

## Ag/Rh Bimetallic Nanoparticles Formed by Self-assembly from Ag and Rh Monometallic Nanoparticles in Solution

Kazutaka Hirakawa and Naoki Toshima\*†

Radioisotope Center, Faculty of Medicine, Mie University, 2-174 Edobashi, Tsu, Mie 514-8507

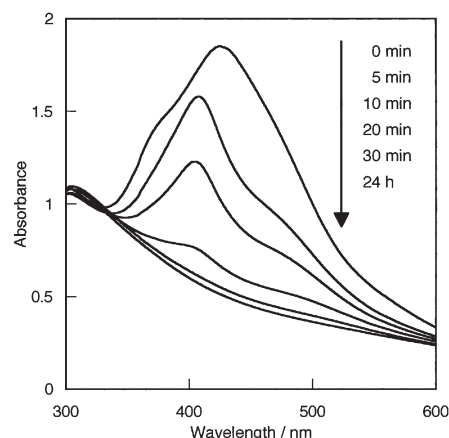
†Department of Materials Science and Environmental Engineering, Tokyo University of Science, Yamaguchi [The former Science University of Tokyo in Yamaguchi], Onoda-shi, Yamaguchi 756-0884

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The plasmon absorption band of colloidal dispersions of poly(*N*-vinyl-2-pyrrolidone)-protected Ag nanoparticles was extinguished within several minutes by the addition of Rh nanoparticles sol. Transmission electron micrographs and X-ray diffraction measurements have shown that this phenomenon is due to that the physical mixture of Ag and Rh nanoparticles spontaneously generates the bimetallic nanoparticles with Ag-core/Rh-shell structure.

Metal nanoparticles have received much attentions as a building block of advanced materials for nanoscience and nanotechnology.<sup>1</sup> Their optical,<sup>2-5</sup> magnetic,<sup>6,7</sup> and catalytic<sup>8-19</sup> properties have recently been reported with great interests. The character of metal nanoparticle can be altered by the addition of other metals. Bimetallic nanoparticles, composed of two different metallic elements, have been reported to show outstanding characters different from the corresponding monometallic nanoparticles.<sup>11-15</sup> For example, catalytic activities of Au-core structured bimetallic nanoparticles, Au/Pt,<sup>11-13</sup> Au/Pd,<sup>13,15</sup> and Au/Rh,<sup>13</sup> for hydrogenation and/or water reduction are higher than Pt, Pd, and Rh monometallic nanoparticles, respectively. Surprisingly, in some cases, a physical mixture of monometallic nanoparticles such as Pt and Ru nanoparticles in solution shows higher catalytic activity than the corresponding monometallic nanoparticles under a certain condition.<sup>16,17</sup> This suggests that an interaction between two kinds of monometallic nanoparticles can produce novel nanoparticles. In this study, we examined the interaction between Ag and Rh monometallic nanoparticles in solution by physical mixing. The main reason for using Ag and Rh nanoparticles is the reported prominent characteristics of Rh nanoparticles as a catalyst,<sup>18,19</sup> and the expected electronic effect of Ag similar to Au upon enhancement of the catalytic activity of Rh.

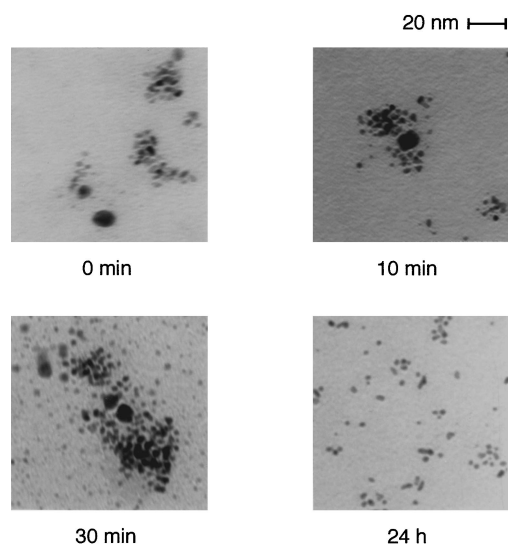
The colloidal dispersions of Ag and Rh monometallic nanoparticles (1 atom-mmol L<sup>-1</sup>) protected by poly(*N*-vinyl-2-pyrrolidone) (PVP) were prepared by an alcohol reduction method.<sup>13,20</sup> Average diameters of Ag and Rh monometallic nanoparticles were 7.5 nm and 2.2 nm, respectively. Colloidal sol of Ag nanoparticles shows characteristic plasmon absorption.<sup>21</sup> The plasmon absorption band of Ag nanoparticles decreased by addition of Rh nanoparticles and was almost completely extinguished within 30 min after mixing (Figure 1). The parts of plasmon absorption in larger wavelength region were preferentially extinguished within 10 min, suggesting that influences of Rh nanoparticles on Ag nanoparticles depend on the size of the Ag nanoparticles. When relatively smaller molar quantity of Rh to Ag was added, the plasmon absorption was not completely extinguished. More than 40 atom-mol% of Rh against to Ag was required to extinguish the plasmon absorption band



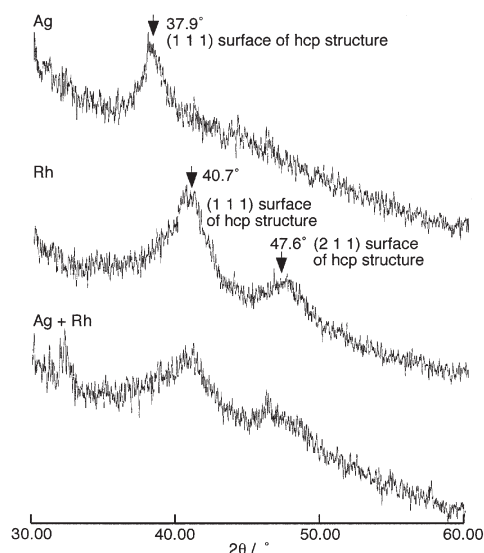
**Figure 1.** UV-Vis spectral change of the physical mixtures of dispersions of Ag and Rh nanoparticles. The aqueous solutions of Ag (1 atom-mmol L<sup>-1</sup>, 50 mL) and Rh (1 atom-mmol L<sup>-1</sup>, 50 mL) nanoparticles were mixed and measured in 0, 5, 10, 20, and 30 min, and 24 h after mixing.

completely.

Figure 2 shows transmission electron micrograph (TEM) photographs of the physical mixtures of Ag and Rh monometallic nanoparticles. The samples for TEM measurement were prepared by drying the aqueous dispersions of the physical mixtures of Ag and Rh nanoparticles under vacuum in 0, 10, and 30 min, and 24 h, respectively, after mixing. Relatively large particles are attributed to Ag nanoparticles, and rather small ones are Rh nanoparticles. The TEM photographs showed that Rh particles gathered around Ag particle to surround within several minutes, comparable period of the extinction of plasmon absorption. Interestingly, these aggregated particles changed into homogeneous small particles (average diameter = 2.7 nm) after 24 h. Preliminary study has shown that the increase of Rh/Ag molar ratio reduces the average diameter and the size distribution of the nanoparticles. The elemental analysis using characteristic X-ray in high-resolution TEM measurement has shown that the particles produced from their physical mixtures in 24 h are composed of Ag and Rh. Figure 3 shows X-ray diffraction (XRD) patterns of PVP-protected Ag and Rh monometallic nanoparticles, and their physical mixture. The sample of the physical mixture of Ag and Rh nanoparticles was prepared by drying the mixtures of their aqueous solutions under vacuum for 24 h after mixing. The XRD pattern of the mixtures of Ag and Rh nanoparticles was similar to that of Rh nanoparticle, suggesting that the surface of the particle produced by mixing Ag and Rh nanoparticles is composed of Rh. Similarly, Au-core/Pt-shell and Au-core/Pd-shell structured nanoparticles have shown the XRD pattern quite similar to that of their surface metals.<sup>22</sup>



**Figure 2.** TEM micrograms of the physical mixtures of Ag and Rh nanoparticles. The aqueous solutions of Ag and Rh nanoparticles (1/1, atom-mol/atom-mol) were mixed, and dried after indicated periods.



**Figure 3.** XRD patterns of Ag and Rh monometallic nanoparticles, and their physical mixture (1/1, atom-mol/atom-mol).

These findings suggest that the aggregation of Rh particles around the Ag particle is involved in the extinction of the plasmon absorption. Henglein et al. reported that Pb atoms transfer from Pb colloidal particle onto the surface of Ag colloidal particle in physical mixing of Ag and Pb colloidal sols.<sup>23</sup> If the extinction of the plasmon absorption is due to coating of the surface of Ag particle by Rh atoms transferred from Rh nanoparticle, at least 28 mol% of Rh to Ag is required assuming that a Ag particle (average diameter = 7.5 nm) is uniformly coated by Rh atoms in a one-atom layer. In the present experiments about 40 atom-mol% of Rh to Ag was required to completely extinguish the plasmon absorption, which is reasonably supporting the above assumption. These observations suggest that the physical mixture of Ag and Rh nanoparticles spontaneously generates Ag/Rh bimetallic nanoparticles with an Ag-core/Rh-shell structure. The disappearance of the XRD peak of Ag nanoparticles suggests that the core of this bimetallic nanoparticles is not

complete Ag, but possibly has a partial Ag/Rh alloy structure. The driving force of the formation of this Ag/Rh bimetallic nanoparticles may be due to the larger binding energy between Ag and Rh atoms than between Rh atoms.<sup>24</sup> Reduction of diameter of the nanoparticle increases not only its surface energy but also number of the binding sites between Ag and Rh atoms, which stabilizes the total energy. Therefore, the shrinking of Ag/Rh bimetallic nanoparticles might be explained by the balance between the binding energy and the surface energy. The size and the rate of formation of the bimetallic nanoparticles can be controlled by the kind and concentration of protective agents.

The self-assembling formation of bimetallic nanoparticle using Ag nanoparticle is applicable to construction of novel nanoparticles. We have examined the catalytic activity of the Ag/Rh bimetallic nanoparticles for visible-light-induced hydrogen generation<sup>12,13,16,17</sup> in an aqueous solution composed of ethylenediamine-tetraacetic acid, tris(bipyridine)ruthenium(II), methyl viologen, and metal nanoparticle catalyst. The activity is clearly higher than the corresponding monometallic nanoparticles and alloy-structured Ag/Rh nanoparticles, suggesting that the Ag-core shows an electronic effect on the surface Rh as in the case of the Au-core<sup>13</sup> and enhances the catalytic activity of the surface Rh. Further studies on the formation mechanism of the Ag/Rh nanoparticles and the catalytic activities are now in progress.

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