Preparation of Ag Core–Cu Shell Nanoparticles by Microwave-assisted Alcohol Reduction Process

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We have succeeded in rapidly preparing Ag core–Cu shell nanoparticles (denoted as Cu/Ag nanoparticles) having 10–40 nm in size by a microwave (MW)-assisted alcohol reduction process. The core–shell nanoparticles were prepared by step-by-step successive reduction of a silver precursor and then of a copper precursor added after the formation of silver nanoparticles in 1-heptanol.

Metal nanoparticles are applied to catalysts,[1] magnetic,[2] electronic,[3] and nonlinear optical materials.[4] Monometallic nanoparticles have been extensively used for these applications. Nowadays, bimetallic nanoparticles, having core–shell and alloy nanostructures, are desired as new materials because new functions and improvements of functions can be expected in catalytic[1] and magnetic properties,[5] that cannot be achieved by monometallic nanoparticles.

Bimetallic nanoparticles having a core–shell nanostructure (denoted as core–shell nanoparticles) have started to attract much attention of researchers. Properties and preparation methods of the core–shell nanoparticles have been reported, e.g., Ag/Au,[6] Pd/Ag,[7] Pt/Au,[8] Ag/Ni,[9] Ag/Co.[9] Ag/Cu nanoparticles have been prepared only by the physical methods such as a laser ablation in ethanol solvent[10] or a thermal evaporation under ultra high vacuum.[11] Chemical preparations in solvents have never been reported for Ag/Cu or Cu/Ag nanoparticles, while chemical preparations of these particles by solution reactions should have advantages in manipulation and tuning of their fine structures. Furthermore, based on the previous reports as to improvements of catalytic and magnetic function of core–shell nanoparticles,[1,5] it is expected that Ag/Cu or Cu/Ag nanoparticles show new and different functions from sole silver or copper nanoparticles.

Our group succeeded in easily preparing silver[12] and copper[13] nanoparticles in long-chain alcohol solvents by a MW-assisted alcohol reduction process. Consequently, we have tried to prepare Cu/Ag nanoparticles by modifying this process to the consecutive ones of the formations of Ag and Cu: first, silver nanoparticles are prepared from a silver precursor in a long-chain alcohol solvent, and then a copper precursor is reduced in the presence of the silver nanoparticles in the same solution. This is the first report on chemical preparation of Ag core–Cu shell nanoparticles in solutions.

Silver myristate and copper myristate used as the precursors for preparing nanoparticles were synthesized according to previous reports.[12,13] Silver myristate (0.1 mmol) was dispersed in 1-heptanol (30 mL) in a three-necked flask. After treated by supersonication for completely dispersing the precursor, the 1-heptanol solution was heated by MW irradiation using an MW apparatus MMG-213VP (Micro Denshi Co., Ltd., 500 W) at 413 K for 5 min under N_2 bubbling (the obtained sample here was denoted as S1). The heating temperature was controlled by on-off irradiation of MW. A 1-heptanol solution (30 mL) including copper myristate (0.2 mmol) was mixed in the S1 1-heptanol solution, and then, heated at 433 K for 5 and 10 min (the samples obtained here were denoted as S2 and S3, respectively).

The sizes and morphologies were characterized by a high-resolution transmission electron microscopy (HRTEM) at 300 kV with a Hitachi H-9000 (Hitachi High-Technologies Corp.) The solution diluted with hexane was dropped onto a copper grid coated with carbon film, and then the grid was dried under vacuum at 323 K. UV–vis spectra of the solutions diluted by tenth with hexane were measured with a V-570 (JASCO Inc.).

Figure 1 shows HRTEM images. An image of the sample S1 is shown in Figure 1a. Nanoparticles having 5 nm in size were demonstrated therein. Observation of electron diffraction (ED) pattern showed face-centered cubic (fcc) structure of silver

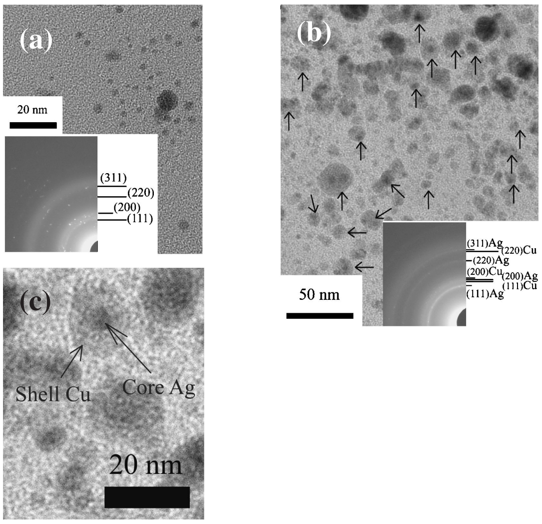

Figure 1. HRTEM images of the samples prepared only silver (a) and at atomic fraction Cu:Ag = 2:1 heated at 433 K for 5 min (b). Figure 1c is magnified image of one particle in Figure 1b. Indicated particles by arrows are nanoparticles having core–shell nanostructure.

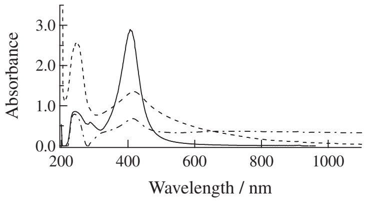

Figure 2. UV–vis spectra of the samples. Silver myristate was heated for 5 min at 413 K in 1-heptanol (solid line). Copper myristate was added into silver nanoparticles solution and then heated for 5 min (dash line) and 10 min (dash dot line). The sample of silver was diluted by twentieth with hexane.

(Figure 1a, inset). This result agreed with a result of Wada et al.[12] showing preparation of silver nanoparticles having 5 nm in size.

An HRTEM image of the sample S2 is shown in Figure 1b. Nanoparticles having 10–40 nm in size were observed. Figure 1c shows a magnified image of the particles in Figure 1b. A particle having 5 nm was observed with a strong contrast inside the particle having 15 nm in size. Thickness of the shell was 5 nm. This inside nanoparticle should be a silver nanoparticle having 5 nm in size because this diameter of the silver nanoparticles was close to those observed in Figure 1a. Furthermore, the shell surrounding the silver nanoparticle should be copper because of lighter contrast than the contrast of the inside nanoparticle. The different contrasts can be understood by difference of atomic numbers: a copper atom (Cu, 29) is lighter than a silver atom (Ag, 47). Therefore, it has been concluded that the nanoparticle in Figure 1c is an Ag core–Cu shell nanoparticle having 15 nm in size successfully prepared by step-by-step reduction of the two precursors. Additionally, nanoparticles of the sample S3 were aggregated forming the large particles over 100 nm in size (see Supporting Information Figure S1).[14]

A lot of Cu/Ag nanoparticles were observed in an image of the wide sight (Figure 1b) as indicated by the arrows. The number of the nanoparticles having the core–shell structure was counted to be 18 in 107. That is, the Cu/Ag nanoparticles were prepared by 17%. From the contrast of each particle, other nanoparticles having homogeneous contrast differing from clear contrast of the Cu/Ag nanoparticles were found. It was difficult to distinguish between silver and copper nanoparticles from the fringes of the particles because of small difference of lattice spacing with 0.3 Å. ED pattern of the prepared Cu/Ag nanoparticles (Figure 1b, inset) showed the copresence of fcc structures of Ag and Cu.

UV–vis spectrum of the sample S1 is shown in Figure 2 (solid line). The UV–vis spectrum had a peak at 407 nm attributed to surface plasmon absorption of silver nanoparticles.[12,15]

Dash line in Figure 2 shows the UV–vis spectrum of the sample S2. Damping, broadening, and red-shifting of the peak around 407 nm were observed. This variation of the spectrum should be caused by variation of mean free path of free electron in silver nanoparticles and dielectric constant surrounding a silver nanoparticle. Cottancin et al.[9] have reported change in the plasmon absorption of Ag nanoparticles by converting them into the core–shell nanoparticles with Co. Our observation in the absorption spectra should indicate that the surface plasmon absorption of silver nanoparticles was varied by change of dielectric constant surrounding the silver nanoparticles owing to deposition of copper nanoparticles onto the surface of the silver nanoparticles. The absorbance at 407 nm was damped by 45% in spite of the presence of Cu/Ag nanoparticles found by 17% in the HRTEM image of Figure 1b. The change of the plasmon absorption seemed complicated and could not be simply explained. Dash dot line in Figure 2 shows the UV–vis spectrum of the sample S3. The absorption at 400 nm was damped. Furthermore, the back ground rose up in the all region caused by scattering of probe light for measuring the UV–vis spectrum, suggesting the formation of large particles due to the aggregation.

In conclusion, we have succeeded in preparing Ag core–Cu shell nanoparticles by an MW-assisted alcohol reduction process in a short period of time. MW-heating is advantageous for this process due to its rapid heating mode.

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