Rapid Formation of Novel Au Core–Ag Shell Nanostructures by a Microwave-polyol Method

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(Received August 8, 2005; CL-051028)

Au core–Ag shell bimetallic nanoparticles, denoted as Au@Ag, have been prepared by a microwave(MW)-polyol method through the two-step reduction of $AuCl_4^-$ and Ag^+ ions in the presence of poly(vinylpyrrolidone) (PVP) as a capping reagent. When single crystal polygonal Au nanoplates and nanorods were used as seeds, a mixture of various Au@Ag core–shell nanostructures was prepared after MW heating for only 2 min. Among them, small amounts of novel polygonal and rod types of Au@Ag nanostructures, in which morphologies of Au core were conserved, were produced.

Recently, Au@Ag bimetallic nanoparticles have attracted considerable interest because of unique optical and catalytic properties relative to those of separate metallic nanoparticles. They were synthesized by chemically reducing $HAuCl_4$ and $AgNO_3$, photochemical reduction of a mixture of $HAuCl_4$ and $AgClO_4$, and radiolytic reduction of $KAu(CN)_2$ and $NaAg(CN)_2$.[1,2] In most cases, spherical Au@Ag core–shell and Au–Ag alloyed nanoparticles were prepared.

We have recently studied fast preparation of Au nanostructures by using a MW-polyol method.[3] $HAuCl_4$ was reduced in ethylene glycol (EG) in the presence of PVP as a polymer capping reagent. Then, single crystal polygonal plates, nanorods, and nanowires, which were difficult to prepare by using a conventional oil-bath heating, were synthesized preferentially. In the present study, we succeeded in preparation of novel Au@Ag bimetallic nanostructures by using these Au nanostructures as seeds and addition of $AgNO_3$ as a source of Ag shell. It was found for the first time that morphologies of Au core are conserved well for the growth of Ag shell.

The MW-polyol method used in this study was essentially identical to that reported previously.[3] 2.4 mM of $HAuCl_4 \cdot 4H_2O$ was resolved in 20 mL of EG solution. Then, 1 M of PVP in term of monomeric units (molecular weight 40,000) was added to the above solution. This solution was heated by MW irradiation in a continuous wave mode (Shikoku Keisoku: 400 W) for 2 min. After cooling down the product solution to a room temperature, 23 mM of $AgNO_3$ was added to the solution. It was heated again by MW irradiation for 2 min. Products particles after the first and second MW irradiation were characterized by using transmission electron microscopy (TEM: JEOL JEM-2010) and UV–visible absorption spectroscopy (Shimadzu UV-2450).

Figure 1 shows a TEM photograph of products obtained after the first MW irradiation, where triangular, square, rhombic, and hexagonal nanoplates, and nanorods are observed. Average edge lengths of polygonal nanoplates were 40–50 nm. When these single crystal Au nanostructures were used as seeds, a mixture of various Au@Ag core–shell nanostructures was prepared after MW heating for only 2 min, as shown in Figure 2. Although most Au@Ag nanostructures consist of single core/single shell, multicore/single shell structures are also obtained as indicated by allows.

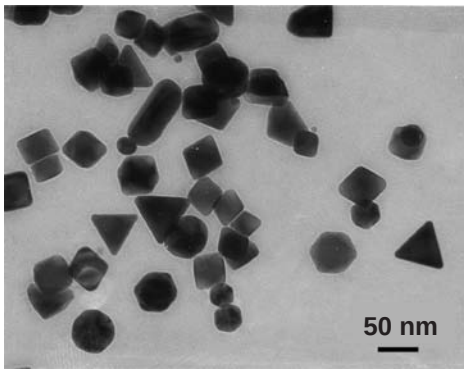

Figure 1. TEM photograph of Au nanoparticles prepared by MW heating of $HAuCl_4 \cdot 4H_2O$/PVP/EG for 2 min.

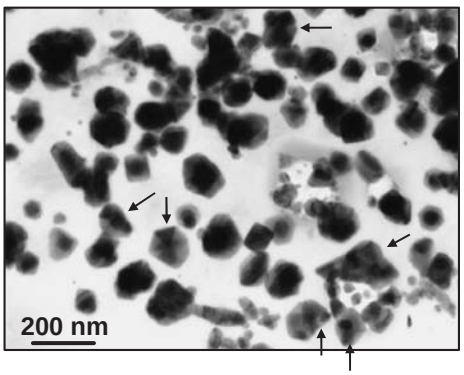

Figure 2. TEM photograph of Au@Ag nanoparticles prepared by MW heating of $AgNO_3$/PVP/EG for 2 min in the presence of Au nanoparticles as seeds. Multicore particles are shown by allows.

It should be noted that among a mixture of various Au@Ag products, small amounts of novel polygonal and rod types of nanostructures were produced (Figures 3a–3f). Some other Au@Ag particles having the same nanostructures were observed, though their sizes were different. Clear contrast between Au core and Ag shell in TEM images indicates that there are no thick Au/Ag alloyed layers between them. Various kinds of new Au@Ag core–shell nanostructures were prepared by using various kinds of single crystal Au nanostructures as seeds. When Au core is truncated triangle, inversed truncated triangle Ag shell structure is formed (Figure 3a). Rhombic, truncated rhombic, and hexagonal cores gave square, truncated rhombic, and hexagonal core–shell structures, respectively (Figures 3b–3d). Rod

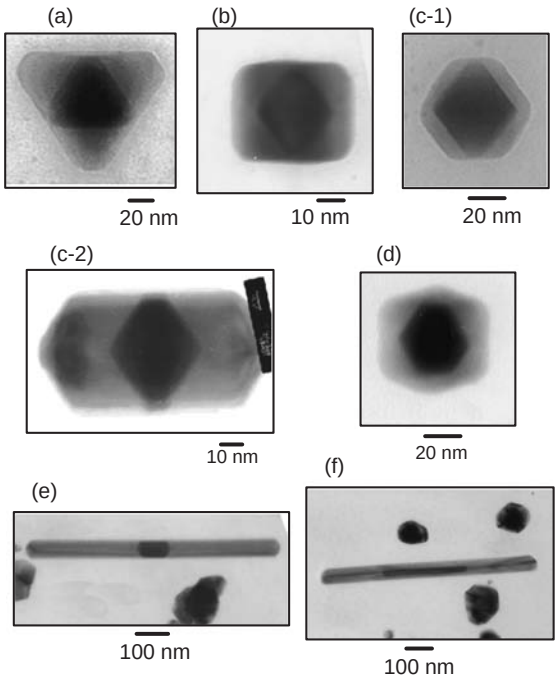

Figure 3. TEM photographs of Au@Ag nanostructures prepared by MW-polyol method.

cores result in either a longer rod (Figure 3e) or a longer and thicker rod (Figure 3f). In Figure 4 is summarized the correlation in morphologies between Au core and Au@Ag core–shell obtained in Figure 3. Similar anisotropic Au@Ag core–shell structures arise from each different shape of anisotropic Au seeds. Their selected area electron diffraction patterns indicated that they consisted of single crystal Au and Ag nanostructures. Gold and silver gave the same face-centered cubic structure and the lattice constants of Au (0.408 nm) and Ag (0.409 nm) are very similar. Thus, similar shapes of Ag shells grow from single crystal Au nanoplates and nanorods as seeds in the presence of PVP under MW heating.

When MW was irradiated to a mixture of the $HAuCl_4 \cdot 4H_2O/AgNO_3$/PVP/EG in the same concentrations, no core–shell structures could be obtained. This indicated that two-step process using Ag seeds is necessary for the preparation of Au@Ag core–shell structures by the MW-polyol method.

In order to obtain information on Au–Ag nanostructures of products, UV and visible absorption spectra of solutions were measured (Figure 5). A surface plasmon resonance (SPR) band of Au nanoparticles with a peak at 560 nm is observed in the 500–700 nm region after the first MW irradiation. When spherical Ag nanoparticles with an average diameter of 40 nm was prepared by MW irradiation to an $AgNO_3$/PVP/EG solution, a SPR band of Ag nanoparticles is observed in the 320–540 nm region with a peak at 420 nm. It is known that Au@Ag core–shell structures give SPR bands with two peaks near the Au and Ag SPR bands, while Au/Ag alloys provide SPR bands with a single peak between them.[2] After the second MW irradiation, a broad SPR band with weak peaks at 420 and 560 nm are obtained in the 320–800 nm region. This finding is consistent with the TEM observation which demonstrated Au@Ag core–shell structures.

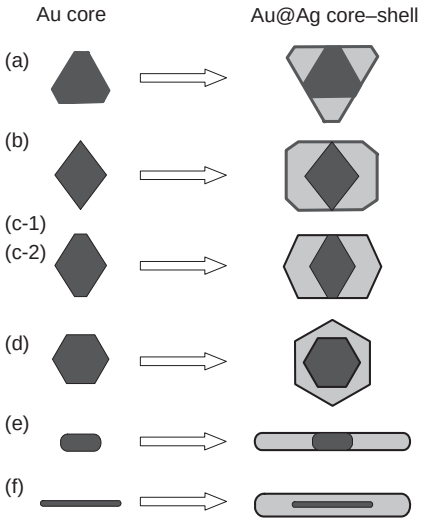

Figure 4. Correlation between Au core and Au@Ag core–shell structures obtained in Figure 3. Black and gray parts represent Au core and Ag shell, respectively.

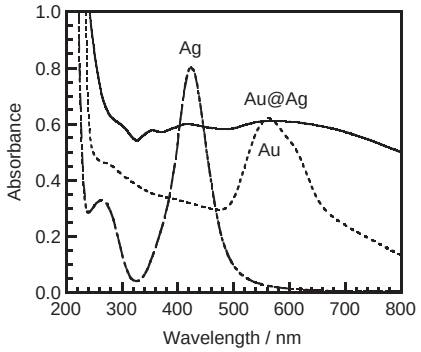

Figure 5. UV and visible spectra of Au, Ag, and Au@Ag nanoparticles obtained by the MW-polyol method.

In summary, a mixture of Au@Ag core–shell structures has been prepared by the MW-polyol method. Among them, small amounts of novel polygonal and rod structures, having a strong correlation between core and shell structures, were produced. A further study is in progress in order to clarify the detailed formation mechanism of each Au@Ag core–shell structures under MW irradiation.

This work was partially supported by a Grant-in-Aid for Scientific Research No. 15651046 from the Japanese Ministry of Education, Culture, Sports, Science and Technology.

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Published on the web (Advance View) October 8, 2005; DOI 10.1246/cl.2005.1518