Preparation of Cu@Ag Core–Shell Nanoparticles Using a Two-step Polyol Process under Bubbling of N_2 Gas

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Cu core–Ag shell nanoparticles, denoted as Cu@Ag, were prepared using a two-step polyol reduction process under bubbling N_2 gas. Formation of Cu@Ag particles with an average size of ca. 80 nm was confirmed using energy-dispersed X-ray spectroscopic (EDS) measurements. The Cu particle oxidation was suppressed greatly by Ag shell covering.

In recent years, metal-coated colloidal core–shell composite particles have received intensive attention for potential application as catalysts, sensors, and substrates for surface-enhanced Raman scattering.[1] In contrast to extensive studies of core–shell particle preparation involving Au, Ag, Pd, and Pt, little work has been done for Cu.[2] Recently, Ag@Cu particles were prepared using laser ablation in ethanol solvent,[3] thermal evaporation under ultrahigh vacuum,[4] and microwave-assisted alcohol reduction processes.[5] Although Cu@Ag core–shell particles were also prepared using two vapor phase deposition techniques,[6] they have not been obtained using a chemical method in solution. Preparation of Cu@Ag particles in solution is expected to be more difficult than that of Ag@Cu because the displacement reaction occurs by the addition of Ag^+ ions to the Cu core solution resulting from the higher standard electrode potential of Ag^+/Ag (+0.80 V) than that of Cu^{2+}/Cu (+0.34 V). Here, the standard hydrogen electrode is used as a reference electrode.

In this study, we prepared Cu@Ag nanoparticles using a two-step polyol reduction method. The Cu core and Ag shell structure formation was confirmed using transmission electron microscope (TEM)–EDS measurements. Although Cu nanoparticles are anticipated for use as new electronic materials because of their lower cost than either Au or Ag, low oxidation resistance limits actual application. We show here that Ag shell coatings can greatly suppress the oxidation rate of the Cu component in solution.

The following techniques and procedures were used to overcome the difficulties described above for preparation of Cu@Ag particles. (a) Copper is easily oxidized by O_2 dissolved in the solution. Therefore, N_2 was bubbled during preparation of Cu cores and Ag shells to suppress oxidation. (b) Because of a replacement reaction occurring between Cu and Ag^+,

$$\mathrm{Cu(s)} + 2\mathrm{Ag}^+ \rightarrow \mathrm{Cu}^{2+} + 2\mathrm{Ag(s)} \qquad (1)$$

Cu cores were partly dissolved as Cu^{2+}. To suppress such a displacement reaction, Ag shell preparation was conducted rapidly at a high temperature because the reduction of Ag^+ occurs more rapidly than reaction 1. (c) Drop-by-drop injection was used to overgrow Ag shells on Cu cores. Using this technique, supersaturation of Ag^0 leading to nucleation and growth of Ag nanoparticles was suppressed.

In actual experiments, 3.33 g of PVP (MW: 10000) was dissolved in 27.5 mL of EG solution by continuous stirring in a 100-mL three-necked flask, which was heated to 110 °C and maintained at that temperature for 1 h by bubbling of N_2 to remove O_2 dissolved in the solution. Then the solution was heated to 196 °C; 2.5 mL of 48 mM $Cu(OAc)_2{\cdot}H_2O$ in EG was added drop-by-drop using a syringe pump at an injection rate of 2 mL/min. The solution was maintained at 196 °C for 2.5 min to prepare Cu core nanoparticles. Subsequently, 4 mL of 15 mM $AgNO_3$ was injected at an injection rate of 6 mL/min to prepare the Ag shell. The final concentrations of $Cu(OAc)_2{\cdot}H_2O$, $AgNO_3$, and PVP in EG were 3.53, 1.76, and 882 mM, respectively. The reagent solution was cooled rapidly using a water bath. During Ag shell fabrication, N_2 was bubbled continuously.

Product solutions were centrifuged at 13000 rpm three times for 15 min each time. The precipitates were collected then redispersed in deionized water. For TEM (JEM-2010 and 2100F; JEOL) observations, samples were prepared by dropping 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–visible (vis) region.

Figures 1a and 1b depict typical TEM images of products obtained after preparation of Cu core seeds and Ag shells, where spherical particles with average diameters of 59 ± 11 and 81 ± 13 nm were obtained, respectively. The greater average diameter implies that Cu@Ag particles might have been formed. Then TEM–EDS was used (Figure 2) for confirmation. Although distinguishing between Cu and Ag from the TEM image contrast depicted in Figure 2a is difficult, EDS data shown in Figures 2b–2d show that Cu@Ag particles were prepared in a high yield (ca. 80%). Figure 3 portrays distributions of the Cu and Ag components along the cross section line shown in Figure 2b. These data imply that uniform Ag shells were overgrown on spherical Cu cores. In separate experiments for preparation of Cu and Ag nanoparticles in EG solutions in the presence of PVP, results showed that the reduction of Cu^{2+} was much slower than that

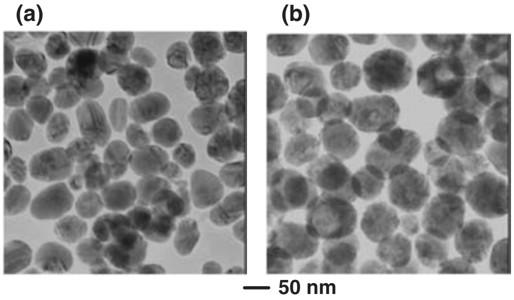

Figure 1. TEM images of (a) Cu and (b) Cu@Ag nanoparticles prepared using polyol reduction in EG.

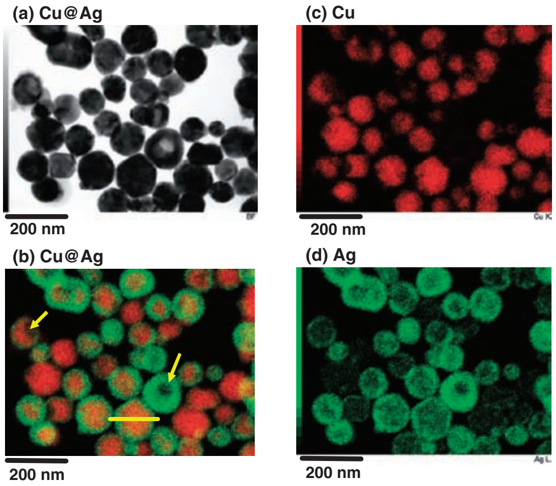

Figure 2. TEM–EDS images of Cu@Ag nanoparticles: (a) original TEM, (b) Cu@Ag, (c) Cu component, (d) Ag component.

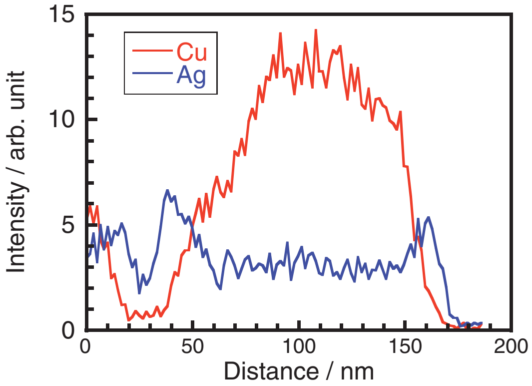

Figure 3. Distribution of Cu and Ag components for a particle shown in Figure 2b along a yellow line.

of Ag^+. In the experiment described herein, the reduction of Ag^+ to Ag^0 on Cu core and the displacement reaction 1 can occur competitively in the second step. Using rapid, high-temperature heating, the former rate is enhanced to suppress the latter reaction. Consequently, Cu@Ag particles were prepared.

There are a few particles which have spherical holes or some vacancy in the cores, as shown in Figure 2b by yellow allows. When distributions of Cu and Ag in such particles were measured, little Cu component was observed in the cores and no Cu/Ag alloys were observed in shells. The formation of hollow particles by such a galvanic replacement reaction as

$$3Ag + AuCl_4^- \rightarrow 3Ag^+ + 4Cl^- + Au \qquad (2)$$

has been reported for the Ag/Au system.[7] It was, therefore, concluded that a similar displacement reaction 1 creates the small quantities of hollow particles obtained for the Cu/Ag system in this study.

The UV–vis spectra were measured to characterize optical properties and to examine oxidation rates of Cu@Ag particles (Figure 4). Absorption spectra of Cu core particles (a) and spherical Ag particles (e) are also shown for comparison. The absorption spectra of Cu core seeds observed immediately after preparation (a) yields a broad absorption spectrum having a surface plasmon resonance peak of Cu at about 600 nm. The absorption spectrum of Cu@Ag (c) strengthens in the 300–800 nm region, although the 600 nm peak related to the Cu component weakens. No sharp peak corresponding to Ag is visible in the 400-nm region.

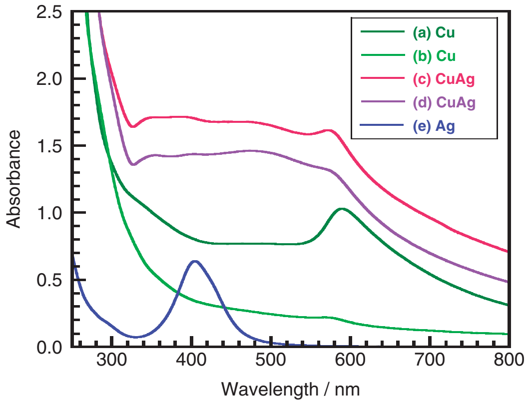

Figure 4. UV–vis spectra of Cu core and Cu@Ag particles: (a) Cu, 2.5 min heating; (b) Cu, 2.5 min heating, after 6 days; (c) CuAg, as prepared; (d) CuAg, after 14 days; (e) spherical Ag nanoparticles.

The Cu peak at 600 nm had almost disappeared because of rapid oxidation when the UV–vis spectra of Cu were measured after 6 days (b). On the other hand, the absorbance of Cu@Ag had reduced by about 20% after 14 days (d). These results show that, by covering Cu cores with Ag shells, particle surfaces gained an antioxidative property.

In summary, we prepared Cu@Ag particles using a two-step polyol reduction method. The thickness of Ag shells obtained by vapor-phase techniques was not uniform, and many peanut-type particles were produced.[6] On the other hand, Ag shells with uniform thickness could be obtained in our chemical method. Thus, it is expected that Cu@Ag particles obtained using the chemical method have higher antioxidative property than those prepared using the vapor-phase techniques.[6] Therefore, they are useful for many industrial applications as a new colloid material.

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