

BIMETALLIC NANOPARTICLES PARALLEL BULK ALLOYING CHARACTERISTICS

Metallic nanoparticles are of increasing interest due to their use in many applications, from catalysis to electronic devices. Bimetallic nanoparticles, comprising two different metallic elements, are of even greater interest. They hold promise as biosensors, which can be used for disease prevention and treatment, ensuring a safe food supply, and environmental monitoring. Researchers from the University of Notre Dame, the University of Missouri-Rolla, and the Illinois Institute of Technology studied the mixing behavior of metallic nanoparticle materials composed of two metallic elements. The impetus for this study came from theoretical comparisons of excess surface free energy versus elastic relaxation within bimetallic nanoparticles. The investigators showed that the metals alloyed in ways that paralleled how their bulk form alloyed; that is, two metals possessing the ability to thoroughly mix and form a single homogeneous phase in their large bulk form (i.e., complete miscibility) also displayed that ability as bimetallic nanoparticles. Likewise, two metals that were completely immiscible in bulk also remained as separate phases when mixed as bimetallic nanoparticles.

Specifically, the group studied bimetallic nanoparticles of platinum-silver (Pt-Ag), which is completely immiscible in bulk, and palladium-silver (Pd-Ag), which is entirely bulk-miscible. In these two systems, the atomic sizes of the components differed (i.e., were mismatched) by 15% and 16%, respectively.

The effect of morphology on the degree of alloying was examined at a core size of 2 nm for spherical shaped Pt-Ag nanoparticles (Fig. 1) and in a diameter of 20 nm for cylindrical-shaped Pd-Ag nanoparticles (or nanowires). Both systems were synthesized radiolytically (irradiated), which allowed for structural control of the particles when experimental parameters were varied.

To determine the alloying of the two disordered bimetallic nanoparticle systems, as well as analyze their local structures (such as interatomic distances, coordination numbers, bond lengths, and bond-length distributions), the collaborators used the technique of x-ray-absorption fine structure (XAFS). The XAFS measurements—taken at the Pt L₃, Ag K, and Pd K edges—were performed at the MR-CAT beamline 10-ID at the APS.

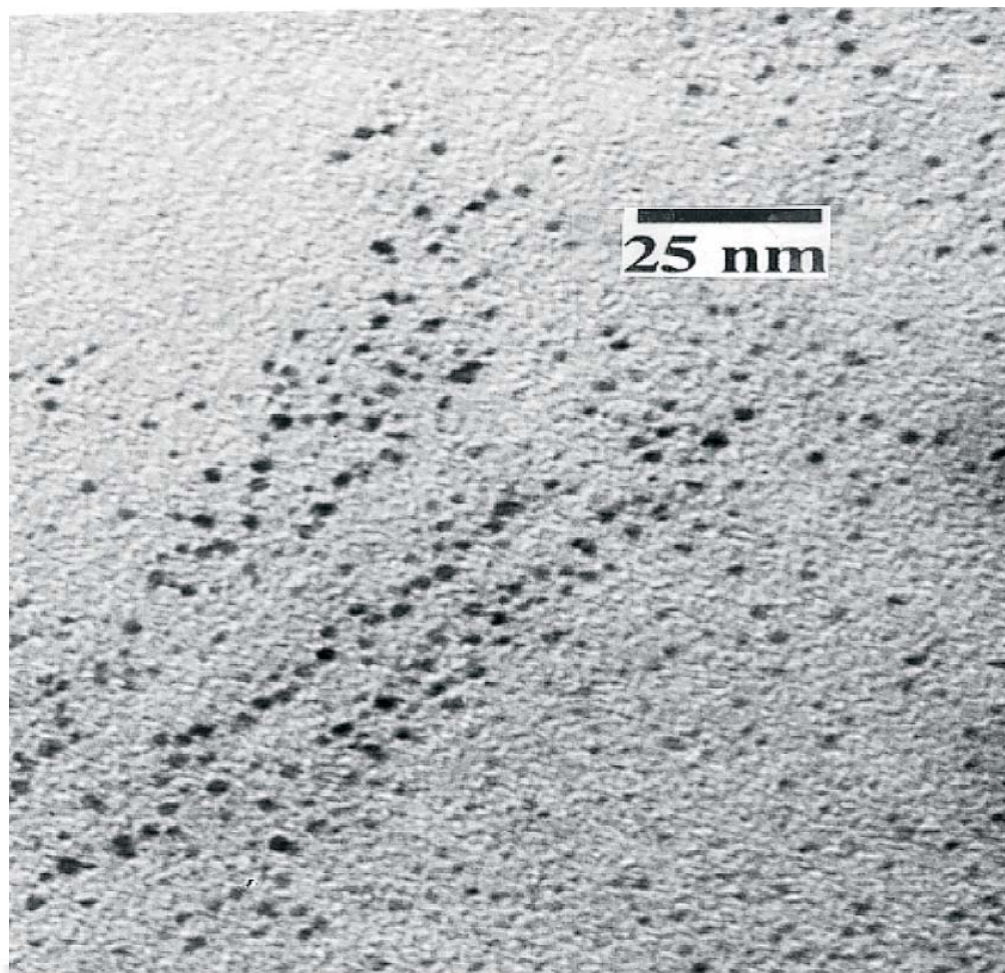


Fig. 1. TEM Image of the 2-nm Pt nanoparticles. The particles were synthesized radiolytically and were used as core for the Pt-Ag particles.

In addition, x-ray appearance near-edge structure (XANES) was used to determine that the absorbing metal atoms of the samples did not oxidize during the measurements, and transmission electron microscopy (TEM) was used to determine the composition, shape, and size of the samples (Fig. 2).

According to the collaborators, when the two bimetallic nanoparticles were mixed, the materials followed their bulk alloying characteristics in all cases. Specifically, the collaborators found—with bimetallic Pt-Ag—that at a diameter of two nanometers and larger, Pt and Ag did not alloy in the nanosized system. Instead, the two metals remained separated in both spherical and cylindrical forms because the tension produced in the Ag-Pt lattice from crystallographic mismatch was greater than the excess surface free energy found in the particle pair. In the case of bimetallic Pd-Ag, the research showed that the cylindrical rods of the nanowires alloy in the nanosized system (as was the case with their spherical equivalents from other, similar studies). With Pd-Ag, the mismatch-induced strain was less than the excess surface free energy found in the small particles. Thus, the two metals did not remain separated.

The collaborators concluded that the morphology of the nanostructures did not directly influence their ability to alloy in these systems and at these very small sizes. The information learned in this study will be important in future research, especially with regard to (1) providing a method to control energies of plasmon absorption bands of metallic mixtures, (2) improving catalytic activities of particles, which sometimes produce new catalysts unknown in bulk form, and (3) alloying component metals in order to make structural alterations that affect the electronic properties of composites, as well as possibly increasing or decreasing Fermi-level equilibration in those composites. Future applications of bimetallic nanoparticles are growing in many diverse fields such as catalysis, biosensing, and electronics. — *William Arthur Atkins*

See: Debdutta Lahiri¹, Bruce Bunker¹, Bhoopesh Mishra¹, Zhenyuan Zhang¹, Dan Meisel¹, C.M. Doudna², M.F. Bertino², Frank D. Blum², A.T. Tokuhira², Soma Chattopadhyay³, Tomohiro Shibata³, and Jeff Terry³, "Bimetallic Pt-Ag and Pd-Ag Nanoparticles," *J. Appl. Phys.* **97**, 094304 (2005).

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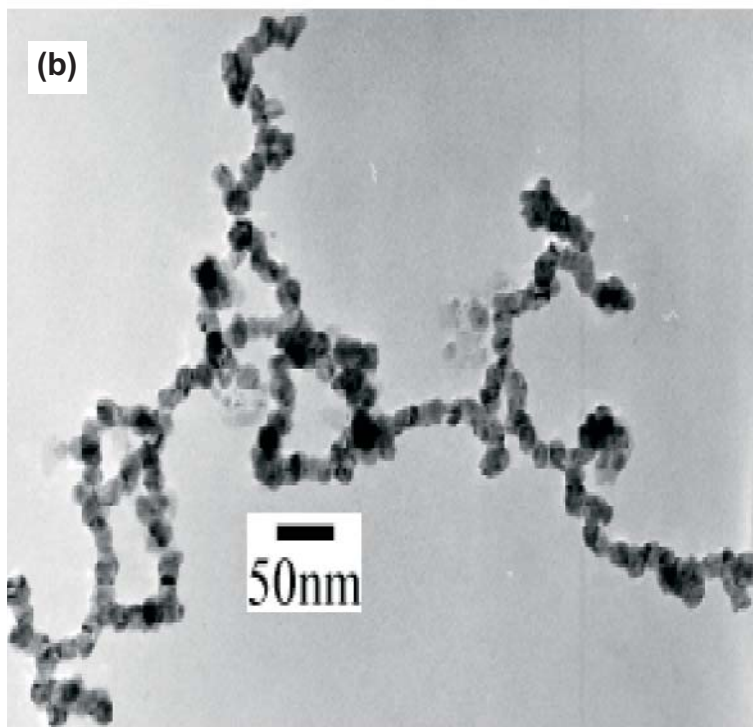
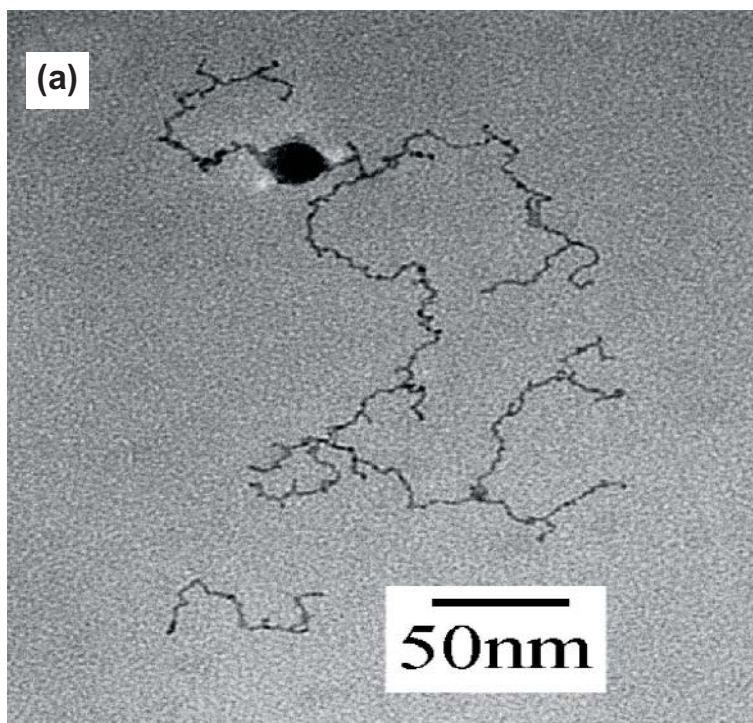


Fig. 2. (a) Bright-field TEM micrographs of Pt-Ag nanowires: A large (20 nm) particle of $85 \pm 5\%$ Ag can be seen at the top of the figure; thin filaments (3-nm diameter) of 50% Ag extend out of the particle. (b) Pd-Ag nanowires: The wire-like particles have a diameter of 20-25 nm and a length of up to 1.5 μm .