XAFS Studies of Au and Au/Ag Nanoparticles in Aqueous Solution

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Introduction

Nanometer-size metallic particles (nanoparticles) show remarkably different behavior from the corresponding bulk materials, and various size effects on the stability of the structures are of great interest. Especially for binary core-shell nanoparticles, the interface structure, e.g., the degree of interdiffusion and alloy formation, is itself an interesting topic from a fundamental viewpoint and is also important for application to bimetallic catalysts.

Methods and Materials

X-ray absorption fine structure (XAFS) is capable of providing local structural information in the region around the specific elements and is suitable to the study of the interface of nanoparticles due to the large fraction of the interface atoms in the particles. These studies involve Au nanoparticles with a deposited Ag shell, (referred to as Au/Ag hereafter). These elements are well-suited for the present study because of a large difference in the XAFS photoelectron backscattering amplitude between Au and Ag; this makes it straightforward to obtain information about Au and Ag around Au and Ag separately by measuring the Au and Ag edges as shown in Fig. 1.

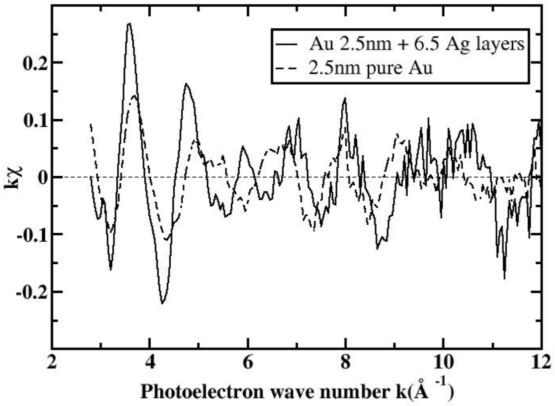

FIG.1 XAFS oscillations at the Au L3 edge for the pure 2.5nm Au nanoparticles and Au/Ag nanoparticles of 2.5nm Au core with 6.5 layer of Ag deposited. The large difference of backscattering phase shift between Au and Ag makes the spectra remarkably different.

Pure Au and Au/Ag nanoparticles with various thicknesses of Ag (1-6 layers) on various sizes of Au cores (2.5 nm to 20 nm in diameter) were synthesized by the radiolysis-initiated reduction. Since we are particularly interested in their natural properties, we measured particles in aqueous solutions without a solid support, which was used in most previous structural studies.[1] For this reason, the typical metal concentration is as low as 5×10^{-4} M in order to avoid coagulation. XAFS was measured at the Au L_3 and Ag K edges at the MRCAT undulator beamline. A harmonic rejection mirror was used, and incident and fluorescence signals were detected by an ion chamber with the mixture of the gas varied depending on the x-ray energy. After initial data reduction using standard methods, the FEFFIT program[2] was used with theoretical scattering paths from FEFF 6.[3]

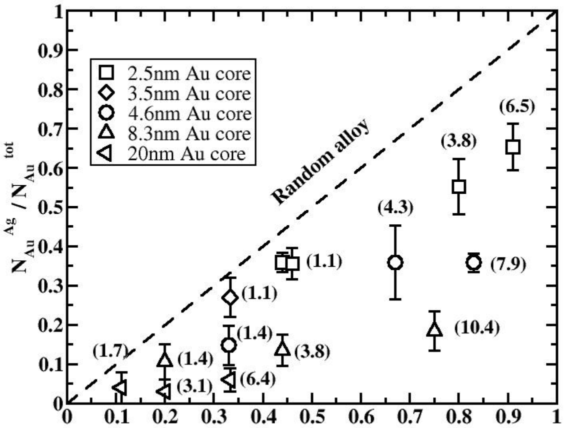

FIG.2 The fraction of the scattering from Ag at the first neighbor of Au divided by the total number of the scattering from metals (no dangling bond included). Different symbols indicate the different initial Au core diameter 20nm, 8.3nm, 4.6nm, 3.5nm and 2.5nm. The number in the bracket is approximate number of Ag layers deposited.

Results

The fraction of the scattering from Ag at the first neighbor of Au among the total scattering from metals, $N_{Au}^{Ag}/ N_{Au}^{tot}$ (no dangling bond included), is shown in Fig. 2 as a function of [Ag]/([Au]+[Ag]), the fraction of Ag in a particle. If a random alloy formation is realized, N_{Au}^{Ag}/N_{Au}^{tot} = ([Ag]/([Au]+[Ag]) should be satisfied (dashed line), while the phase segregation occurs, N_{Au}^{Ag}/N_{Au}^{tot} should remain as a small value slightly depending on the Au core size. The samples of the different initial Au core sizes are depicted as a different symbols in Fig. 2, and the different ([Ag]/([Au]+[Ag]) with the same symbol means the different degree of Ag deposition on the same Au core. The results from the separate fit at the Ag edge, Au edge, and the simultaneous fit at Au and Ag edge data are consistent. We see clearly the size-dependent alloy formation. When Ag is deposited on the 20 nm Au core, N_{Au}^{Ag}/N_{Au}^{tot} remains as a small value with little dependence on the degree of Ag deposition, indicating the Ag stays outside the core. When we decrease the size of the Au core to 2.5 nm, N_{Au}^{Ag} approaches random alloy formation and strongly depends on the degree of Ag deposition.

Discussion

To show these results more quantitatively, we calculated the penetration of Ag into the Au core assuming that the time (*t*) evolution of the alloy formation follows a three-dimensional diffusion model. Here we used a parameter (*Dt*), *D* being the diffusion coefficient, to explain the coordination results; *Dt*~2 to 15 Å^2/sec depending on the degree of Ag deposition and is larger for smaller nanoparticles. For all sizes of nanoparticles, we obtained some alloying effect at the interface, however, the degree of alloying strongly depends on the particles size. For the 4.6 nm Au nanoparticles, the alloying occurs within 15 Å (6 layers) around the interface, and a further deposition of Ag contributes to the formation of the shell on the nanoparticles. The diffusion region is not much changed for larger nanoparticles of the 8.3 nm Au core, and the region of the pure Au core and the pure Ag shells remains with Ag deposition. On the other hand, for the smaller nanoparticles of 2.5 nm Au core, by the deposition of Ag to 6.5 layers, the alloy formation occurs to the center of the shell and having a pure Au core is difficult.

These experimental results definitely indicate a size dependency not explained by a mere bulk diffusion. Since the bulk diffusion coefficient in a miscible Au-Ag alloy is of the order of D~10-16 Å^2/sec at room temperature, the order of 10^{17} seconds should be assumed to explain the data. This is not consistent, because we measured XAFS within several days after the synthesis of the nanoparticles. In addition, the size dependence of Dt cannot be explained by a bulk diffusion model.

Summary

We successfully measured XAFS of Au/Ag nanoparticles in a dilute aqueous solution. The data indicate striking size changes in the alloy structure, which are not explained by a bulk diffusion process.[4]

Acknowledgments

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