes,[10] displays recognizable redox-like electrochemical behavior. Those results will be reported in a future paper. *A core size-dependent transition of Au_N electrochemistry between double-layer capacitance and redox behavior is potentially regarded, for metal surfaces, as simply exposing different facets of the same phenomenon whose appearance is determined by the scale of matter on which charge transfer is being effected.*

Fan and Bard[11] have recently achieved an electrochemical coulomb staircase based on nanometer-sized electrodes.

Supporting Information Available: Details of sample preparation and purification and MALDI characterization (3 pages). See any current masthead page for ordering and Internet access information.

JA972319Y

(6) (a) Weaver, M. J.; Gao, X. *J. Phys. Chem.* **1993**, *97*, 332. (b) Roth, J. D.; Lewis, G. J.; Safford, L. K.; Jiang, X.; Dahl, L. F.; Weaver, M. J. *J. Am. Chem. Soc.* **1992**, *96*, 6159.

(7) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987,** *109,* 3559.

(8) Chen, S.; Murray, R. W., unpublished research, University of North Carolina, 1997.

(9) Taylor, K. J.; Pettiette-Hall, C. L.; Cheshnovsky, O.; Smalley, R. E. *J. Chem. Phys.*, **1992**, *96*, 3319.

(10) Li, Q.; Wudl, F.; Thilgen, C.; Whetten, R. L.; Diederich, F. *J. Am. Chem. Soc.,* **1992**, *114*, 3994.

(11) Fan, F.-R. F.; Bard, A. J. *Science* In press.