

Electrochemical deposition on Layered Au Nanoparticle Films: Bimetallic Clusters by Underpotential Deposition

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We describe the construction of bimetallic clusters on indium tin oxides (ITOs), employing well-defined underpotential deposition (upd) systems on layered gold nanoparticle (AuNP) thin films, linked with difunctional 1,6-hexanedithiol (HDT). Monolayered or multilayered AuNP films are constituted by the alternate accumulation of AuNPs and HDT molecules, following the previous report.¹ The procedure is illustrated in Scheme. Under the electrochemical deposition of upd metals on AuNPs, there are at least three possible shapes such as core-shelled, locally deposited, and alloyed particles in the structures of bimetallic clusters.

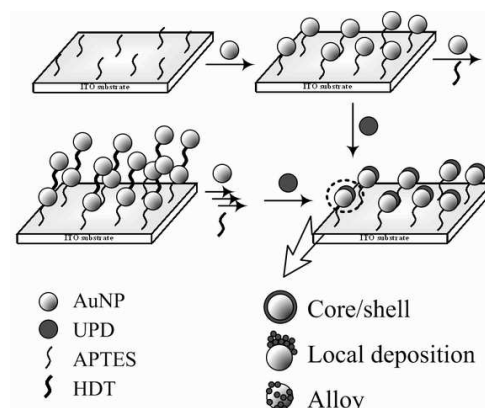
Scanning electron microscopy informs the morphological structures of layered films accumulated by stepwise immersion into citrate-stabilized AuNP and HDT solutions. Although cyclic voltammograms of metal upd, dependent upon the order of crystal orientation of a substrate, show that colloidal AuNP layers are considerably polycrystalline, X-ray diffraction implies that those are close to Au(111) properties. As the AuNP layers are piled up on ITO, faradaic currents for upd adsorption increase linearly, indicating the entire accessibility to individual AuNPs, and hence the mass transfer is plausible in the AuNP frameworks.

This electrochemical approach affords an alternative route to the construction of bimetallic clusters. Ag on AuNP and Cu on AuNP exhibit similar features with that onto the bulk metal film. Noticeably, the Tl and Pb upd tend to reveal more enhanced adsorption currents and particularly irreversible CVs, explicating their strong binding properties to AuNPs.

Therefore, we conclude that Ag or Cu onto AuNPs sustains a core-shelled structure, while Pb or Tl onto AuNPs transforms to an alloyed structure. Moreover, bimetallic clusters of Tl and Pb onto AuNPs will play a prominent role for oxygen catalysis in a fuel cell because they hold their own electrocatalytic activities on the oxygen reduction.

Reference:

1. Schiffrin, D. J. et al., *Langmuir* **14**, 5425 (1998).



Scheme. Illustrative cartoon for the modification of ITO substrates and representative bimetallic structures after electrochemical deposition.