

# ION-INDUCED QUANTIZED CHARGING OF IMMOBILIZED HYDROPHILIC GOLD CLUSTERS

Sulay D. Jhaveri<sup>a</sup>, Daniel A. Lowy<sup>b</sup>, Edward E. Foos<sup>c</sup>,  
Arthur W. Snow<sup>c</sup>, Mario G. Ancona<sup>d</sup>, and  
Leonard M. Tender<sup>a</sup>

<sup>a</sup>Center for Bio/Molecular Science and Technology,  
Naval Research Laboratory, Washington DC 40375

<sup>b</sup>Nova Research, Inc., Alexandria, VA 22308

<sup>c</sup>Chemistry Division, Naval Research Laboratory

<sup>d</sup>Electronics Science and Technology Division, Naval  
Research Laboratory

## INTRODUCTION

Metallic nanoclusters have potential for nanometer-scale electronics, sensors, and electro-optics applications. When they are very small, the clusters exhibit a strong electrical non-linearity via the Coulomb blockade mechanism and this physics is strongly sensitive to local changes associated with electrical gating, or with adsorption of a chemical species of interest.

In this study we describe the self-assembly of water-soluble gold nanoclusters (2 nm diameter) coated with a tri(ethylene oxide) shell, AuEO3 [1] onto a gold electrode modified with a mixed monolayer of alkane thiol/dithiol. The interaction of this system with the hydrophobic anion,  $\text{PF}_6^-$ , is explored by CV and ACV, performed in aqueous supporting electrolyte. Gold nanoclusters that are soluble in water may readily be functionalized with bio-molecules, and the resulting bio-nanoconjugates can be used as sensor elements.

Chen and Pei [2] investigated the ion-induced rectification of the quantized capacitance charging of alkanethiol protected nanoclusters adsorbed onto the surface of bare Au electrodes. The new type of gold clusters and the novel architecture described in this paper allow for faster electron transfer in aqueous media than for the previously reported system.

## EXPERIMENTAL

Working electrodes were gold disks ( $0.04 \text{ cm}^2$ ) or coiled gold wires ( $0.5\text{-cm}^2$ ). Mixed monolayers were obtained with 1-octane thiol (OT, 99%) and 1,9-nonane dithiol (NDT, 98%), self-assembled on the clean gold surface from 10:1 mol/mol solution in ethanol (total thiol concentration: 2.2 mM), for 16 h at room temperature (RT). Gold clusters AuEO3 were prepared according to previously reported methods [1] and were attached to modified Au electrodes, from aqueous solution (12 h at RT).

Three-electrode mode electrochemical measurements were performed with a chemically modified Au working electrode, a Pt counter, and Ag/AgCl, 3 M KCl reference, Ag(RE). Supporting electrolyte was 0.1 M  $\text{NH}_4\text{PF}_6$  in de-ionized water, buffered to pH 7 with 0.01 M phosphates.

Cyclic voltammetry (CV) was recorded from -0.30 to 0.50 V vs. Ag(RE), at  $0.100 \text{ V s}^{-1}$ . AC voltammograms (ACVs) were acquired in the stepped mode, with 10 mV rms amplitude. Data points were recorded every 10 mV at fixed frequency values (1-10000 Hz). CV and ACV were performed with a Model 660a Electrochemical Workstation (CH Instruments, Austin, TX) equipped with a Faraday cage.

## RESULTS

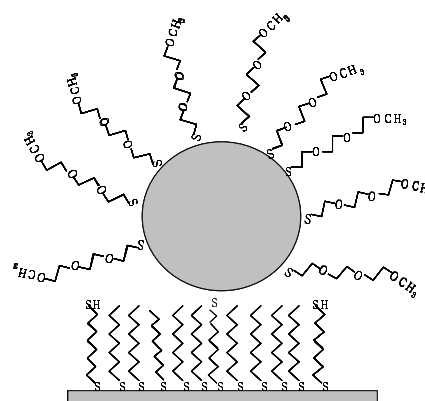
Fig. 1 displays the schematic of the self-assembled system. AuEO3 gold clusters are anchored to a mixed OT-NDT monolayer via the free thiol group of NDT, by an exchange reaction.

The ACV in Fig. 2 shows small peaks related to the presence of the hydrophobic  $\text{PF}_6^-$  anion in the supporting electrolyte. No such peaks have been observed in media based exclusively on phosphates.

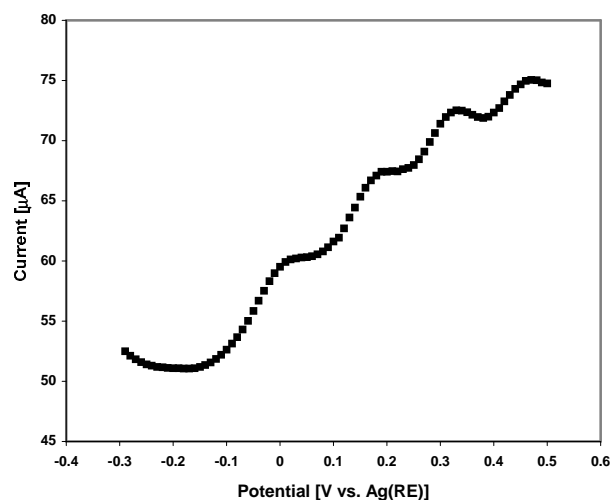
The rate constant of the electron transfer between the clusters and the electrode surface was derived from ACV scans taken at different fixed frequencies by plotting the  $I_p/I_b$  against frequency (where  $I_p$  is the peak current and  $I_b$  is the background current), according to Wooster and Creager [3].

Due to the hydrophilic coating of the electron transfer in the system is approximately 4 times faster than that reported for the alkanethiol-coated clusters [2].

A possible explanation of the enhanced charge transfer rate may reside in the partitioning of  $\text{PF}_6^-$  ions between the hydrophilic coating layer of the Au clusters and the bulk phase (i.e., aqueous supporting electrolyte).



**Fig. 1:** Schematic of the Au clusters with hydrophilic coating tethered to a SAM-coated gold electrode



**Fig. 2:** ACV recorded with the system in Fig.1 (200 Hz)

## REFERENCES

1. E. E. Foos, A. W. Snow, M. E. Twigg and M. G. Ancona, *Chem. Mater.* (submitted),
2. Sh. Chen and R. Pei, *J. Am. Chem. Soc.*, **123**, 10607 (2001).
3. S. E. Creager and T. T. Wooster, *Anal. Chem.*, **70**, 4257 (1998).