Au/Rh Nanoparticles Synthesized under High Temperatures and High Pressures

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Small size gold (Au) and rhodium (Rh) nanoparticles have been produced by flowing the solution containing Au(III) and Rh(III) ions with poly(*N*-vinyl-2-pyrrolidone) through a high-temperature and high-pressure reactor. Au, mostly monometallic, particles (7.5 nm) are produced together with the smaller Rh nanoparticles (2.5 nm) within a few seconds, of which the structure and sizes are identified by the transmission electron micrograph (TEM) images and the extended X-ray absorption fine structure (EXAFS).

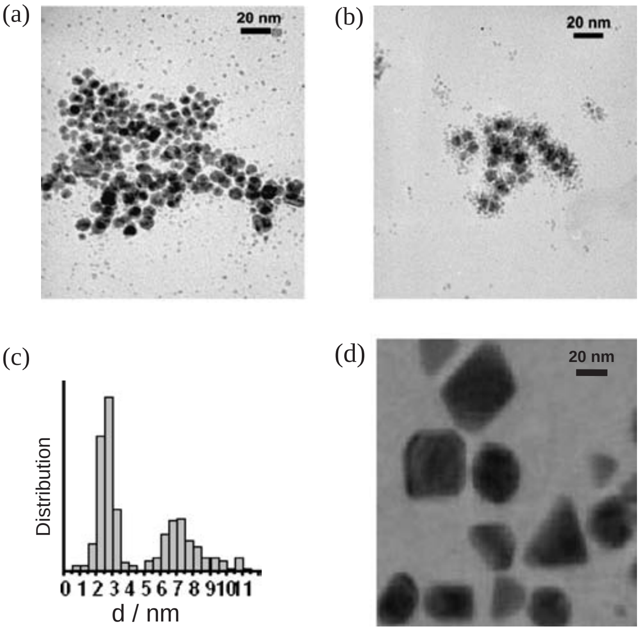

Figure 1. TEM images of nanoparticles produced by the reduction both of Au and Rh salts in water and ethanol 1/1 mixture with PVP at 25 MPa, (a) 150 °C and (b) 200 °C. Size distribution of (a) is shown in (c). For the comparison, TEM image (d) of Au nanoparticle produced under 25 MPa and 200 °C is on the lower right.

Recently, small size particles of nanoscale have collected much attention from the view points of both science and industry because of their remarkable properties in catalytic, magnetic, and optical fields.[1] Among various kinds of metals, gold (Au) is one of the most popular species under investigation. Nowadays, synthetic methods of Au nanoparticles and bimetallic particles containing Au species as a component have been extensively investigated.[2] However, because of quite high stability of Au,[3] precursors of Au monometallic particles or bimetallic particles of Au with another metallic species easily form aggregates of relatively large diameter ranging to even 100 nm in synthetic methods using bulk solutions. The most common strategy is the use of protective reagent. In the case of Au, however, the thermal reduction of Au(III) in the presence of a weak protective reagent such as poly(*N*-vinyl-2-pyrrolidone) (PVP) does not work well, which is commonly used in the synthesis of noble metal nano-particles.[4]

We have recently developed a new synthetic method of noble metal nanoparticles using a high-temperature and high-pressure reactor.[5] We have succeeded in producing platinum (Pt) or rhodium (Rh) nanoparticles of a few nm diameter with small distribution by the thermal reduction of Pt(IV) or Rh(III) ionic solution with PVP at 25 MPa above 200 °C within a few seconds.[5,6] We have also demonstrated that bimetallic Pt/Rh nanoparticles with random structure are produced by the high-temperature and high-pressure synthesis in contrast to the Pt-core/Rh-shell structure produced by the ordinary method.[7] In this work, we will present the results of synthesizing small size of Au nanoparticles in the presence of Rh ions.

The synthetic procedure and the high-temperature and high-pressure reactor are described elsewhere.[5] The colloidal dispersions of nanoparticles protected by PVP have been synthesized by flowing the solutions (1/1 volume mixture of water and ethanol) containing Au(III) ion or Au(III) and Rh(III) ions through the reactor[8] at high temperature and high pressure in a few seconds (25 MPa, 150–200 °C) by an HPLC pump (Jasco Co., PU-1580). The temperature was monitored by a thermocouple immersed in the cell, and controlled by a heat blocks. The pressure was regulated by a back-pressure regulator (JASCO Co., SCF-BPG). As sources of metal ions, sodium chloroauric acid(III) and rhodium chloride(III) (Nacalai Tesque) were used. In the mixture solutions of ions, the mole ratio of Au to Rh was 1. The total ionic concentration was 1.5 mM, and the concentration of PVP was 1.5 g dm^{-3}.

Figure 1 shows typical TEM images of nanoparticles produced under high-temperature and high-pressure conditions. Figure 1d shows Au nanoparticles produced at 25 MPa and 200 °C. As is shown in Figure 1d, particles tend to have a large size more than 50 nm, although the diameter of Rh monometallic particles produced by the same method is relatively small (2.7 nm).[6] Figures 1a and 1b show TEM images of products from the mixture solution of Au and Rh ions, which indicates that two kinds of particles with obviously different sizes are produced. Relatively small particles (about 2.5 nm) are seen around larger particles (about 7.5 nm) gathering each other.

In order to investigate the metallic composition of each nanoparticle, we have measured the EXAFS spectra of colloidal dispersions at KEK-PF (BL-10B and 9A). EXAFS spectra were measured in a transmission mode, and analyzed in a standard manner using Au and Rh foils as the reference samples to extract

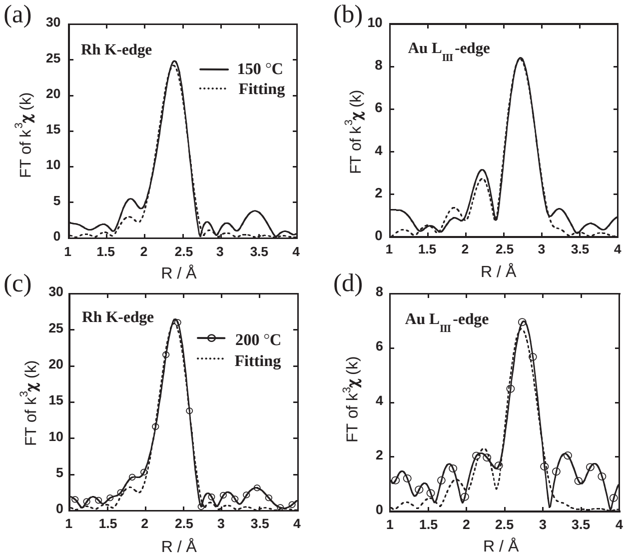

Figure 2. Fourier transforms of EXAFS oscillations of nanoparticles produced by the reduction of both Au and Rh ionic solution with PVP at 25 MPa, (a), (b) 150 °C and (c), (d) 200 °C. The results of Rh K-edge and Au L$_{III}$-edge are shown in (a), (c) and (b), (d), respectively. The solid lines represent the experimental results and the broken lines represent the theoretical fit.

Table 1. Coordination numbers from EXAFS analysis of nanoparticles produced by the reduction of both Au and Rh ions in water and ethanol 1/1 mixture with PVP at 25 MPa and various temperatures

Sample	Edge	Bond	Coordination Number	
			150 °C	200 °C
Au/Rh (1/1)	Au–L$_{III}$	Au–Au	9.4 ± 2.9	8.9 ± 2.2
	Rh–K	Rh–Rh	6.6 ± 2.3	7.3 ± 2.5

the back scattering amplitudes and phase shifts.[9] Figure 2 is the Fourier transforms of Rh K-edge and Au L$_{III}$-edge of EXAFS spectra, respectively, for the concentrated colloidal solutions produced at 25 MPa and (a), (b) 150 °C and (c), (d) 200 °C in water and ethanol 1/1 mixture.

As is shown in the figure, both absorption edges of the samples are almost successfully fitted to a single atomic species using the reference foils while a little gap can be seen in the peak of 2.2 and 2.7 Å on Au L$_{III}$-edge at 200 °C. This result indicates that the cluster unit of each nanoparticle is composed of almost single atomic species of Au or Rh, respectively. Table 1 shows the coordination number (C.N.) obtained from the fitting. From the average C.N., the particle sizes are around 1.0 nm for the Rh K-edge, while those from Au L$_{III}$-edge around 2.0 nm, using the truncated octahedral structure model.[10] Average size probed by EXAFS is known to be generally smaller than that of particles observed in the TEM image because it is attributed to the structure of a monocrystalline cluster unit which composes nanoparticles.[4b] From these results it is difficult to identify the particles in the TEM image, although the smaller one is expected to be a Rh particle and the larger one to be Au one from the results of the syntheses for single metal component. Preliminary analysis of high-resolution TEM images taken very recently suggests that the lattice constant of the larger particle created at 150 °C is slightly larger (ca. 7%) than that of smaller one, as is expected from the difference of the lattice constant between Au (4.078 Å) and Rh (3.716 Å) at 25 °C. This indicates that the larger particle is composed of Au and the smaller one of Rh. The detail will be presented in the near future.

Our observation is similar to the case of the size reduction of Ag nanoparticle by Rh nanoparticles.[11] In their case, Ag nanoparticles with larger size (7.5 nm) were decomposed to smaller ones (2.7 nm) with the treatment of Rh nanoparticle (2.2 nm). They also suggested that the nanoparticle has partially alloy structure of Ag/Rh. They consider that the reason of the self-assembling formation is due to the large binding energy between Ag and Rh. Similar kinds of effect may work during the production of Au and Rh nanoparticles in the present system. The deviation in the fit of the EXAFS spectra of Au L$_{III}$-edge at 200 °C suggests that Au particles are partially alloyed with Rh as in the case of Ag/Rh.

In conclusion, in the present work we have succeeded in the reduction of particle size of Au nanoparticles by the thermal reduction in bulk solutions. The present method may also open the way to the synthesis of Au/Rh alloy nanoparticles which are more interesting in its catalytic feature.

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