Electrochemical resolution of 15 oxidation states for monolayer protected gold nanoparticles

Bernadette M. Quinn,* Peter Liljeroth, Virginia Ruiz, Timo Laaksonen and Kyösti Kontturi

Laboratory of Physical Chemistry and Electrochemistry, Helsinki University of Technology, P.O. Box 6100, FIN-02015 HUT, Finland

RECEIVED DATE (will be automatically inserted after manuscript is accepted

Thiol protected gold nanoparticles, so called *monolayer protected clusters* (MPCs), can behave as multi-valent redox species as charge injection to the core is quantized.[1] Resulting single electron transfer events are termed quantized double layer charging (QDL).[1b] Here, hexanethiol capped Au (C6S-Au) particles were prepared by the Brust method[2a] using the modifications proposed by Murray and co-workers[2b] to obtain particles of small core radius (r = 0.81 nm, Au_{147})[2c] and improved monodispersity. Following a recent report by Hicks et al.[3], four preparations were further annealed to improve dispersity. MPC redox properties were investigated using electroanalytical techniques (cyclic voltammetry (CV), differential pulse voltammetry (DPV), and chronoamperometry) at a Pt microelectrode (diameter 25μm). Results shown here are representative of more than ten MPC preparations over a two-year period.

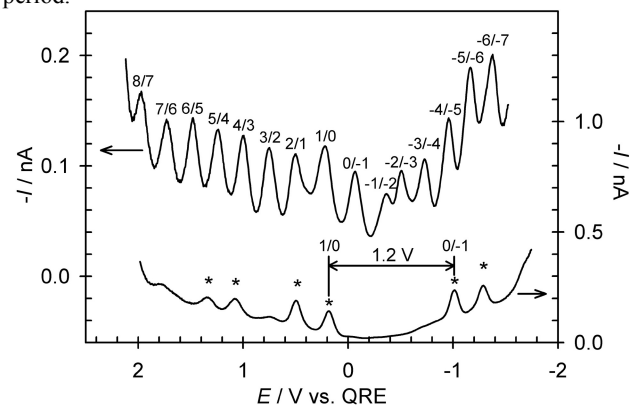


Figure 1. DPV responses for MPC solutions measured at a Pt microelectrode; as prepared 177 μM C6S-Au_{147} (upper) showing 15 high resolution QDL peaks and 170 μM C6S-Au_{55} (lower) showing a HOMO-LUMO gap. It can be seen that the as prepared solution contains a residual fraction of Au_{55} that smears out the charging response in E regions where QDL peaks overlap. The electrode potential scanned negative to positive.[4]

A typical DPV response for the as prepared Au_{147} MPCs showing 15 evenly spaced (ΔV) peaks characteristic of charge injection to the metal core is given in Figures 1. The peak potentials can be taken as the formal redox potential $E^{0'}$ for each MPC $z/z\pm1$ "redox couple".[1b] Here, as prepared Au_{147} particles are assigned charge state z = -1[5] thus, the 1st oxidation and reduction peaks are for the 0/-1 and -1/-2 redox couples, respectively. This is the first report of 15 QDL peaks at room temperature (T = 295 K) and is a clear confirmation that MPCs are indeed multi-valent redox species. The number of observable charge states was limited by the size of the available potential window and additional QDL peaks are anticipated in controlled atmosphere and reduced temperature conditions.

The reason for the increased current response for 0/1 & 1/2 and -4/-5 & -5/-6 peaks became clear after particles of smaller core size were isolated.[6] An example of a DPV for the smaller MPC fraction given in Figure 1 shows a clear HOMO-LUMO gap of 1.2 V with two and four QDL reduction (ΔV = 0.3 V) and oxidation (ΔV = 0.27 V) peaks, respectively, on either side of the band gap. Allowing for the charging energy (estimated as the difference between the two reduction peaks), the band gap is 0.9 V, in excellent agreement with that obtained for Au_{55} (r = 0.55 nm[1c]) from spectroscopic data.[1] It can be seen that the first and second oxidation peaks for C6S-Au_{55} overlap with those for the as prepared C6S-Au_{147}, giving rise to a characteristic increase for the 0/1 and 1/2 current peaks. The level of interference is dependent on the relative mole fractions present in the as-prepared particles and this varied from slight (as in Figure 1) to severe (Supporting Information). Concentrations and diffusion coefficients of both C6S-Au_{55} (D = 2×10^{-6} cm^2 s^{-1}) and C6S-Au_{147} MPCs (D = 1.8×10^{-6} cm^2 s^{-1}) were determined by chronoamperometry using the method proposed by Shoup and Szabo.[7]

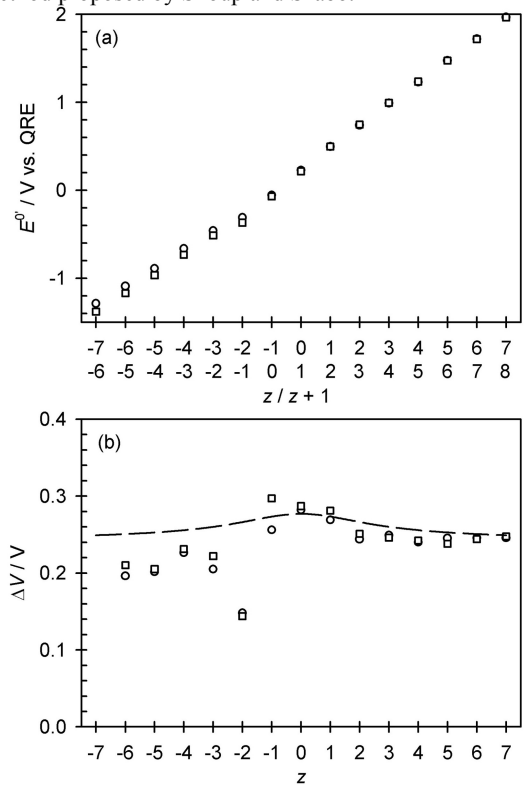


Figure 2. (a) Z-plot of $E^{0'}$ vs. redox couple charge ($z/z\pm1$) and (b) peak voltage spacing ΔV vs. charge state z for (□) 177 μM (○) 760 μM C6S-Au_{147}. Values were obtained from the DPVs given in Figures 1 and 3. The dashed line is the predicted theoretical response.

The Z-plot for C6S-Au_{147} where $E^{0'}$ is plotted vs. redox couple charge ($z/z\pm1$) was linear ($R^2 > 0.999$) as expected (Figure 2a).[1b] However, plotting ΔV vs. z (Figure 2b) reveals that although the voltage spacing is extremely regular at positive electrode potentials, reasonably regular at negative potentials there is variation at intermediate potentials. This type of plot was typical for most C6S-Au_{147} MPCs prepared and post-preparation annealing[3] did not have a significant effect on the response.

Typically, the spacing between -1/0 and 0/1 peaks is greater when compared to those obtained at higher values of z. In addition, ΔV reaches a constant value at high z. To explain this behavior, we considered a simple theoretical model, where the diffuse double layer outside the protecting monolayer is included (Supporting Information).[1c,3b,8] The numerical solution of the Poisson equation with appropriate boundary conditions is shown with a dashed line in Figure 2b (values of the parameters used: core radius 0.81 nm[1c], thickness of the protecting monolayer 0.77 nm, relative permittivity of the monolayer and solvent 3.6 and 10.24, respectively). At positive potentials, there is good agreement between theory and experiment while there is deviation at negative potentials.

This deviation could not be rationalized in terms of residual polydispersity as this would affect positive and negative potential regions equally.[1c] In many instances however, when high concentrations of MPCs were added to solution, CVs characteristic of film formation were obtained at electrode potentials in this region (Supporting Information). Oxidation DPVs recorded at different concentrations under identical experimental conditions are given in Figure 3. It can be clearly seen that $E^{0'}$ is independent of MPC concentration at positive electrode potentials as expected, while there is a marked dependence in the negative potential region. At high MPC concentrations, the -1/0 oxidation peak current is enhanced and peaks are shifted negative by a constant factor. However, comparison of ΔV vs. z for both concentrations (Figure 2b) reveals that with the exception of ΔV value for z = -1, the plots are comparable. From the derivative of the CV response (Supporting Information), there was evidence of film deposition on the electrode surface at the first MPC reduction (peak -1/-2 for particles used here), which was then stripped when the electrode potential was reversed past the first oxidation peak (peak -1/0). This indicates that the electrode is modified by an electroactive MPC film at potentials more negative that the -1/-2 peak. This is the first report of reversible electrodeposition of MPC films. It is likely that the negatively charged MPCs associate with the base electrolyte cation and the resulting ion pair precipitates on the electrode surface at high MPC concentrations. At low MPC concentrations (170 μM), film formation is not apparent in the voltammetric response. However, association with the base electrolyte cation will influence the peak potentials relative to the case where association is absent.[8b] This may be the reason why the average spacing is less by ca. 40 mV for reduction compared to oxidation. A detailed study of association between MPCs and base electrolyte ions will provide more fundamental information.

The results given here are consistent with electrostatic charging of a metallic core.[1c,8a] Irregularities in ΔV reported recently at negative and positive electrode potentials[3] were not noted. As noted by Waters et al.[9], it is problematic to purify MPCs prepared by the Brust method and adsorption/surface phenomena may give additional responses at macro electrodes. As the voltammetric response at a microelectode is at steady-state, interference from these transient phenomena is avoided.

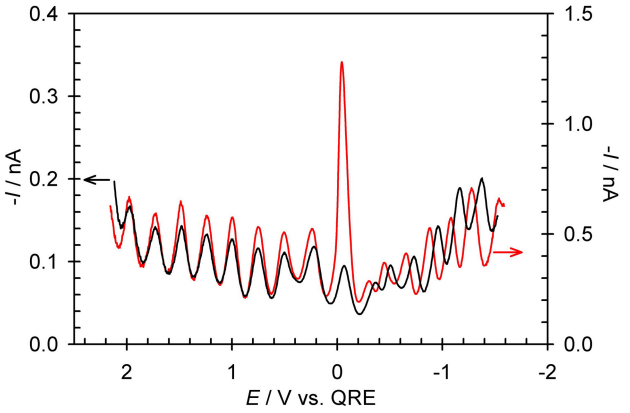


Figure 3. DPV response of as prepared C6SAu_{147} at 760 μM (red) and 177 μM (black) concentrations illustrating how the QDL response in the negative potential region is dependent on the MPC concentration. The sharp peak at ca. 0 V is a stripping peak. Potential scanned negative to positive. Experimental conditions were as in Figure 1.

Acknowledgment. Research funding provided by the National Technology Agency, Finland and The Academy of Finland.

Supporting Information Available: Additional experimental details, DPVs, and theory for the charging behavior of the nanoparticles. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Chen, S.; Ingram, R. S.; Hostetler, M. J.; Pietron, J. J.; Murray, R. W.; Schaaff, T. G.; Khoury, J. T.; Alvarez, M. M.; Whetten, R. L. *Science* **1998**, *280*, 2098. (b) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, *33*, 27. (c) Chen, S.; Murray, R. W.; Feldberg, S. W. *J. Phys. Chem. B* **1998**, *102*, 9898. (d) Quinn, B. M.; Liljeroth, P.; Kontturi, K. *J. Am. Chem. Soc.* **2002**, *124*, 12915.

(2) (a) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *Chem. Commun.* **1994**, 801. (b) Pietron, J. J.; Hicks, J. F.; Murray, R. W. *J. Am. Chem. Soc.* **1999**, *121*, 5565. (c) Schaaff, T. G.; Shafigullin, M. N.; Khoury, J. T.; Vezmar, I.; Whetten, R. L *J. Phys. Chem. B*. **2001**, *105*, 8785.

(3) (a) Hicks, J. F.; Miles, D. T.; Murray, R. W. *J. Am. Chem. Soc.* **2002**, *124*, 13322. (b) Miles, D. T.; Murray, R. W. *Anal. Chem.* ASAP article.

(4) CVs, DPVs and chronoamperograms were recorded using a CHI 900 potentiostat (CH Instruments, Austin, TX). A two-electrode arrangement was used where a Pt microelectrode was used as the working electrode and a silver wire served as both counter and quasi-reference electrode. The particles were dissolved in 10 mM bis-(triphenylphosphoranylidene) ammonium tetrakis-(pentafluorophenyl)borate (BTPPATPBF_{20}) 1,2-dicloroethane (DCE) solution. All measurements were performed at room temperature. Solutions were degassed and a blanket of N_2 was maintained over the solution during the measurements.

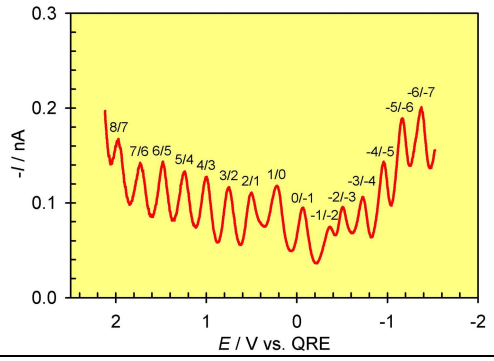
(5) This is a reasonable assumption as $NaBH_4$ used in the particle preparation is a very strong reducing agent and the MPCs formed can also be reduced.

(6) Hexanethiol protected C6S-Au_{55} MPC were isolated following the annealing method proposed by Hicks et al.[3] with the difference that instead of a 1:50 mole ratio of thiolate to incoming hexanethiol, an excess of thiol was added (> 500 fold).

(7) (a) Shoup, D.; Szabo, A. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *140*, 237. (b) For potential steps to z = 0, +1 and +2 charge states (troughs in the DPV response), the accuracy of this method was dependent on the level of Au_{55} impurity but is not significant for steps to z > +3 at relatively minor levels of impurity

(8) (a) Weaver, M.J.; Gao, X.; *J. Phys. Chem.* **1993**, *97*, 332. (b) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamentals and Applications*; 2nd ed.; John Wiley & Sons: New York, 2001.

(9) Waters, C. A.; Mills, A. J.; Johnson, K. A.; Schiffrin, D. J. *Chem. Commun*. **2003**, 540.



The first observation of 15 voltammetric quantized charging peaks for a solution of hexanethiol capped gold nanoparticles (so-called monolayer protected clusters MPCs) at room temperature is reported where the variation in peak spacing with increasing charge stored in the metal core is discussed in terms of MPC capacitance.