Electrocatalysis on Gold Clusters

DOI: 10.1002/ange.200905614

Aqueous CTAB-Assisted Electrodeposition of Gold Atomic Clusters and Their Oxygen Reduction Electrocatalytic Activity in Acid Solutions**

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Dedicated to Dr. Gollakota Prabhakara Rao and in memory of Sarukkai Krishnamachari Rangarajan

In a modification of Reetz's electrochemical production of metal nanoparticles from surfactant solutions,[1,2] Yu et al.[3] observed the generation of gold nanorods exhibiting both transverse and longitudinal surface plasmon resonance (SPR). This method uses a gold metal sheet as anode and platinum as cathode in a mixed surfactant solution of cetyltrimethylammonium bromide (CTAB) and a rod-shape-inducing co-surfactant. This observation triggered a flurry of activity in nanocatalysis and plasmonic sensors. However, the aspects of particle growth and evolution of nanostructures remain unexplored. Interesting questions to ask are: 1) is the growth of different Au nanostructures preceded by the formation of stable gold clusters of a few atoms (zone between molecular and nanoscale structures); and 2) how (electro-) catalytic are these clusters? Nanosized gold particles have been examined extensively as active catalysts for CO oxidation[4–7] and the oxygen reduction reaction (ORR).[8,9] However, most of the earlier studies were concerned with Au nanoparticles that are larger than 2 nm in diameter. The high catalytic activity of clusters of about ten gold atoms (ca. 0.5 nm in diameter) towards CO oxidation[10] suggests that subnanometer-sized clusters represent a unique class of catalysts.

In situ spectroscopic investigations of gold electrooxidation/re-reduction in CTAB-containing solutions in the present work have provided some of the most intriguing glimpses of the initial stages of nanoparticle production. We observed molecule-like absorption bands typical of gold clusters of a few atoms, examined by using a UV/Vis optical-fiber probe placed near the gold working electrode. The total absence of the SPR bands suggested an interesting possibility that the initial products are not nanoparticles but clusters of a few atoms.[11]

Herein, we show that the clusters deposited on gold and glassy carbon exhibit 1) molecule-like voltammetric features typical of the redox chemical character of smaller core clusters;[12] and 2) a smooth transition from an electrocatalytic four-electron to a bulk-type two-electron reduction pathway in the catalytic behavior towards a structure-sensitive reaction such as oxygen reduction, depending on the CTAB concentration used during the electrochemical synthesis of gold atomic clusters (AuACs).

When a clean gold-disk electrode is cycled in a solution containing CTAB (less than the critical micelle concentration (cmc), 0.1 mM, or >cmc, 50 mM) in a potential region from 0.48 to 1.88 V versus the standard hydrogen electrode (SHE) for 50 cycles at a scan rate of $100\,mV\,s^{-1}$, AuACs are generated on the electrode surface. An orange-yellow film was seen on the gold electrode when [CTAB] = 50 mM (see the Supporting Information), whereas no visually distinguishable film was obtained when [CTAB] = 0.1 mM. Simultaneously, the course of potential cycling was monitored by using an in situ UV/Vis probe, which exhibited the signature features of molecule-like subnanometer gold clusters.[13–15]

The optical spectrum (Figure 1) is more structured within each of the bands and gives major and minor bands at 393,

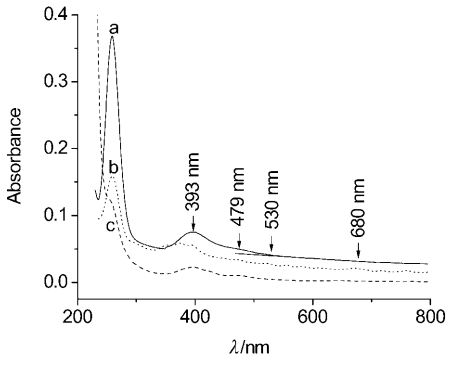

Figure 1. UV/Vis spectra of AuACs a) in CTAB/H_2O (——), b) in Bu_4NClO_4/CH_2Cl_2 (••••), and c) deposited on glassy carbon and dissolved in Bu_4NClO_4/CH_2Cl_2 (----).

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[**] C.J. thanks CSIR for a research fellowship, K.L.N.P. acknowledges financial support from DST-India (SR/S1/PC-37/2004), and we thank Sridevi Iyer and Prajakta Pednekar, Piramal Life Sciences–Mumbai, for MALDI-TOF mass spectrometry analysis. CTAB = cetyltrimethylammonium bromide.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200905614.

479, and 680 nm etc. These bands may be attributed to the interband (sp←d) and intraband (sp←sp) electronic transitions. The band at 680 nm results from an intraband electronic transition and is similar to the excitonic transition observed with semiconducting quantum dots.[16] The spectral responses for the dispersions of this orange-yellow film in H_2O/CTAB and CH_2Cl_2/Bu_4NClO_4 are very similar, and show a molecule-like behavior that is entirely different from the SPR band for the spherical gold nanoparticles.[17] For particles below about 1.5 nm in size, the SPR band is totally absent and the spectrum consists of continuously increasing absorbance with decreasing wavelength.[14] For very small clusters (Au_n, $n <$ 10–20 atoms), discrete, molecule-like bands similar to those observed in Figure 1 are expected. Based on the band-gap trend observed for these clusters,[14] the present experiments suggest the generation of Au_n clusters of $n \lesssim 13$ atoms. We speculate that the structure of these clusters is such that the smallest are protected by oligomeric motifs.[18] Also, the optical spectra of gold clusters have a band edge at about 530 nm, which corresponds to a HOMO–LUMO gap of the clusters that works out to be 2.34 eV.

In differential pulse voltammetry (Figure S1 in the Supporting Information), the redox chemical character of AuACs and a large featureless central gap of 2.5 V are the result of the molecule-like electronic energy structure of small clusters arising from their subnanometer core dimensions with a rather substantial HOMO–LUMO gap.[12] This gap agrees well with that observed in the optical spectra described above.

The core-size range of clusters indicated in the above experiments was confirmed by mass spectrometry. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry is emerging as an authentic tool for positive identification of nanocluster core size.[15,19,20] Figure 2 displays the mass spectrum of the electrolyzed samples, directly showing the presence of AuACs of 1034 (Au_5), 1178 (Au_6), 1791 (Au_9), 2255 (Au_{11}), and 2542 Da (Au_{13}) corresponding to a cluster size range of $5 \le n \le 13$, Au_5 being the most abundant cluster. As we employed a mild laser along with an organic matrix (α-cyano-4-hydroxycinnamic acid), the results are free from fragmentation. Peaks arising from the protective CTAB are not seen because its interaction with Au is weak. The Au 4f core-level photoelectron spectra of the deposits on an Au-foil electrode (Figure S2 in the Supporting Information) exhibit a positive shift of $4f_{7/2}$ binding energy from that of the bulk, which suggests the presence of small clusters surrounded by CTA^+Br^-, as carbon and bromine are also detected in the spectra. These clusters could not be imaged by analytical transmission electron microscopy, as they are too small (see the Supporting Information).

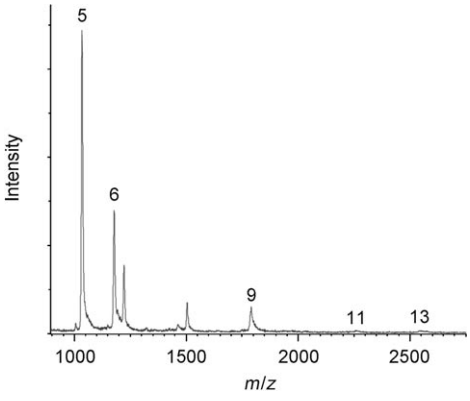

Figure 2. MALDI-TOF mass spectrum of the gold-cluster sample (index numbers indicate *n*, the number of atoms per cluster).

From the electrocatalytic point of view, bulk gold is poorly active towards the ORR in acidic media since the reduction leads not to water but only to H_2O_2 by two-electron addition. In an interesting development, Zhang et al.[21] demonstrated the replacement of a third of the platinum surface with AuACs, without affecting the electrocatalytic activity to the ORR. Other recent reports that demonstrated high ORR electrocatalytic activity through a direct four-electron addition deal with AuACs/carbon-supported particles[8,14] and Au_n ($n = 11$–140)[15] in acidic and alkaline solutions, respectively. The smallest clusters were found to yield the highest rate constant.

Figure 3 shows a comparison of the linear-sweep voltammograms for the ORR in oxygen-saturated 0.5 M H_2SO_4 solutions on 1) bulk polycrystalline gold substrate and

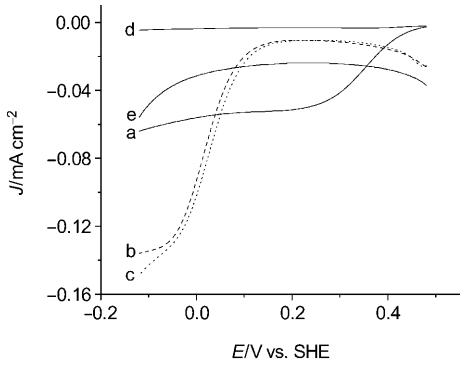

Figure 3. Linear-sweep voltammograms for the ORR in oxygen-saturated 0.5 M H_2SO_4 solution: a) on bulk polycrystalline gold substrate (——); b) on AuACs electrodeposited from 50 mM CTAB solutions (-----); and c) on Nafion-coated AuACs (•••••). d,e) Voltammograms equivalent to those in (a) and (b), respectively, in nitrogen-saturated H_2SO_4. Scan rate: 5 mVs^{-1}; scan direction: cathodic.

2) AuACs electrodeposited from 50 mM CTAB solutions. The voltammetric current density for the ORR on AuACs is twice that of the bulk gold electrode,[22] thus indicating that oxygen reduction takes place through the direct four-electron pathway. A half-wave potential of 0.025 V versus SHE of the four-electron oxygen reduction wave is approximately 0.3 V more anodic than that reported by Rodríguez-Vázquez et al.,[14] which confirms the strong electrocatalytic activity of the nanoclusters in the present work.[23] These nanoclusters reduce oxygen directly to water, as also proved by hydrodynamic voltammetry.

Rotating ring-disk electrode (RRDE) studies yield a value of four for the number of electrons involved in the reduction of oxygen, and a level of $\le 1\,\%$ for the percentage

of hydrogen peroxide generated (measured at 0.03 V vs. SHE where its generation is expected to be maximum). The current waves in the rotating disk electrode (RDE) voltammograms (Figure S5 in the Supporting Information) are very well defined, in contrast to those obtained with larger gold nanoparticles. In fact, the voltammetric patterns are akin to those observed with Pt or Pt–M bimetallic electrocatalysts.[24]

The Koutecky–Levich plots ($\omega^{-1/2}$ vs. i^{-1}) at various electrode potentials corresponding to the RDE voltammograms (Figure S5 in the Supporting Information) are perfectly linear, with slopes remaining nearly constant over a potential range of 0.22 to 0.14 V versus SHE and parallel to each other, which suggests favorable electrode kinetics of the ORR at different electrode potentials. The calculated kinetic limiting current density (J_k) and rate constant are $32\,mA\,cm^{-2}$ at 0.18 V versus SHE and $6.6\times10^{-2}\,cm\,s^{-1}$, respectively.[25]

Some theoretical studies[26,27] have shown that a decrease in the core size of Au nanoclusters results in narrowing of the d bands shifting towards the Fermi level. The work of Metiu et al.[28] shows that roughness arising from the edges of a planar Au cluster ($n \leq 13$) acts by localizing electron density at the site, thus facilitating electronic charge transfer to the π^* orbital of O_2 which leads to bonding. The disordered nature of the CTAB micellar protecting layers on the planar Au clusters most likely exposes the catalytically active edge or defect sites. In addition, preference for O_2 binding may also depend on the cluster being neutral or negatively charged.

Gold clusters deposited from solutions of CTAB below its cmc present us with the possibility of witnessing another interesting feature of ORR electrocatalysis. The linear-sweep voltammograms presented in Figure 4 were obtained from

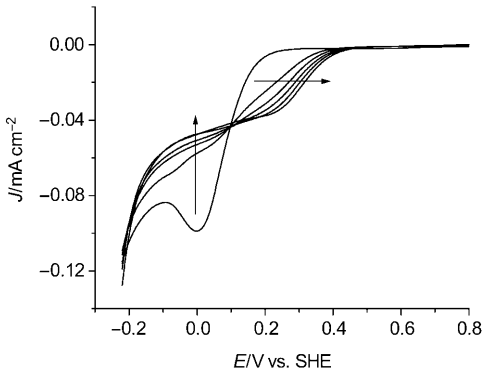

Figure 4. Successive linear-sweep voltammograms for the ORR in oxygen-saturated 0.5 M H_2SO_4 solutions on AuACs electrodeposited from 0.1 mM CTAB solutions. Scan rate: $5\,mV\,s^{-1}$; scan direction: cathodic. Arrows indicate the direction of shift of current/potential.

several consecutive runs recorded for the ORR on AuACs electrodeposited by potential cycling in 0.1 mM CTAB solutions in a potential region of 0.48 to 1.88 V versus SHE. The first scan yields a current peak at 0.01 V. In the subsequent runs using the same AuAC-covered electrode, there is a gradual decrease in current with associated: a) splitting of the current wave into two; b) shifting in the potential of the first split peak to less cathodic and of the second peak to more cathodic potentials; and c) total disappearance of the second wave because of the obvious loss of catalytic activity for H_2O_2 reduction to water. The curves corresponding to the subsequent runs cross the curve of the first run at its near mid-point. This result clearly shows that the mechanism changes to two-step two-electron reduction from what is initially a direct four-electron reduction.

This mechanism changeover also points to a possible transformation of atomic clusters to nanoparticles, an observation unprecedented in the literature of AuACs and electrochemical reactions. That the transition is caused only by the AuACs and not by the exposure of the gold substrate is proved in a control experiment with cluster-modified glassy carbon electrodes (see the Supporting Information). This dependence of the nature of the AuACs on the concentration of CTAB used in the electrosynthesis is suggestive of ineffective stabilization of AuACs at a concentration of 0.1 mM as much as when it is 50 mM, possibly because of "electrochemical sintering".

In summary, we have demonstrated that CTAB-assisted aqueous electrodeposition yields AuACs (with Au_5 being abundant) that: 1) are molecule-like; 2) electrocatalyze the reduction of oxygen to water through a direct four-electron pathway in acidic solutions; and 3) show a transition of the ORR mechanism from four-electron to two-electron reduction, which reflects the transformation of AuACs possibly to nanoparticles. From the surface science point of view, pertinent issues, such as cluster-phase formation at the electrode surfaces, the mechanism of transformation[29] of planar atomic clusters to nonplanar three-dimensional clusters or nanoparticles, and their stability under reaction conditions, need immediate attention. Work to elucidate these aspects using electrochemical-STM is underway in our laboratories.

Experimental Section

Absorbance studies of AuACs in CTAB/water and Bu_4NClO_4/CH_2Cl_2 were performed with a Cary 500 scan UV/Vis–near-IR spectrophotometer with incident light normal to the 1 cm path length quartz cuvette. For in situ observation of absorption bands during electrochemical cycling, a combination of a fiber-optic SD-2000 spectrometer with a dip-probe and DH-2000-BAL light source (Ocean Optics) was employed.

A conventional three-electrode cell was used for the electrochemical studies. The gold-disk working electrode was polished with 4/0 grade emery sheet and alumina slurry, cleaned well with Millipore water, sonicated, and then pretreated by potential cycling in sulfuric acid solutions. This clean electrode was used for electrogeneration of AuACs on its surface. Pt foil was used as counter electrode. Electrochemical measurements were performed using mercury/mercurous sulfate and quasi-silver reference electrodes. However, all the potentials reported herein are referred to the SHE, unless otherwise stated. CTAB dissolved in water played a dual role as the supporting electrolyte and surfactant stabilizer for AuACs. The cyclic/linear-sweep voltammetric experiments were carried out using a BAS-100B instrument (Bioanalytical Systems, Inc.), BIPOT module of the Autolab potentiostat/galvanostat, and RRDE setup (Pine Instruments) for hydrodynamic voltammetry. For studies on the ORR, oxygen-saturated H_2SO_4 solutions were used with an oxygen blanket maintained throughout the electrochemical measurement. All the

solutions were prepared with Millipore water (18.2 MΩ cm) and the temperature was maintained at 25 °C.

Received: October 7, 2009
Revised: November 25, 2009
Published online: February 9, 2010

Keywords: cluster compounds · electrocatalysis · gold · oxygen electroreduction · reaction mechanisms

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