

Potential and Particle-Size Dependent Charge Transfer Across Ligand-Protected Au Nanoparticle Thin Layers

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This paper reports a very interesting finding on the charge transfer across octanethiol-protected Au nanoparticle (NP) thin layers formed on glassy-carbon (GC) electrode. It is found that the charge-transfer kinetics through the NP thin layers depends on the electrode potential as well as the particle size. Similar behavior has also been observed on Au and Pt electrodes. Three samples of octanethiol-protected gold NPs, with average particle size of 1.7, 2, and 3.5 nm respectively, were investigated. For each sample, an aliquot of 5 μ l of a 10mg/ml solution of NPs dissolved in toluene was drop-cast on the GC working electrode and air-dried. The electrochemical measurements were performed in a three-electrode electrochemical cell, Pt wire as counter electrode, and Ag/AgCl (3M NaCl) as reference electrode. Differential pulse voltammograms (DPVs) are presented in Fig.1. They show very distinct features in the positive vs. the negative potential regions. In the positive potential region, the characteristic quantized-double-layer (QDL) charging-discharging waves [1] still show up for smaller NPs and the peak interval still depends on the particle size, being larger for smaller NPs. But, the peak interval between two consecutive charging peaks, $E_{z,z-1}$, becomes smaller compared with the value measured in a solution phase, reflecting changes in the dielectric environment around the NPs and/or non-negligible NP-NP interaction. At negative potentials, however, the QDL charging waves disappear and the three samples behave very similarly. We hypothesize that this interesting behavior is most likely related to a potential-dependent charge transfer across the NP thin layers. This hypothesis was tested by using the well-known redox waves of $[\text{Fe}(\text{CN})_6]^{3-}$ [2] in the positive potential region and $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ [3] in the negative potential region, which are presented in Fig.2 and 3 respectively. Remarkably, the redox waves of the $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ at -0.24 V and -0.5 V are almost not affected by the presence of the NP thin layers but those of $[\text{Fe}(\text{CN})_6]^{3-}$ at the positive potentials do. Specifically, the peak-to-peak separation (ΔE_p) increases from 59 mV for bare GC to 112, 136, and 300 mV for 3.5 nm, 2 nm, and 1.7 nm respectively. This indicates that the presence of the NP thin layers dramatically modifies the charge transfer kinetics at the positive potential region in which a bigger effect is noticed for smaller particles. The implications between the ΔE_p and the charge transfer kinetics will also be discussed.

References

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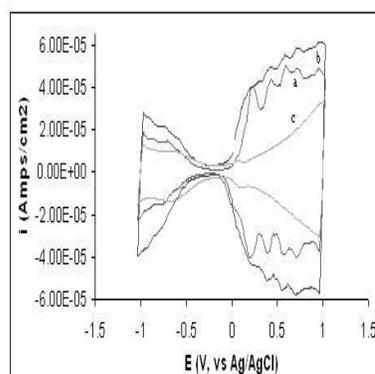


Fig.1 DPVs of a thin-layer of octanethiol-protected gold NPs deposited on the GC working electrode; electrolyte /solvent: 0.1 M Bu_4NClO_4 in acetonitrile; (a) 1.7 nm Au NP; (b) 2 nm Au NPs; (c) 3.5 nm Au NPs.

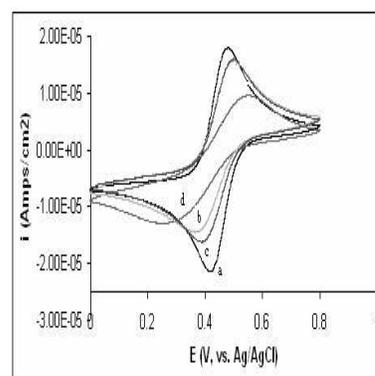


Fig 2. CVs of 1mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ in 0.5 M H_2SO_4 before (a) and after the deposition of the 3.5 nm (b), 2 nm (c) and 1.7 nm (d) Au NPs on the GC electrode.

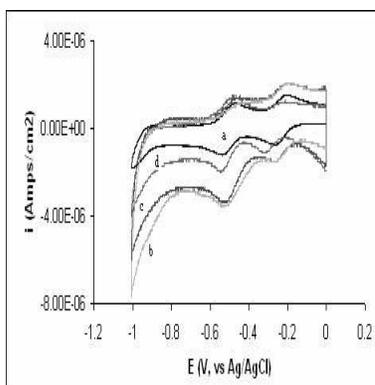


Fig 3 CVs of 10^{-4} M $\text{K}_4\text{SiW}_{12}\text{O}_{40}$ in 0.1 M LiClO_4 before (a) and after the deposition of the 3.5 nm (b), 2 nm (c) and 1.7 nm (d) Au NPs on the GC electrode.