Preparation of Gold Nanoplates by a Microwave-polyol Method

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Triangular, square, and hexagonal gold nanoplates with diameters of 30–90 nm have been prepared through a microwave-polyol method. These nanoplates gave new plasmon band of Au in the 550–800 nm region. It was concluded that nonthermal effect plays a significant role for the formation of Au nanoplates under microwave irradiation.

Microwave (MW) dielectric heating is a new promising technique for preparation of size-controlled metallic nanoparticles because of its rapid heating and penetration. Preparation of gold nanoparticles under MW heating (480–1100 W) has recently been studied by three research groups.[1–3] When $HAuCl_4/3H_2O$ or $HAuCl_4$ was reduced in methanol, ethanol, or *N*,*N*-dimethylformamide for 0.5–5 min, spherical nanoparticles with diameters below 11 nm were synthesized. Gold nanoplates have recently been synthesized by a few research groups by reduction of $HAuCl_4$ with salicylic acid in aqueous solution[4] and by photoreduction of $NaAuCl_4$.[5] We report here the first preparation of polygonal gold nanoplates by a MW-polyol method.

An 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 an MW oven and connected to a condenser. A resolved solution of $HAuCl_4$ (20 mg) in ethylene glycol (20 mL) containing polyvinylpyrrolidone (PVP: average molecular weight: 40000, 0.572 g) was irradiated by MW in a continuous wave (CW) or pulse mode (Shikoku Keisoku: 400 W). PVP acts as a stabilizer of small Au metal particles. For comparison, the same solution was heated in a conventional oil bath (500 W). Products particles were characterized by using UV–vis absorption spectroscopy and transmission electron microscopy (TEM).

Figure 1 shows temperature profiles of the $HAuCl_4$–PVP–ethylene glycol solution for different heating time with CW or pulse mode of MW irradiation and in an oil bath. For the solution irradiated by CW MW, the temperature increases linearly and abruptly with a fast heating rate and reached 196 °C after 1 min. The solution was kept at 196 °C for 1 min. For the same solution heated in the oil bath, the temperature increases more slowly. The solution needed 18 min heating in the oil bath to reach 196 °C. Then, the solution was kept at 196 °C for 1 min. When a pulse mode of MW was used, the solution temperature was controlled by a microcomputer in order to obtain a similar slow heating rate to that in the oil bath, as shown in Figure 1.

It is expected that Au metal particles are produced from the following reactions in the MW-polyol process.

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

$$6CH_3CHO + 2Au(III) \rightarrow 2Au + 6H^+ + 3CH_3COCOCH_3 \quad (1b)$$

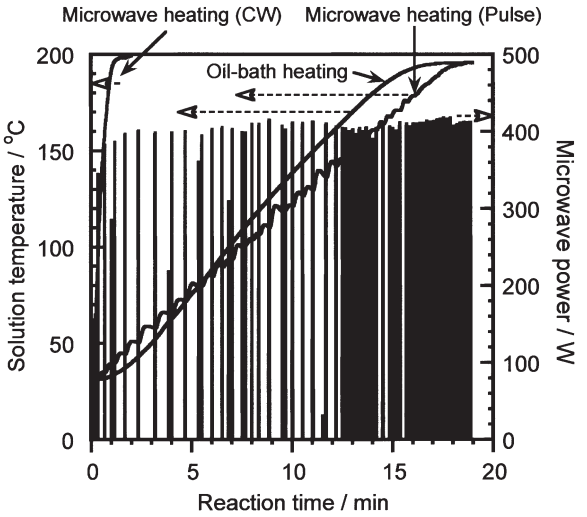

Figure 1. Dependence of temperature on the reaction time for $HAuCl_4$–PVP–ethylene glycol solution heated by CW or pulsed MW and in an oil bath. MW pulses used are also shown.

Reagent solution exposed to MW irradiation was sampled at different times and then the samples were characterized by UV–vis absorption spectrometry (Figure 2). The reactant spectrum is composed of an absorption peak of $AuCl_4^-$ at 328 nm. Although this peak disappears after MW irradiation for 40 s, a broad surface plasmon band of Au appears in the 500–800 nm region. Af-

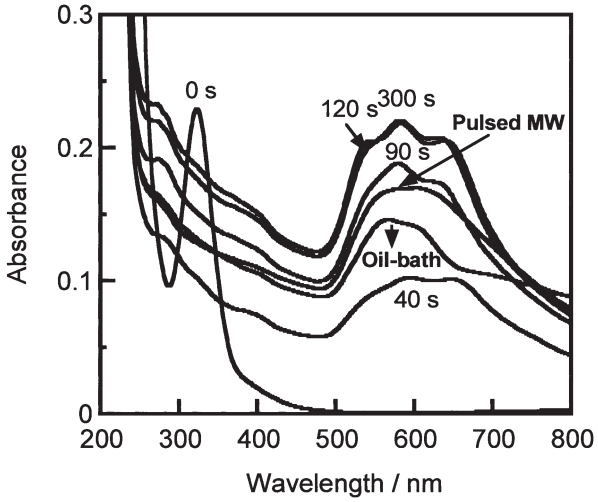

Figure 2. Absorption spectra of the original solution and solutions obtained after CW MW heating at various reaction times (s), oil-bath heating (19 min), and pulsed MW heating (19 min). Sample solutions are diluted by a factor of 50.

ter MW irradiation for 120–300 s, the plasmon band consists of three peaks at 545, 590, and 645 nm. A similar plasmon band of Au nanoparticles with a peak at 570 nm is observed in the oil-bath heating, though its peak shifts to blue and the relative intensity in the 550–700 nm region becomes weak in comparison with that in the CW MW heating. It is known that a surface plasmon band of Au sphere nanoparticles appears in the 500–600 nm with a sharp peak at about 520 nm.[3,4] Thus, the enhancement of longer-wavelength component of Au plasmon band under MW heating suggests a high possibility of the formation of nanoparticles with different morphologies.

In order to examine morphologies of Au nanoparticles obtained by CW MW and oil-bath heating, TEM photographs are measured, and the size and shape distributions of Au nanoplates are determined (Figures 3 and 4). In recent studies, Malikova et al.[4] obtained a mixture of flat triangular/hexagonal nanoplates with diameters of 50–200 nm and smaller close-to-spherical Au particles, while Ibano et al.[5] synthesized hexagonal Au nanoplates with diameters of 200–500 nm. In this study, square nanoplates as well as triangular and hexagonal nanoplates with smaller diameters of 30–90 nm than those in the previous studies[4,5] are produced under CW MW irradiation. In the oil-bath heating, the distribution of large spherical particles (>100 nm) becomes large and a small amount of rod is also formed. Particles and plates in the oil-bath heating have less sharp edges than those formed under CW MW heating. The fact that dominant products in the oil-bath heating are spherical particles is consistent of the observation of a typical plasmon band of Au spherical particles with a peak around 550 nm.[3,4] A comparison between UV-absorption spectra and TEM led us to conclude that the longer-wavelength component in the 550–800 nm region arises from surface plasmon bands of polygonal Au nanoplates.

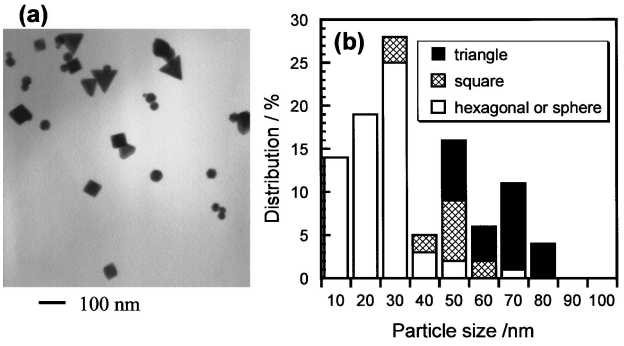

Figure 3. (a) TEM photograph of nanoplates and (b) their distributions prepared by CW MW heating for 1 min.

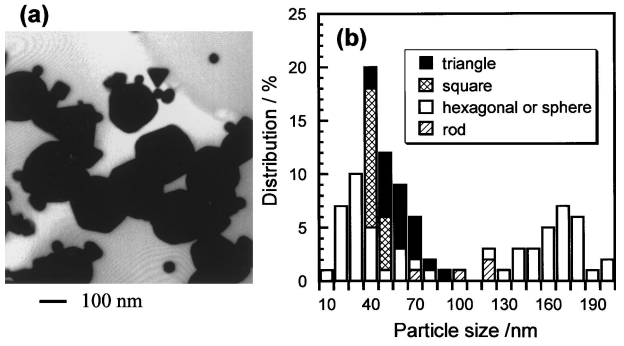

Figure 4. (a) TEM photograph of nanoparticles and (b) their distributions prepared by oil-bath heating for 19 min.

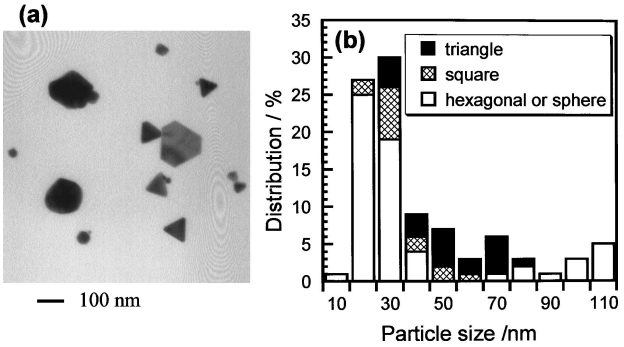

Figure 5. (a) TEM photograph of nanoplates and (b) their distributions prepared by pulsed MW heating for 19 min.

Electron diffraction (ED) patterns of triangle nanoplates were measured. The ED spot array gave the hexagonal symmetry, which was very similar to that reported previously for Au nanoplates.[4,5] On the basis of this finding, it was concluded that product nanoplates are single crystals and the incident electron beams are perpendicular to {111} facets of the plates.

We found that morphology of Au particles was different between CW MW and oil-bath heating. In order to examine the effects of MW irradiation, temperature profile under MW irradiation was controlled to be similar to that in the oil-bath heating by using a pulse mode (Figure 1). TEM photograph of products under pulsed MW, shown in Figure 5, indicates that fractions of smaller polygonal plates below 110 nm are larger than those in the oil-bath heating. This is consistent with a higher relative intensity of the longer-wavelength component in the pulsed MW heating than that in the oil-bath heating (Figure 2). On the basis of these facts, it was concluded that nonthermal effect such as superheating of Au under MW heating plays a significant role for the formation of Au nanoplates.

In summary, we succeeded in a fast preparation of Au polygonal plates by the MW-polyol method. In addition to previously synthesized triangular and hexagonal nanoplates, square nanoplates were prepared for the first time. One reason for the lack of formation of nanoplates in the previous MW-polyol methods[1–3] may be lower reaction temperatures in methanol (bp 65 °C), ethanol (78 °C) and *N*,*N*-dimethylformamide (156 °C) than that in ethylene glycol (198 °C) used in this study. We are planning to extend this technique as a new method for manipulating the shapes of polygonal Au nanoplates.

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