

**Double Layer Charging and Ligand Chemistry of
Monolayer-protected Gold Clusters**

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Gold nanoparticles containing less than 200 atoms have been of recent interest because they represent the bulk-to-molecule transition region. We have studied in particular $\text{Au}_{140}(\text{SC6})_{53}$ and $\text{Au}_{38}(\text{SC2Ph})_{24}$, whose voltammetry shows, respectively, quantized double layer charging capacitance (QDL) and a molecule-like band gap. The effects of supporting electrolyte concentration, temperature and solvent on QDL behavior of the hexanethiolate-protected gold cluster $\text{Au}_{140}(\text{SC6})_{53}$ have been analyzed with double layer theory including diffuse layer effects. Phenylethylthiolate coated gold cluster $\text{Au}_{38}(\text{SC2Ph})_{24}$ shows a doublet of oxidation waves in addition to the electrochemical band gap in square wave voltammetry. The spacing between the doublet peaks is affected by the electrolyte medium in a manner similar to that for $\text{Au}_{140}(\text{SC6})_{53}$. Meanwhile, the ligand exchange kinetics of the $\text{Au}_{38}(\text{SC2Ph})_{24}$ nanoparticles have been examined in comparison to that known for $\text{Au}_{140}(\text{SC6})_{53}$, as a study of the effect of nanoparticle size on chemical reactivity. Finally, the diffusion coefficient of $\text{Au}_{38}(\text{SC2Ph})_{24}$ in dichloromethane was also measured.

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