Fabrication of Au–Ag Alloy Nanoprisms with Enhanced Catalytic Activity

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Au–Ag alloy nanoparticles with prismatic structure have been prepared in aqueous solution by photoinduced conversion of spherical Au–Ag alloy nanoparticles. All the particles have compositions close to those expected from the starting ratio of metal compounds. These nanoprisms showed pronounced catalytic activity in the reduction of 4-nitrophenol by $NaBH_4$.

Multimetallic nanoparticles with alloy or core–shell structures are attractive materials because of their composition-dependent optical, catalytic, electronic, and magnetic properties.[1] In particular, bimetallic nanoparticles are of special importance in the field of catalysis, since they often exhibit better catalytic properties than their monometallic counterparts.[2] Such nanostructures have been prepared by various methods including simultaneous chemical reduction of mixed metal ions,[3] successive reduction of one metal ion on the surface of another metal particle,[4] and electrochemical reduction.[5] However, most of studies on the fabrication of bimetallic nanostructures have concentrated on isotropic spherical structures. Very few methods have been reported for making bimetallic nanoparticles with anisotropic structures.[6]

Anisotropic nanoparticles have been a subject of intense research in recent years because their specific geometries lead to unusual physical and chemical properties[7] and they can be promising building blocks for the creation of nanostructured materials.[8] Among various geometries, triangular nanoprisms have been intensely studied owing to their characteristic optical and electrical properties and the recent development of photochemical and thermal methods for preparing bulk quantities of them.[9] However, there are few reports on the preparation of bimetallic alloy nanoprisms.[6c] Herein, we present a strategy for making Au–Ag alloy nanoprisms in the form of a colloidal suspension. The catalytic properties of the alloy nanoprisms for reduction of an aromatic nitro compound are also reported.

Spherical Au–Ag alloy nanoparticles were prepared by simultaneous reduction of $HAuCl_4$ and $AgNO_3$ by $NaBH_4$ in aqueous solution.[10] Figure 1a shows absorption spectra for several Au–Ag alloy nanoparticles prepared from the aqueous solutions of $HAuCl_4/AgNO_3$ mixtures in molar ratios of 5/95, 10/90, 15/85, and 20/80. The alloy formation is concluded from the facts that the each optical absorption spectrum shows only one plasmon band and that a linear relationship is found between plasmon maximum λ_{max} and the gold mole fraction x_{Au} (inset of Figure 1a).[3] Transmission electron microscopy (TEM, JEOL JEM-2010, 200 kV) images of the colloids show that nanoparticles possess spherical shapes with average sizes of <10 nm (not shown).

The alloy solutions are then irradiated with a conventional 45-W fluorescent light. For the Au/Ag = 5/95 and 10/90 sam-
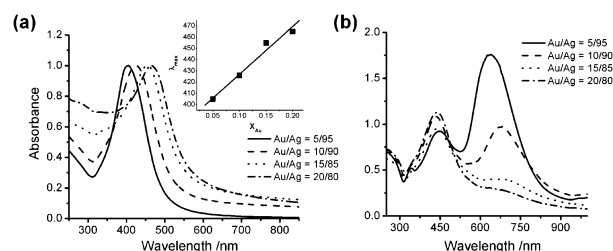

Figure 1. UV–vis spectra of Au–Ag alloy nanoparticles: (a) before and (b) after irradiation (15 h). The inset of (a) shows the positions of surface plasmon bands plotted against the x_{Au} in alloy nanoparticles.

ples, the color of the dispersions turned from yellow to greenish blue and bluish green, respectively, after they had been irradiated for 15 h (Figure S1).[10] We could not observe any color change for the Au/Ag = 15/85 and 20/80 samples. This photoinduced change was also reflected in their absorption spectra (Figure 1b). For instance, in the case of the Au/Ag = 10/90 system, three new bands centered at 340, 435, and 677 nm appeared and the characteristic surface plasmon band of spherical nanoparticles at 426 nm disappeared after irradiation. There is no noticeable change in the spectra of the Au/Ag = 15/85 and 20/80 samples. Referring to the previous reports on the photoinduced conversion of silver nanoparticles into triangular nanoprisms,[9a] the observed results can be assumed to be a result of certain structural change of the particles.

TEM observations show that nearly all of the initial spherical alloy particles were converted to prismatic structures that appear in two dimensions as truncated triangles for the Au/Ag = 5/95 and 10/90 samples (Figure 2). For Au/Ag = 10/90 nanoprisms, average edge size is determined to be ≈84 nm. Upon evaporation of solvent, some nanoprisms assemble into stacks on the TEM grids (inset of Figure 2a), which allow measurement of their thickness (8.8 ± 3.0 nm). The energy-dispersive X-ray (EDX) analyses (Figure 2) and X-ray photoelectron spectroscopy measurements (Figure S2)[10] from prism particles authenticate that all the particles are homogeneous and that a final particle composition is close to that expected from the starting ratio of metal compounds. Moreover, X-ray diffraction patterns of the samples show characteristic feature of face-centered cubic structure (Figure S3),[10] indicating that the prepared alloy nanoprisms are well crystallized. These experimental results imply that homogeneous Au–Ag alloy nanoprisms can be prepared in high-yield by the photochemical approach. Contrast to the cases of Au/Ag = 5/95 and 10/90 particles, we could not observe regular shape change of particles for the Au/Ag = 15/85 and 20/80 samples (Figure S4).[10] In fact, we also could not identify any spectral or shape changes upon light irradiation for the par-
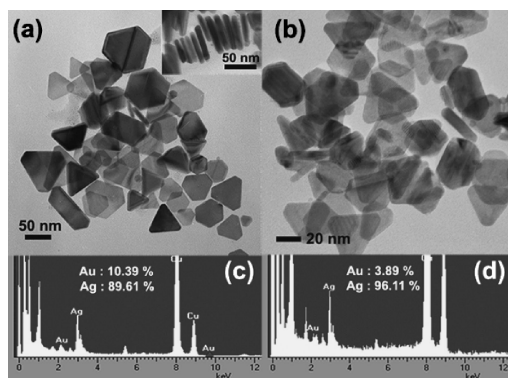
Figure 2. TEM images of (a) Au/Ag = 10/90 and (b) Au/Ag = 5/95 alloy nanoprisms. Inset of (a) shows the assembly of nanoprisms into stacks on the TEM grid upon solvent evaporation. EDX spectra of (c) Au/Ag = 10/90 and (d) Au/Ag = 5/95 alloy prisms. Cu peaks are due to the Cu grid.

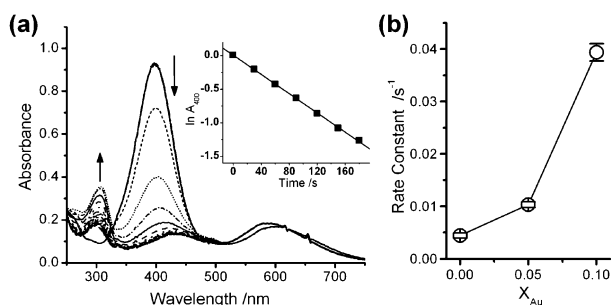**Figure 3.** (a) Successive UV–vis absorption spectra (30 s interval) of the reduction of 4-NP by $NaBH_4$ in the presence of Au/Ag = 10/90 alloy prisms. The inset shows the plot indicating the variation of $\ln A_{400}$ vs. time. (b) Plot of rate constant vs. x_{Au} in nanoprisms for the reduction of 4-NP.

ticles with higher x_{Au} such as Au/Ag = 25/75, 50/50, 75/25, and 100/0 samples. Although exact reason for this difference is not clear yet, we could conclude tentatively that alloy nanoprisms with $x_{Au} > 0.1$ cannot be realized by photoinduced conversion of alloy nanospheres because of relatively low reactivity of Au toward light.

　　For investigating application aspects of the alloy nanoprisms, catalytic activity of the nanoprisms was examined for the reduction of 4-nitrophenol (4-NP) by $NaBH_4$ in aqueous solution. We have chosen this system as a model reaction because this reaction is rapid and can be easily characterized.[11] The reduction is inert to $NaBH_4$ if it is used alone. However, the metal nanoparticles effectively catalyzed the reaction by acting as an electron relay system. Figure 3a shows successive UV–vis absorption spectra of the reduction of 4-NP (5.0×10^{-5} M) by $NaBH_4$ (5.0×10^{-2} M) in the presence of Au/Ag = 10/90 alloy prisms (amount of metal = 12.5 μM). In the absence of any particles, the peak due to 4-NP at 400 nm remains unaltered. The reduction can be visualized by the disappearance of the 400-nm peak with the concomitant appearance of a new peak at 300 nm which can be attributed to 4-aminophenol. Pseudo-first-order kinetics with respect to 4-NP could be used to evaluate the catalytic rate. A good linear correlation with time, that is, $\ln A_{400}$ vs. time plot, was obtained (inset of Figure 3a). Here, A_{400}

stands for the absorbance at 400 nm at any time. The pseudo-first-order rate constant determined from this plots is 3.93 (± 0.17) $\times 10^{-2}$ s^{-1}. We have also performed similar experiments with the Au/Ag = 5/95 alloy particles and Ag nanoprisms prepared by photoinduced conversion of Ag spherical nanoparticles and obtained similar spectral changes.[12] The estimated rate constants are plotted in Figure 3b. The dependence of kinetics on the composition of nanoparticles is nicely demonstrated in this plot. The reaction rate increases with increasing x_{Au} in the nanoprisms. The enhanced catalytic activity of the alloy nanoprisms may be ascribed to the modified electronic structure and/or increased resistance to corrosion and poisoning by loading of a small amount of Au metal. Furthermore, our rate constant value is much higher than those obtained with spherical monometallic Au and Ag, and Au–Ag alloy nanoparticles (Figure S5).[10] This can be understood by the fact that nanoprisms have more well-defined edges and corners than do spheres. These active regions can serve as effective catalytic sites. The detailed studies on the mechanism of the shape and composition-dependent catalytic activity are underway.

　　In summary, we have presented an aqueous room temperature method for the production of homogeneous alloy nanoprisms with pronounced catalytic activity. We envision that the prepared alloy nanoprisms can also be useful in other interesting researches such as the fabrication of high-order nanostructures with tunable optical and optoelectronic properties.

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10　See Supporting Information. It is available electronically on the CSJ-Journal web site; http://www.csj.jp/journals/chem-lett/.
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12　For exact comparison of the catalytic activities, total amounts of metal were adjusted to the same value for each sample, i.e., 12.5 μM.