

Electrochemical dealloying of gold-silver alloy nanoparticles - selective dissolution of the lesser and more-noble species

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Dealloying is most commonly associated with the selective oxidative etching of the lesser-noble species in a bulk metal alloy. Extensive research has been devoted to understanding this process as it relates to industrial corrosion,¹ but it has also been utilized as a technique for creating unique nanomaterials. The tunable electronic properties of alloys have been well recognized for their potential to produce improved catalysts,² but there has also been interest in dealloying catalytically relevant alloys to manipulate their surface structure and composition and increase their activities.

For bulk gold-silver alloys, chemical etching of silver with nitric acid produced intricate nanoporous gold (NPG) structures with high surface areas³ that have shown improved catalytic properties.^{4,5} Dealloying studies have been extended to a variety of bulk alloy systems, but the dealloying of nanoparticles (NPs) has received far less attention. Sieradzki et al. showed through Monte Carlo simulations that surface roughness and porosity associated with silver dealloying could be induced in gold-silver alloy NPs ($\text{Au}_x\text{Ag}_{1-x}$ NPs) as small as 4 nm in diameter.⁶ This required an overpotential to increase the dissolution rate above the diffusion rate of the more-noble metal to prevent passivation of the core.

Experimental data for silver dealloying potentials in gold-silver alloy NPs were not found in the literature. In the alloy NPs systems that have been dealloyed, very few studies have looked at NPs with diameters <10 nm where quantum size effects and high surface energies are expected to significantly influence their electrochemical behavior.⁷ Two notable papers have shown the dealloying behavior of small Pt-alloy NPs.^{8,9} Both groups showed that electrochemical dealloying only penetrated within ~1 nm of the NP surface, although the surface-enrichment was shown to improve their catalytic activities for the oxygen reduction reaction (ORR).

Here, we report that aqueous gold-silver alloy nanoparticles (NPs) were synthesized by reduction with borohydride using adenosine-5'-triphosphate as a capping ligand. UV-Vis spectroscopy (UV-Vis) and high-resolution transmission electron microscopy (HRTEM) showed the formation of alloy NPs at all Au:Ag ratios in the <8 nm diameter size range. The NPs were immobilized into a transparent indium-tin oxide (ITO) electrode using a layer-by-layer (LbL) technique which was verified by X-ray photoelectron spectroscopy (XPS). Lesser-noble silver was dealloyed from the alloy NPs by cyclic voltammetry

(CV) in sulfuric acid. Dealloying of the gold atoms from the NP LbLs was also performed by CV in sodium chloride. Silver oxidation to insoluble silver chloride allowed the more noble gold atoms to be dealloyed as tetrachloroaurate ions while retaining cohesive silver in the NPs. Both silver oxidation as well as gold dealloying shifted toward higher potentials with increasing gold content, and both processes converged in samples with >60% gold. Reversible silver redox behavior persisted at its thermodynamic potential beyond the first cycle.

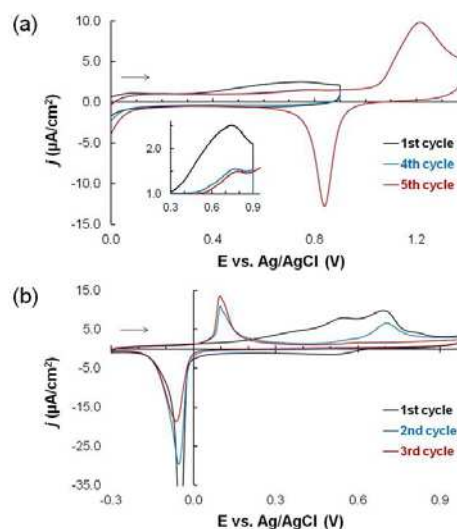


Figure 1. CVs [10 mV/s scan rate] of ITO-NP LbL films showing (a) Ag-dealloying for ATP-Au₆₀Ag₄₀ NPs over 5 cycles (Ag-oxidation enlarged in inset) in 0.1 M H₂SO_{4(aq)}. (b) Au-dealloying over 3 cycles for ATP-Au₄₀Ag₆₀ NPs in 0.1 M NaCl_(aq).

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