

Studying the Interdiffusion of Au and Pd using Nanoparticle Diffusion Couples and Transmission Electron Microscopy

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Bimetallic nanoparticles are important as candidate materials for applications in catalysis, plasmonics, and biomedical research [1]. At elevated temperatures, the constituent atoms can inter-diffuse, leading to changes in surface composition and structure, which then affects the properties of these nanostructures. Despite the importance of atomic diffusion in controlling nanoparticle morphology, much of what we know about the process is extrapolated from bulk measurements or thin film studies. A well-known reaction that takes place during the interdiffusion of two metals across an interface is the Kirkendall effect [2]. Due to the difference in interdiffusion rates between the two components, there is a net vacancy flux towards the side with the faster diffusing species. The subsequent clustering of these vacancies can lead to the formation of voids. The Kirkendall effect has also been used to explain the formation of hollow nanostructures when monometallic nanoparticles oxidize [3]. Our understanding of the Kirkendall effect in nanoscale bimetallic systems is, however, more limited.

Here, we report results from annealing experiments where we studied the interdiffusion of Au and Pd in nanoparticles synthesized with a core-shell geometry (see Figure 1). We heated these samples at fixed time intervals and then characterized the same nanoparticles with scanning transmission electron microscopy. Chemical mapping using energy dispersive x-ray indicate that Pd diffuses through Au faster than Au diffuses through Pd. We also observed the formation of small voids near the bimetallic interface. However, there is a noticeable difference between core-shell particles that have Au cores and those that have Pd cores. For those with Au at the center, the interface roughens within a few minutes of heating and the voids are frequently seen. On the other hand, particles with Pd at the center tend to have smaller voids and do not always evolve into nanostructures with an internal void, contrary to what's expected from the nanoscale Kirkendall effect [3].

Experiments involving real-time observations of these nanoparticles during heating suggest that the voids are mobile and can be annihilated at the nanoparticle surface. We will further discuss the role of strain relaxation in causing the motion of these nanoscale voids.

References:

[1] K.D. Gilroy *et al.*, Chem. Rev., **116** (2016) p.10414

[2] A.D. Smigelskas and E. Kirkendall, Trans. AIME, **171** (1947) p.130

[3] W. Wang, M. Dahl, and Y. Yin, Chem. Mater., **25** (2013) p. 1179

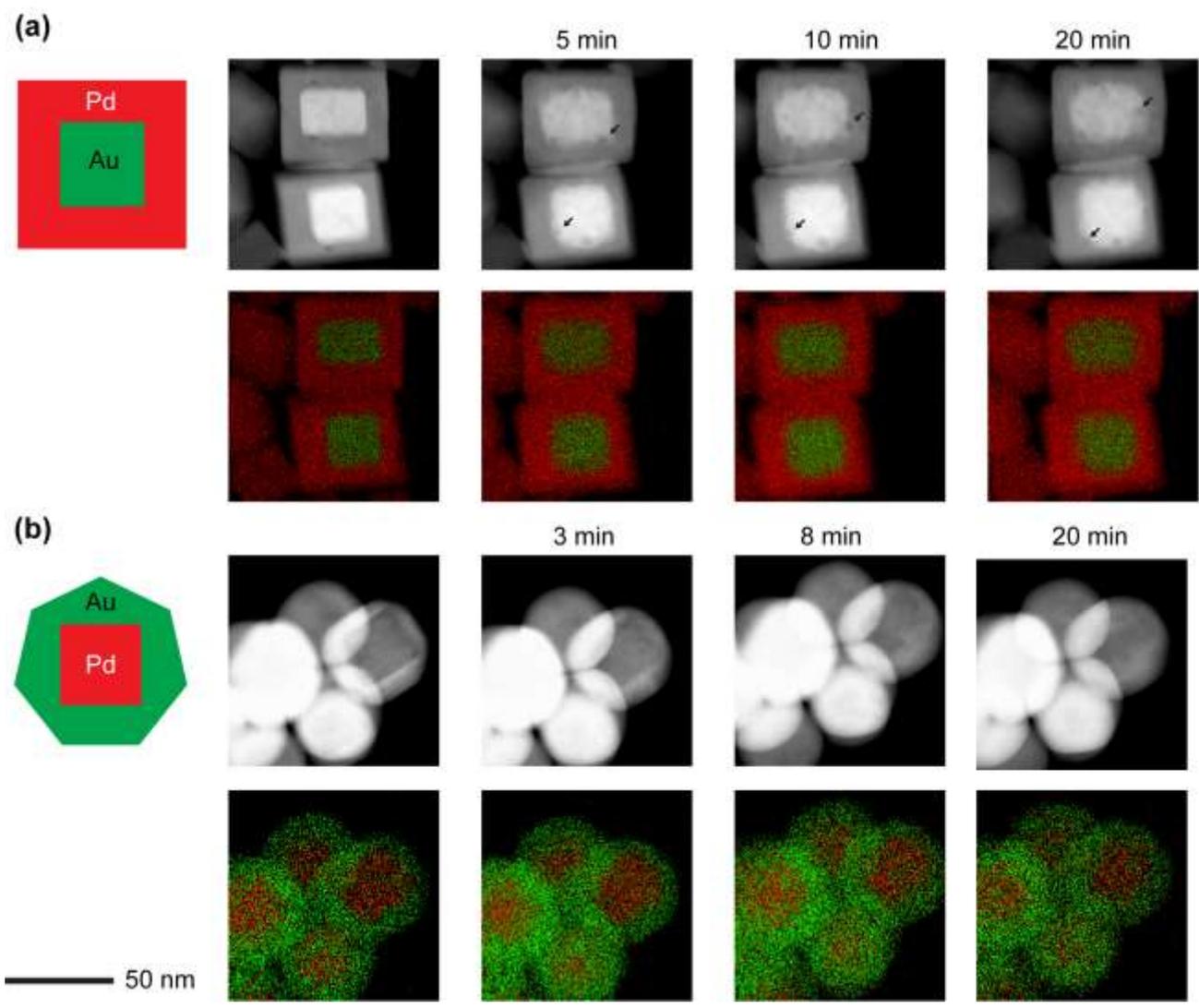


Figure 1. Scanning transmission electron microscopy (STEM) and energy dispersive X-ray (EDX) spectroscopy of nanoparticles with (a) a cuboid Au core (green) and Pd shell (shell) and (b) a cuboid Pd core (red) and Au shell (green) that were annealed under vacuum at the 500 °C for different time intervals. Arrows in (a) depict the apparent void motion between frames.