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Ion-induced discrete charging of immobilized water-soluble gold nanoclusters

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Hydrophilic gold nanoclusters were immobilized onto monolayer-modified gold electrodes and PF_6^--induced rectification and stepwise capacitance charging was studied in aqueous supporting electrolyte by cyclic voltammetry and ac voltammetry.

Metallic nanoclusters have potential for nanometer-scale electronics,[1] sensors,[2] and electro-optics applications.[3] When very small (diameter < 2 nm), they exhibit strong electrical nonlinearity *via* the Coulomb blockade mechanism,[4] and are sensitive to chemical adsorption.[2] In this paper we examine 1.8 nm diameter water-soluble gold nanoclusters coated with tri(ethylene oxide)thiol, AuEO3, immobilised on a modified gold electrode, Fig. 1.[5] Such water-soluble gold nanoclusters may eventually be functionalized with biomolecules, and the resulting bionanoconjugates used as electronic biosensor elements. Here we report their interaction with PF_6^-, in aqueous supporting electrolyte, explored by cyclic voltammetry (CV) and AC voltammetry (ACV).[6] The novel water-soluble nanoclusters, immobilized by the strategy employed here, demonstrate PF_6^--sensitive rectification and stepwise charging similar to that previously reported for water-insoluble nanoclusters immobilized on bare gold electrodes[7] but with significantly faster electron transfer kinetics.

AuEO3 were immobilized onto gold wire electrodes modified with a mixed monolayer of 1-octanethiol (OT) and 1,9-nonanedithiol (NDT).[8] For comparison, 1.8 nm diameter water-insoluble nanoclusters coated with OT, AuC8(1 : 1), prepared according to previously reported procedures,[9] were also immobilised onto OT/NDT modified gold wires.[8]

In the CV of AuEO3, Fig. 2 (black line), the small well-defined peaks result from the stepwise charging of these nanocluster assemblies, similar to that previously reported for water insoluble nanoclusters.[7,10] Oxidation of AuEO3 facilitates ion pairing with PF_6^- resulting in expulsion of water from the cluster/electrolyte interface, thereby increasing interfacial charging.[7] Voltammetric steps were observed to a lesser extent in the presence of ClO_4^- (a smaller anion), but were absent from CVs recorded in phosphate buffer without either anion. The CV also exhibits PF_6^--sensitive rectification, *i.e.*, increasing charging current with increasing applied voltage, as previously observed (albeit to a greater extent) for water-insoluble nanoclusters.[7]

CV of immobilised AuC8(1 : 1), Fig. 2 (grey line), exhibits PF_6^--dependent stepwise charging and rectification similar to that described for the same nanoclusters immobilised on bare gold.[7]

Comparison of the CVs in Fig. 2 highlights the effect of different encapsulating monolayers on the voltammetric properties of immobilised nanoclusters. Firstly, the similarities in physical properties of these assemblies are evinced by the calculation of average interfacial capacitance attributed to a single nanocluster (‘molecular capacitance’). Voltammetric step spacing yielded molecular capacitance values of 1.1 aF for both AuEO3 and AuC8(1 : 1).[11] Secondly, the extent of rectification is greater for the AuC8(1 : 1) than for AuEO3. At

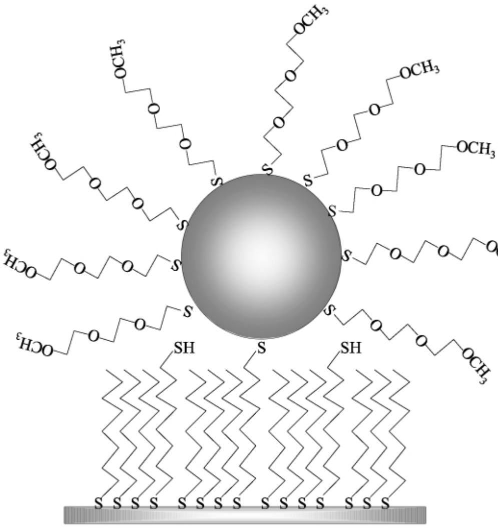

Fig. 1 Schematic of the AuEO3 tethered to a modified gold electrode. AuEO3 are anchored to a mixed OT/NDT monolayer *via* the free thiol groups of NDT, by an exchange rection.

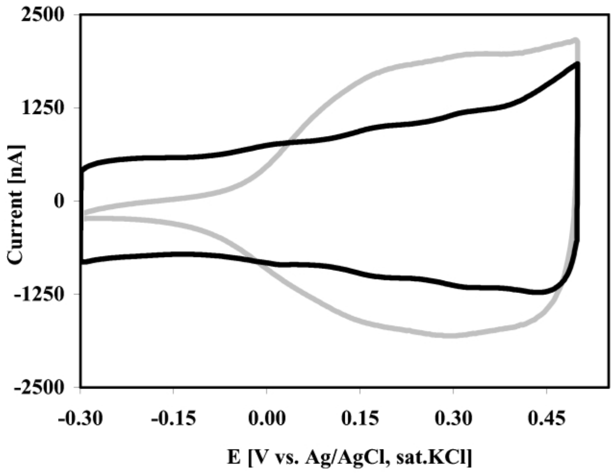

Fig. 2 CVs of AuEO3 (black line) and AuC8(1 : 1) (grey line) in the presence of 0.1 M NH_4PF_6 in buffered aqueous solution (pH 7); scan rate 0.100 V s^{-1}.

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negative applied potentials the charging current is much smaller for AuC8(1 : 1) than for AuEO3, suggesting that PF_6^- partitions to the interfacial region of AuEO3 even when uncharged. Thirdly, the voltammetric steps of AuC8(1 : 1) are less resolved compared to those of AuEO3. This result is consistent with slower kinetics of the electron transfer between AuC8(1 : 1) and the underlying electrode relative to that of AuEO3, as measured by ACV.

AC voltammetry, Fig. 3, emphasises the differences in electron transfer kinetics of AuEO3 and AuC8(1 : 1). At 1 Hz, peaks corresponding to the stepwise charging of AuEO3 are clearly resolved, whereas those for AuC8(1 : 1) are barely discernable. Even at 10 000 Hz, discrete peaks were visible in the ACV for AuEO3 (not shown).

Following Creager and Wooster, ACVs were recorded over a range of frequencies, and the ratio of peak current to background current, (I_p/I_b) was plotted as a function of frequency for the three peaks associated with the discrete charging of the clusters (Fig. 4). Simulated curves based on a Randles equivalent circuit, were used to fit the data and the resulting parameters pertaining to the resistance to charge transfer, $R_{ct,}$ and adsorption pseudo-capacitance, C_{ads}, were used to calculate values for rate constant, $k_{ET} = (2.25 \pm 0.56) \times 10^4\ s^{-1}$, and coverage, $\Gamma = 3.2 \times 10^{-12}$ mol cm^{-2}.[12,13] The magnitude of the k_{ET} is consistent with values previously reported for ferrocene tethered to the electrode surface by 9–10 carbon atom spacers.[13–15]

The difference in magnitudes of k_{ET} for AuEO3 and AuC8(1 : 1) [$k_{ET} = 2\ s^{-1}$] correlates with the difference reported for bulk electrical conductivities.[5] Furthermore, the k_{ET} for AuEO3 is *ca*. 3000 times faster than previously reported for alkanethiol (C_6)-coated clusters in aqueous media.[7] The solubility of AuEO3 and fast kinetics in aqueous solutions may potentiate their use as elements of a bioelectrochemical sensor.

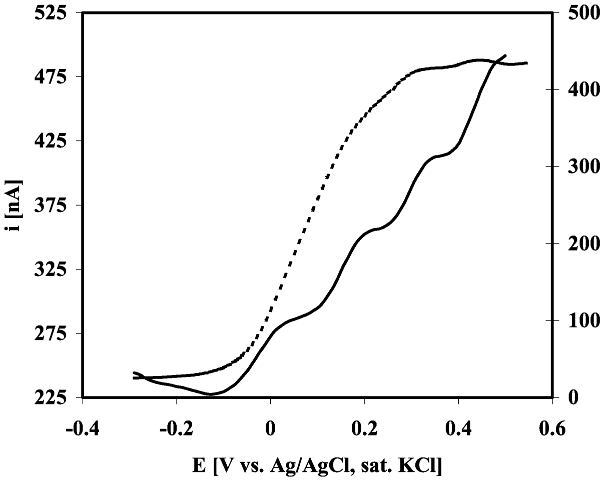

Fig. 3 ACVs of clusters in the presence of PF_6^-, at 1 Hz: AuEO3 (solid line, primary *y* axis); AuC8(1 : 1) (dotted line, secondary *y* axis).

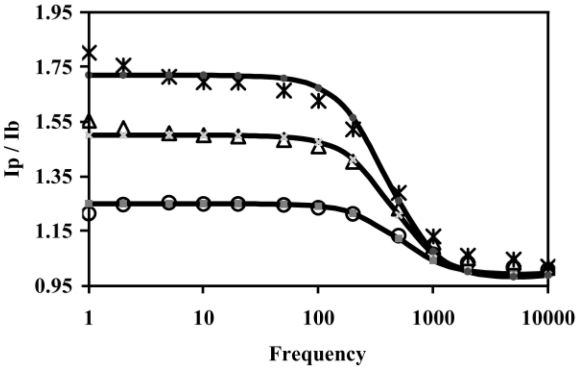

Fig. 4 I_p/I_b *vs*. frequency curves: Average current ratios from three electrodes and simulated curves (solid lines) for peak 1 (○), peak 2 (△) and peak 3 (*).

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6 Electrochemical measurements were performed using a Model 660 electrochemical workstation (CH Instruments, Austin, TX) equipped with a Faraday cage. A Pt counter electrode and a Ag/AgCl, 3 M KCl reference electrode were employed. Supporting electrolyte consisted of 5 mL of 0.1 M NH_4PF_6 and 0.01 M potassium phosphates in deionised water (pH 7). ACV was carried out with an AC-amplitude of 10 mV. Working electrodes were 32 mm length, 0.5 mm diameter coiled gold wires.

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8 Mixed monolayers were obtained with OT (99%) and NDT (98%) on the clean gold surface from 10 : 1 mol/mol solution in ethanol (total concentration of thiols: 2.2 mM), for 2 h at room temperature (RT). AuEO3 (prepared according to Foos *et al.*, *cf.* ref. 5) were immobilised by immersion of the wire in aqueous solution of AuEO3 for 1 h at RT. AuOT(1 : 1) were immobilized from a dichloromethane solution for 1 h at RT. As a control for non-specific adsorption of gold clusters, electrodes modified solely with OT monolayer were exposed to both types of nanoclusters. CVs of these systems showed neither stepwise charging nor rectification.

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