

Monitoring Galvanic Replacement of Ag Nanoparticles by Pd using Low Dose *In Situ* Liquid S/TEM

Katherine Jungjohann¹, Stoyan Bliznakov², Radoslav Adzic² and Eli Sutter¹

¹. Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY, USA.

². Department of Chemistry, Brookhaven National Laboratory, Upton, NY, USA.

Hollow nanoparticles present high surface area nanostructures that have displayed improved catalytic activity for the oxygen reduction reaction [1]. Formation of hollow nanoparticles can be achieved in a spontaneous reaction known as galvanic replacement, where the atoms in a metal nanoparticle are displaced by metal ions in solution having a higher reduction potential. The general mechanism for the formation of the hollow nanostructures includes a pit formation followed by diffusion of the interior metal atoms out from the pit [2]. During the replacement, the morphological and compositional changes are not well understood. In order to control the hollow structure formation for catalysis applications, a deep understanding of the pitting process is necessary.

One of the main abilities provided by *in situ* liquid scanning/transmission electron microscopy (S/TEM) is to monitor liquid-state reactions of nanoparticles. Growth of nanoparticles from metal ion precursors using liquid cell S/TEM can be controlled by the electron dose for aqueous solutions [3]. Electron irradiation of the water within the liquid cell will create redox species, of which the aqueous electron is known to reduce metal ions for the synthesis of metal nanoparticles [4]. To limit the formation of redox species, low dose imaging conditions allow for reduced beam induced reactions and charging for the observation of spontaneous reactions without an external stimulus.

In this study, a dedicated liquid cell TEM holder [3] sealed a sample solution of silver nanoparticles mixed with a dilute PdCl₂ solution for imaging in TEM and STEM using a FEI Titan Environmental TEM operated at 300 kV. Polystyrene beads, 90 nm in diameter, were dried at the windows corners to define the spacing between two 30 nm SiN membrane windows within the cell. Low dose conditions were achieved by imaging at reduced beam current and magnification, for an electron dose per frame of $\sim 5.2 \text{ e}^-/\text{\AA}^2$ in TEM and $\sim 40.9 \text{ e}^-/\text{\AA}^2$ in STEM. Figure 1 shows the *in situ* galvanic replacement of a 35 nm Ag nanoparticle upon exposure to 10 μM PdCl₂ using dark-field STEM imaging. Initial pit formation occurred within the first 5 seconds of imaging as observed on the bottom edge of the nanoparticle. Over the following 40 seconds, a stable morphology was observed with an increase in the size of the pit and the nanoparticle diameter, caused by simultaneous deposition and diffusion. Although the electron dose is reduced, reducing species formed by electron irradiation of water molecules promote the redeposition of the Ag ions onto the nanoparticle surface. Diffusion of the bulk nanoparticle volume was observed between 50 to 70 seconds, where the pit size increased, as shown by the variation in contrast between the top and bottom edges of the hollow nanoparticle in the final frame. In comparison of the reacted nanoparticles exposed and unexposed to the electron beam, the resulting structures and compositions were equivalent, Fig. 2. This demonstrated that the pitting process observed during *in situ* liquid cell STEM imaging was comparable to the native process for homogeneous alloy formation of Ag-Pd by interdiffusion of the metals in solution [5].

References:

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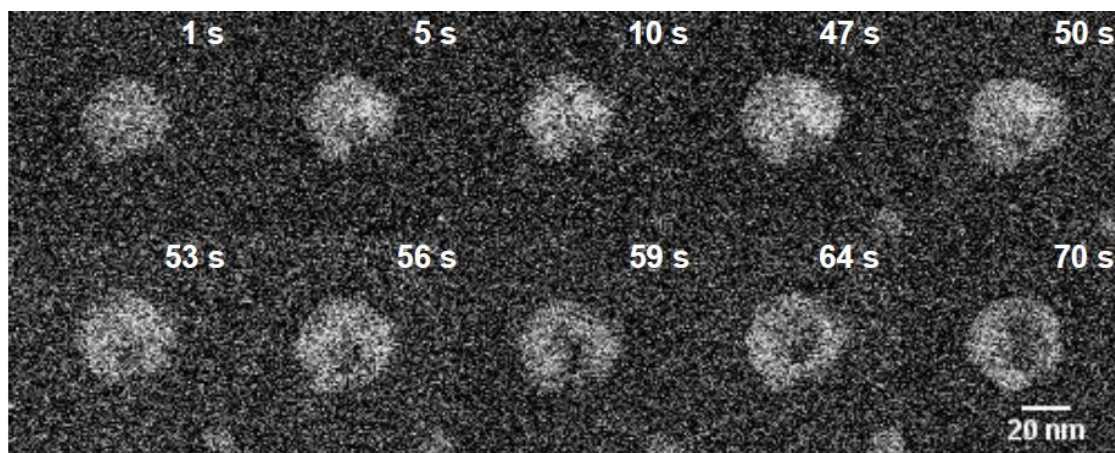


Figure 1. *In situ* dark-field STEM image series of a silver nanoparticle exposed to a PdCl₂ solution for the observation of galvanic replacement within a hermetically sealed liquid cell. Time stamp in the top right corner of each frame defines the time passed in seconds from the initial exposure to the electron beam.

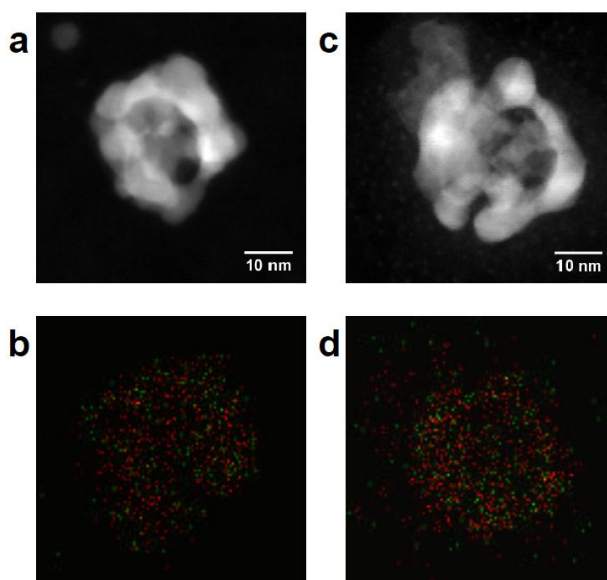


Figure 2. a) Dark field STEM image of a hollow Ag-Pd nanoparticle after *in situ* imaging. b) Energy dispersive x-ray spectroscopy (EDS) map of nanoparticle in (a) displayed a homogeneous alloy, 85% Ag. c) Dark-field STEM image of a hollow Ag-Pd nanoparticle after 2 hours of reacting outside of the microscope. d) EDS map of nanoparticle in (c), 85% Ag.