JOURNAL OF APPLIED PHYSICS **97**, 094304 (2005)

# Bimetallic Pt–Ag and Pd–Ag nanoparticles

Debdutta Lahiri, Bruce Bunker,[a] and Bhoopesh Mishra
*Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556*

Zhenyuan Zhang and Dan Meisel
*Radiation Laboratory and Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556*

C. M. Doudna, M. F. Bertino, Frank D. Blum, and A. T. Tokuhiro
*Departments of Physics, Chemistry and Nuclear Engineering, University of Missouri–Rolla, Missouri 65409*

Soma Chattopadhyay, Tomohiro Shibata, and Jeff Terry
*Department of Biological, Chemical, and Physical Sciences (BCPS), Illinois Institute of Technology, Chicago, Illinois 60616*

(Received 23 June 2004; accepted 17 February 2005; published online 19 April 2005)

We report studies of bimetallic nanoparticles with 15%–16% atomic crystal parameters size mismatch. The degree of alloying was probed in a 2-nm Pt core (smallest attainable core size) of Pt–Ag nanoparticles (completely immiscible in bulk) and 20-nm-diameter Pd–Ag nanowires (completely miscible in bulk). Particles were synthesized radiolytically, and depending on the initial parameters, they assume spherical or cylindrical (nanowire) morphologies. In all cases, the metals are seen to follow their bulk alloying characteristics. Pt and Ag segregate in both spherical and wire forms, which indicates that strain due to crystallographic mismatch overcomes the excess surface free energy in the small particles. The Pd–Ag nanowires alloy similar to previously reported spherical Pd–Ag particles of similar diameter and composition. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1888043]

## INTRODUCTION

There has been a great deal of interest in the size dependence of electronic and thermodynamic properties of metallic nanoparticles because of their potential use in many applications from catalysis to electronic devices. The electronic structure of a metallic nanoparticle undergoes major deviation from that of bulk.[1,2] Crystallographic parameters in these large clusters might be significantly different from those of the bulk, partially because of increased surface energy and partially because of capping agents that are always present when the particles are generated from suspensions in solution.[3] A significant impetus to study metallic nanoparticles comes from their ability to store excess electrons.[4] These stored electrons can reduce substrates in solution via multielectron-transfer processes, e.g., produce hydrogen from water. Bimetallic nanoparticles, composed of two different metal elements, are of greater interest since they offer a method to control the energy of the plasmon absorption band of the metallic mixture, which becomes a versatile tool in biosensing.[5] They may also improve the catalytic activity of the particles, sometimes creating new catalysts unknown in the bulk size.[6] Furthermore, structural changes can be created in small bimetallic nanoparticles as a result of alloying of the component metals, even though they remain segregated in bulk dimensions at ambient temperature. This may affect the electronic properties of the composite and may enhance or inhibit Fermi-level equilibration in such systems.[7]

Binary phase diagrams for bulk metals are a well-established, commonly utilized tool.[8] However, it is doubtful that they can be extended to the nanometer size regime because of the presence of the large bimetallic interface, the large surface area, and the possible presence of defects at the interface. A significant fraction of the total atoms present in the nanoparticles resides at the surface and contributes to the excess Gibbs free energy, thereby modifying the bulk binary phase diagram.[9,10] Similarly, a large fraction of the atoms occupies the bimetallic interface thereby affecting the miscibility of the metals in one another. Other factors that contribute to the modified alloying characteristics of the two metals are the depression of the melting point in clusters[11,12] and the presence of defects at the bimetallic interface of the particles that enhances the interdiffusion of the metals.[13] Both of these factors lead to an enhanced diffusion rate within the small particles, as much as nine orders of magnitude faster than in the bulk.[14] Size-dependent alloying in Au–Ag core-shell nanoparticles, at room temperature, had been reported by our group earlier.[13] At 2-nm Au core and variable thickness Ag shell, rapid random alloying has been observed at ambient temperature. However, for Au nanoparticles of >8-nm core size a distinct interface between the core and the Ag shell was maintained. In this context it should be noted that Au and Ag are bulk miscible at every ratio at elevated temperatures and they have essentially identical lattice parameters.

In the present report we explore the mixing behavior of Pt–Ag and Pd–Ag nanoparticles. In these systems the atomic sizes of the components differ by 15% and 16%, respectively, and the melting points of Pt and Pd are higher than that of the previously studied Au. In the bulk such a mis-

---

[a] Electronic mail: bunker.1@nd.edu

0021-8979/2005/97(9)/094304/8/$22.50