

Self and directed assembly of metallic nanoparticles via PLiD and STEM/ EELS characterization of plasmon-related effects

Yueying Wu¹, Guoliang Li², Charles Cherqui³, Nicholas W. Bigelow³, Jon P. Camden², David J. Masiello³, Jason D. Fowlkes⁴, Philip D. Rack^{1,4}

1 Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN37996, USA

2 Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN46556, USA

3 Department of Chemistry, University of Washington, Seattle, WA98195, USA

4 Oak Ridge National Laboratory, Center for Nanophase Materials Science, Oak Ridge, TN37831, USA

Email: prack@utk.edu

Metallic nanostructures form the basis for a wide range of applications such as ultrasensitive detection, plasmon-assisted solar energy harvesting, nano-electronics and catalysis, and nonlinear spectroscopy. Recently, the self and directed assembly of metallic thin films via pulsed-laser induced dewetting (PLiD) has proven to be an effective route for the synthesis of single-element and alloy nanoparticles. In our recent study, the physical properties and liquid dynamics underlying metallic thin film dewetting were investigated for the purpose of understanding how initial boundary conditions facilitate precise assembly. Consequently, the crystalline structure and plasmon spectra of resultant nanoparticles were examined using a transmission electron microscope (TEM) and Electron energy loss spectroscopy (EELS). Simulation using the full-wave electron-driven discrete-dipole approximation (e-DDA) software package was performed to interpret the experimentally observed plasmonic behavior. Specifically, we demonstrate the self-assembly of truncated $\text{Au}_x\text{Ag}_{1-x}$ alloy nanospheres on a supporting substrate via PLiD. The PLiD process yields ultrasmooth nanoparticle surfaces and uniform alloy compositions over the entire binary Au–Ag composition range. The dielectric functions of the $\text{Au}_x\text{Ag}_{1-x}$ alloys were experimentally measured for a precise theoretical analysis of the plasmonic behavior of the alloy nanoparticles. The size and composition effects on the substrate-dressed LSPR modes of the identically synthesized truncated nanospheres are investigated using EELS for the first time. The result reveals a progressive red-shift of all LSPR modes as a function of size and a linear red-shift of the modes as the atomic fraction of Au is increased (See figure 1 for an overview of synthesized $\text{Au}_x\text{Ag}_{1-x}$ nanoparticles, measurement/ simulation set up, and the dependence of plasmonic energy on size and alloy composition). Finally we will present some concepts for advanced optical devices based on directed assembly of complex nanoparticle arrays.

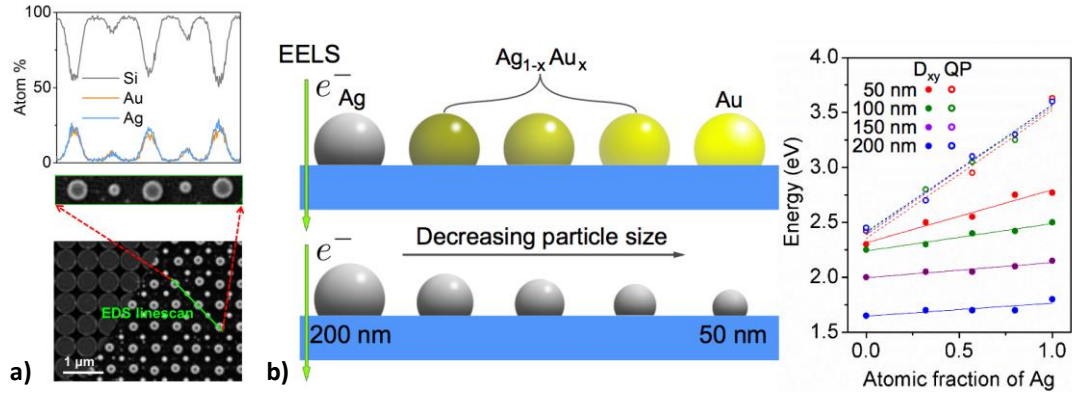


Figure 1. (a) Lithographically patterned Au_{0.5}Ag_{0.5} film (left) and resultant ordered Au_{0.5}Ag_{0.5} 2-d nanoparticle array (right) formed via PLiD. Top panel of a) Au, Ag and Si EDS line scans of the Au_{0.5}Ag_{0.5} nanoparticle array. (b) Left panel contains schematics of the composition- and size-dependent EELS experiments performed on the PLiD synthesized alloy nanoparticles. The right panel demonstrates the dependence of the D_{xy} and QP mode energies on alloy composition and particle size.