Synthesis of Bicompartmental Ag/Cu Nanoparticles Using a Two-step Polyol Process

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Bicompartmental (BC) Ag/Cu nanoparticles were synthesized using a two-step polyol reduction process. Initially, Ag nanoparticles with an average diameter of 21 ± 3 nm were prepared from $AgNO_3$ using a microwave (MW)–polyol method. Then, $Cu(OAc)_2 \cdot H_2O$ was added dropwise under MW or oil-bath heating. The formation of BC Ag/Cu nanoparticles with an average size of 29 ± 6 nm in high yield (98%) was confirmed using energy-dispersive X-ray spectroscopic (EDS) measurements.

In recent years, bimetallic nanoparticles have received intense attention, owing to their different optical, electronic, magnetic, and catalytic properties relative to those of the individual metals.[1,2] We have recently synthesized Cu core Ag shell particles, denoted as Cu@Ag, using a two-step polyol method under bubbling N_2 gas.[3] They showed higher antioxidative properties than Cu particles. Ag@Cu particles, having an inverted core–shell structure compared to Cu@Ag particles, have also been prepared using thermal evaporation under ultrahigh vacuum[4] and microwave-assisted alcohol reduction processes.[5]

In this study, we prepared Ag/Cu bimetallic nanoparticles using a two-step polyol reduction method. We succeeded in synthesis of BC Ag/Cu nanoparticles which have different shapes from those described in previous reports.[4,5] The formation of BC structure was confirmed using transmission electron microscope (TEM)–EDS measurements.

Ag seeds were prepared using a polyol method under fast MW heating. A mixture of 2 mM $AgNO_3$ and 1 M poly(vinylpyrrolidone) (PVP: $M_w = 10000$) in 20 mL of ethylene glycol (EG) was heated from room temperature to 195 °C for 75 s under MW irradiation (μReactor; Shikoku Instrumentation Co., Ltd.). Then, Ag/Cu bimetallic nanoparticles were prepared using a polyol method under MW heating or conventional oil-bath heating. In the case of MW heating, 10 mL of 4 mM $Cu(OAc)_2 \cdot H_2O$ in EG was added dropwise for 10 min using a syringe pump at an injection rate of 1 mL min^{-1}. A similar experiment was carried out under oil-bath heating. During injection of $Cu(OAc)_2 \cdot H_2O$ in both MW and oil-bath heating, a continuous flow of Ar or N_2 was used to suppress oxidation of Cu particles.

For TEM (JEM-2010 and 2100F; JEOL) observations, samples were prepared by placing colloidal solutions of the products onto carbon-coated Cu or Au grids. Absorption spectra of the product solutions were measured using a spectrometer (UV-3600; Shimadzu Corp.) in the UV–vis region.

Figures 1a and 1b depict typical TEM images of products obtained after preparation of Ag seeds and Ag/Cu particles under MW heating, where spherical particles with average diameters of 21 ± 3 and 29 ± 6 nm were obtained, respectively. The greater average diameter implies that some Ag/Cu bimetallic nanoparticles might have been formed in the second step. Then TEM–EDS was used (Figure 2) for confirmation. Although distinguishing between Ag and Cu from the TEM image contrast depicted in Figure 2a is difficult, EDS data shown in Figures 2b–2d show that the number of the Ag/Cu nanoparticles occupied 98% in the total products.

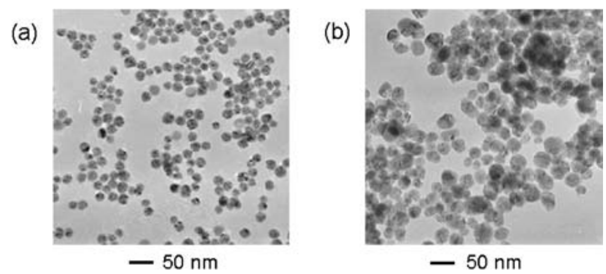

Figure 1. TEM images of (a) Ag and (b) Ag/Cu nanoparticles prepared using polyol reduction in EG.

Figure 3 portrays distributions of the Ag and Cu components along the cross section line of a typical particle shown in Figure 3a. These data imply that BC Ag/Cu nanoparticles were formed. Although Ag@Cu core–shell particles were prepared in previous studies,[4,5] anisotropic heterostructures were prepared in high yield in our present experiments.

The UV–vis spectra were measured to characterize optical properties of Ag/Cu particles (Figure 4). Absorption spectra of Ag seeds and spherical Cu particles are also shown for comparison. The absorption spectrum of Ag seeds gives a typical surface plasmon resonance (SPR) band of Ag from 320 to 500 nm with a peak at about 405 nm. On the other hand, Cu nanoparticles give a broad SPR band with a weak peak at 580 nm. A broad absorption spectrum of Ag/Cu is observed in the 300–800-nm region, where the 400-nm peak corresponding to Ag component and the 580-nm peak related to the Cu component weaken.

There are a lot of biphasic particles such as Janus particles, bicompartmental, dumbbell-like (hetero-doublets or asymmetric dimers), snowman-like, acorn-like, and half-raspberry-like particles.[6] On the basis of TEM–EDS analyses, Ag/Cu particles obtained here can be ascribed to phase separated type of BC particles. The most significant finding in this study is that BC nanoparticles are produced and that no Ag@Cu core–shell particles are prepared under the present experimental conditions.

Figures S1 and S2 (Supporting Information; SI)[7] show TEM–EDS and UV–vis spectra data of Ag/Cu particles prepared under oil-bath heating. These data indicate that similar BC Ag/Cu nanoparticles were prepared under oil-bath heating and that the Ag component at 405 nm decreases, whereas the Cu component at 570 nm increases with increasing the [Cu]/[Ag] molar ratio.

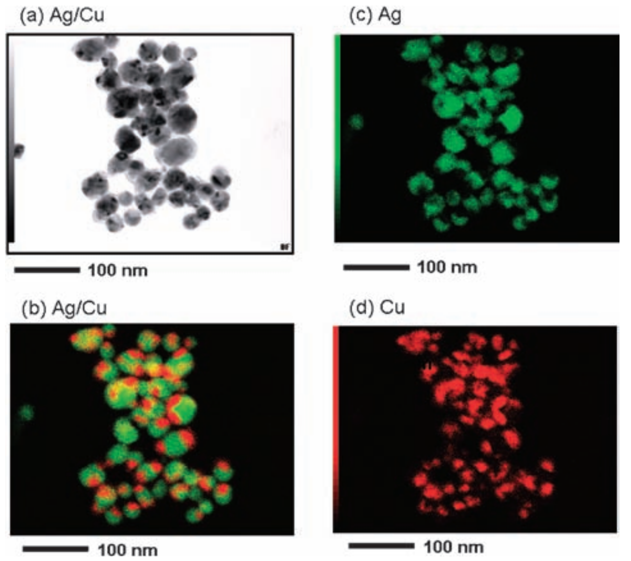

Figure 2. TEM–EDS images of Ag/Cu nanoparticles: (a) original TEM, (b) Ag/Cu, (c) Ag component, and (d) Cu component.

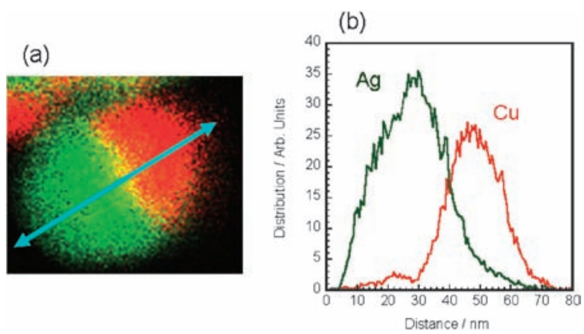

Figure 3. Distribution of Ag and Cu components for a typical BC Ag/Cu particle along a blue line.

The average size of Ag/Cu nanoparticles (29 ± 6 nm) was larger than that of Ag seeds (21 ± 3 nm). Most BC Ag/Cu particles consist of one large Ag component and one small Cu component as shown in Figure 3. Besides them, there are some large particles where more than two Cu components are involved in one Ag/Cu nanoparticle (Figure S3).[7] If spherical Cu particles are produced and attached to spherical Ag seeds, acorn-like or snowman-like structures[6] are expected to be formed to keep spherical structure of Ag seeds. However, on the basis of EDS data (see Figures 2 and 3), both Ag and Cu have nonspherical shapes and combined structures of Ag and Cu components are quasi-spherical shapes in most cases. This indicates that shapes and sizes of Ag seeds change during the second step. One possibility is that small Ag seeds melt and combine into larger particles in the second step at 195 °C. When Ag seeds were heated again in EG for 20–60 min, an increase in particle sizes and broadening of SPR band due to fusion were observed in TEM images and UV–vis spectra (Figure S4).[7] Thus, the increase in sizes of BC Ag/Cu particles and formation of more than two parts of Cu component in one particle for some particles can be explained by melting of Ag particles during the second step, and the melting of Ag seeds is responsible for the formation of anisotropic BC Ag/Cu nanoparticles.

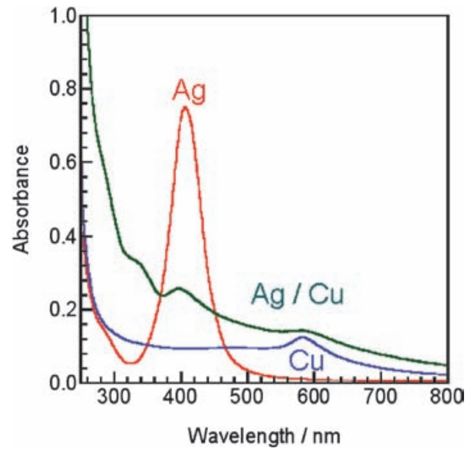

Figure 4. UV–vis spectra of (a) Ag seeds, (b) Ag/Cu particles, and (c) spherical Cu nanoparticles measured at the same concentration of 0.04 mM.

Figures S5 and S6 in SI[7] show selected area diffraction pattern (SAED) patterns and high-resolution TEM image of BC Ag/Cu particles. We could observe many ED spots of (111) and (200) facets and some other facets of Ag and Cu in SAED patterns. Most of the observed lattice fringes fitted well with the Ag{111} and Cu{111} planes. On the basis of these findings, it was concluded that BC Ag/Cu particles are not amorphous but polycrystals having {111} facets as main facets.

In summary, we synthesized BC Ag/Cu particles using a two-step polyol reduction method. Anisotropic Ag/Cu structures arise from melting of Ag seeds in the second step. We are planning to a further detailed study to clarify the formation mechanism of BC Ag/Cu particles under the polyol reduction process.

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References and Notes

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7 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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