Syntheses of Silver Nanofilms, Nanorods, and Nanowires by a Microwave-polyol Method in the Presence of Pt Seeds and Polyvinylpyrrolidone

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$AgNO_3$ was reduced by ethylene glycol (EG) in the presence of Pt seeds and polyvinylpyrrolidone (PVP) under microwave heating. In addition to spherical nanoparticles, single-crystalline silver nano-films, rods, and wires were produced. The relative number ratio of nanorods and nanowire to the total silver nanostructures was <14%. The formation mechanism of anisotropic silver nanostructures was discussed.

Recently, microwave (MW) dielectric heating has been used for preparation of size-controlled metallic nanostructures because of its rapid heating and penetration. The MW-polyol method has been used to the syntheses of silver nanostructures.[1–4] Pastoriza-Santos and Liz-Marzán[1] prepared spherical silver nanoparticles in *N*,*N*-dimethylformamide solution of $AgClO_4$ in the presence of PVP. Komarneni et al.[2] synthesized spherical silver nanoparticles with diameters below 50 nm by reduction of $AgNO_3$ in EG for 15 min in the presence of PVP. In addition, they obtained a small amount of short nanorods with aspect ratios below 5. He et al.[3,4] synthesized polychrome silver nanoparticles and silver dendrites under MW irradiation from solutions of $AgNO_3$ in the presence of PVP. Although syntheses of spherical particles, triangular nanoplates, and dendrites of silver under MW irradiation have been studied, no work has been reported on the syntheses of silver nanofilms and nanowires. Here, we define nanofilms as thin nanoplates with thickness less than 5 nm, and nanorods and nanowires as materials with aspect ratios of 2–20 and >20, respectively.

In the present study, we have attempted a one-pot synthesis of silver nanostructures by a MW-polyol method. In addition to known isotropic spherical silver nanoparticles, silver nanofilms, nanorods, and nanowires could be synthesized under continuous wave (CW) MW heating for 1–8 min with the assistance of Pt seeds and surfactant PVP.

A MW oven was modified by installing a condenser and thermocouple through holes of the ceiling and a magnetic stirrer coated with Teflon at the bottom. A 100-mL glass flask was placed in a MW oven and connected to a condenser. In a typical synthesis, 0.77 mL of $H_2PtCl_6{\cdot}6H_2O$ solution (1.5×10^{-4} M in EG) was added to 19.23 mL of EG (0.278 mol). Then, $AgNO_3$ (78 mg: 0.46 mmol) and PVP (average molecular weight: 40000, 73 mg: corresponding to 0.66 mmol in term of monomeric units) were added to the above solution. $H_2PtCl_6{\cdot}6H_2O$ and PVP should act as a precursor of Pt seeds for nucleation of silver metal and a stabilizer of silver nanostructures, respectively. The reagent solution was irradiated by MW in a CW mode (Shikoku Keisoku: 400 W) for 0.5–8 min.

For the solution irradiated by CW MW, the temperature increased linearly and abruptly with a fast heating rate and reached 198 °C after only 1 min owing to a large dielectric constant of EG. The solution was kept at 198 ± 1 °C for 0.5–7 min. Product particles were characterized by transmission electron microscopy (TEM: JEOL JEM-200CX) and UV–vis absorption spectroscopy (Shimadzu UV-2450). Before measurements of TEM photographs, PVP was separated from silver nanostructures by centrifugation. In this case, the reaction mixtures was diluted with water and centrifuged at 13000 rpm for 30 min.

When a mixture of $AgNO_3$/PVP in EG was irradiated by MW for 1–8 min without adding $H_2PtCl_6{\cdot}6H_2O$, only uniform spherical silver nanoparticles with diameters of ≈80 nm were obtained, and little anisotropic structure was obtained. Figures 1a and b show TEM photographs of products obtained after MW irradiation to a mixture of $AgNO_3$/PVP/$H_2PtCl_6{\cdot}6H_2O$ in EG for 1.5 and 8 min, respectively. It should be noted that besides spherical nanoparticles, nanofilms, nanorods, and nanowires of silver are produced after MW irradiation for 1.5 min. Most of silver nanofilms are triangular and appear as larger aggregated films, as shown by arrows in Figure 1a. Although exact thickness of nanofilms was not measured, it will be <5 nm on the basis of their weak contrast in the TEM photographs. To the best of our knowledge, this is the first observation of silver nanofilms and the first preparation of silver nanowires by the MW-polyol method. Although these films disappear in TEM photograph obtained under MW irradiation for 8 min (Figure 1b), larger numbers of nanorods and nanowires are grown. The diameters and lengths of nanorods and nanowires were 30–140 nm and 0.3–10 μm, respectively. Figures 2a and b show the distribution histograms of nanorods and nanowires prepared under MW irradiation for 8 min, respectively. The distribution of nanorods and nanowires decreases with increasing the aspect ratio from 2 to 140. The branching fractions of nanorods and nanowires were 86 and 14%, respectively, and

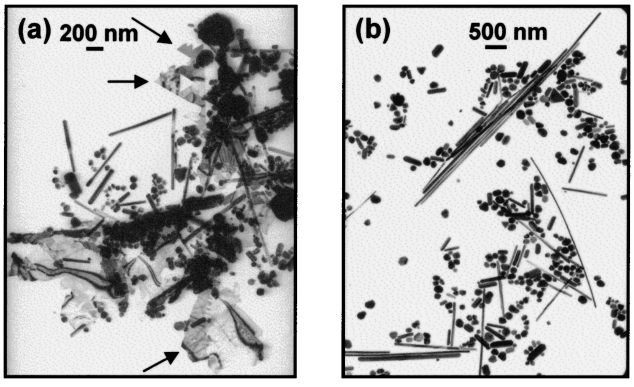

Figure 1. TEM photographs of silver nanostructures prepared by MW heating for (a) 1.5 min and (b) 8 min.

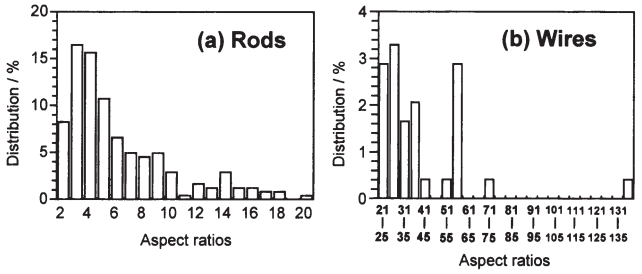

Figure 2. Distributions of (a) nanorods and (b) nanowires prepared by MW heating for 8 min.

the relative number ratio of nanorods and nanowires to the total nanostructures including spherical particles was 14% under MW irradiation for 8 min.

When selected-area electron diffraction (SAED) patterns of nanofilms, nanorods, and nanowires were measured, similar patterns were obtained, as shown in Figure 3 for the case of the nanofilm. The SAED pattern showed face-centered cubic single crystal nature and the corresponding XRD pattern agreed well with reported data of Ag (JCPDS No. 04-0783). On the basis of these findings, it was concluded that produced nanofilms, nanorods, and nanowires consist of Ag single crystal.

It is known that spherical silver nanoparticles give a surface plasmon band in the 350–500 nm region with a peak at about 410 nm.[1,6–8] When spherical particles vary to anisotropic nanorods, two surface plasmon bands appear below and above 400 nm. With increasing the aspect ratio of nanorod, the major longitudinal band significantly shifts to red, while the minor transverse band slightly shifts to blue. UV–vis spectra of products, obtained from the $AgNO_3/H_2PtCl_6{\cdot}6H_2O$/PVP mixture in EG at different irradiation times, are shown in Figure 4. The spectra obtained after 1, 1.5, 3, and 8 min irradiation consist of main band in the 320–600 nm region on account of spherical particles. In addition, a weak shoulder due to transverse bands of nanorods and nanowires is observed at ≈360 nm in the spectra obtained after 1.5, 3, and 8 min irradiation, as shown by an arrow. The spectra obtained after 3 and 8 min irradiation are broader than that obtained after 1.5 min because of a long tail band above 600 nm. This is explained by an increase in the contribution of the longitudinal band of nanorods and nanowires above 3 min.

The formation of anisotropic silver nanostructures initiates by reducing $H_2PtCl_6{\cdot}6H_2O$ with EG.

$$CH_2OH\text{–}CH_2OH \rightarrow CH_3CHO + H_2O \quad (1a)$$

$$4CH_3CHO + Pt^{4+} \rightarrow Pt + 4H^+ + 2CH_3COCOCH_3 \quad (1b)$$

As a result of the above reduction process, very small Pt nanoparticles (≈2 nm) are initially formed as seeds. These Pt nanoparticles served as nuclei for the epitaxial growth of silver nanostructures, because crystal structures and lattice parameters match

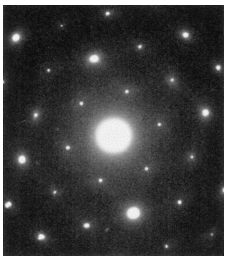

Figure 3. Electron diffraction pattern of nanofilm in Figure 1a.

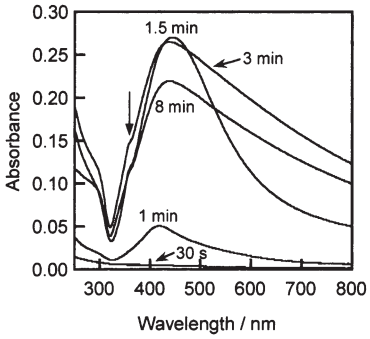

Figure 4. UV and visible spectra of silver nanostructures prepared by MW heating for 0.5–8 min.

closely. Similar reduction processes leading to Ag nanostructures occur for $AgNO_3$ as competitive reduction process.

$$2CH_3CHO + 2Ag^+ \rightarrow 2Ag + 2H^+ + CH_3COCOCH_3 \quad (2)$$

The nucleation and growth processes of silver occur with the assistance of Pt seeds. According to the TEM observation of products, spherical silver nanoparticles with diameters of 10–30 nm were formed after 1 min irradiation. Some of these nanoparticles were grown into larger nanopartilces, nanofilms, or nanorods after 1.5 min irradiation (Figure 1a). Nanofilms disappeared after 3–8 min irradiation, and nanorods, nanowires, and small spherical nanoparticles were produced (Figure 1b). It should be noted that only spherical nanoparticles with diameters of ≈80 nm were formed without the addition of $H_2PtCl_6{\cdot}6H_2O$. On the basis of these findings, it was concluded that initial formation of small nanoparticles with the assistance of Pt seeds and polymeric surfactant PVP plays a significant role for the formation of such anisotropic silver nanostructures as films, rods, and wires. The PVP adsorbed on specific crystalline surfaces could significantly decrease their growth rates and lead to a highly anisotropic growth. One reason for the lack of nanowires in the previous studies will be the high PVP/$AgNO_3$ molar ratios.[1–4] A heavy coverage of PVP on the surfaces of nanoparticles results in an isotropic growth mode of products. The disappearance of nanofilms at longer irradiation time may be due to the fact that rod-shaped and wire structured silvers are more stable than film-shaped ones.

In summary, we succeeded in a one-pot syntheses of single-crystalline silver nanofilms, nanorods, and nanowires by the MW-polyol method with the assistance of Pt seeds and PVP. A further study is in progress in order to enhance the yields of these nanostructures in the products and to control morphology of anisotropic products.

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