

The Metal-Metal Interface in Nanoparticles

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We report on the stability of the metal-metal interface in bimetallic nanoparticles. Core-shell nanoparticles were prepared but the particles spontaneously alloy at room temperature and in aqueous suspension at a rate that depends on their size. Various Au-core sizes, 2.5-20 nm diameter, and Ag shell thickness were synthesized using radiolytic and redox wet techniques (1,2) and the equilibrium structures of these particles were determined in the suspensions. The size-dependence of the equilibrium structure and the alloy formation of silver-coated gold nanoparticles suspended in aqueous solution were studied using X-ray absorption fine structure spectroscopy (in collaboration with B. Bunker and T. Shibata (3)). We observed remarkable size dependent diffusion of the two metals into one another. The interdiffusion is limited to the sub-interface layers of the bimetallic particles and the rate depends on both the core size and the total particle size. For small particles (≤ 4.6 nm Au core size), the two metals are nearly randomly distributed within the particle. However, even for these small Au-core particles, the interdiffusion occurs primarily in the vicinity of the original interface. Features from the Ag shells do remain. For the larger particles, the boundary is maintained to within one monolayer. A possible explanation to these observations is the well-documented size dependence of the melting temperature of the metals. This may in turn lead to size dependent diffusion coefficient of one metal into the other (4). The melting point of silica-encapsulated gold particles of 2-20 nm sizes was measured using differential thermal analysis in combination with the thermal gravimetric technique (Figure 1). Assuming Arrhenius dependence of the diffusion coefficient of Au and Ag on temperature, and assuming that the diffusion coefficient at the melting temperature is independent of size one can calculate the dependence of the diffusion on size. This dependence is also shown in Figure 1. However, the alloying results can not be explained either by enhanced diffusion, which results from depression of the melting point with size, or by surface melting of the nanoparticles. We propose that defects, such as vacancies, at the bimetallic interface enhance the radial migration, as well as displacement around the interface, of one metal into the other. Molecular dynamic calculations (in collaboration with D. Gezelter and C. Vardeman) correctly predict the activation energy for diffusion of the metals in the absence of vacancies and show an enormous dependence of the rate of mixing on defect levels (5). The calculations also suggest that only a few percent of the interfacial lattice sites need to be vacant to explain the observed mixing.

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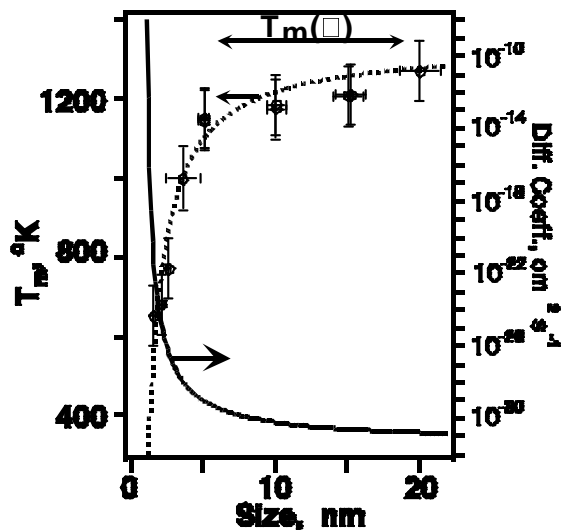


Figure 1: Size dependence of the melting point and diffusion coefficient of silica-encapsulated gold particles. The dotted curve from our experiment indicates that the melting point of Au nanoparticles is size-dependent. The solid curve (right-hand axis) is the calculated Au self-diffusion coefficient (From Ref. 4).