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Fabrication of silver nanoparticles by highly intense laser irradiation of aqueous solution

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Abstract Silver (Ag) nanoparticles were fabricated by highly intense femtosecond laser irradiation of aqueous solutions of silver nitrate ($AgNO_3$) with various concentrations. After irradiation, a broad absorption peak at around 420 nm originating from surface plasmon resonance of Ag nanoparticles was observed in 30 and 300 mM solutions. Transmission electron microscopy revealed that Ag nanoparticles produced in 300 mM $AgNO_3$ solution had a typical size in the range of 2 to 20 nm and a mean size of 4 nm. The addition of 1.0×10^{-2} wt% polyvinylpyrrolidone as a dispersant to the 300 mM solution caused a narrower particle size distribution as well as a narrower absorption peak width after the laser irradiation. As a result, Ag nanoparticles with a mean particle size of about 2 nm were fabricated.

1 Introduction

Noble metal nanoparticles have been intensively studied due to their unique optical, electrical, and catalytic properties. Among them, silver (Ag) nanoparticles are one of the most popular catalysts for oxidation of ethylene [1] and have higher electrical and thermal conductivities than other nanoparticles. Moreover, silver has strong inhibitory and bactericidal effects, and a broad spectrum of antimicrobial activities; these properties have been exploited for a long time to prevent and treat a wide variety of diseases [2–5].

The main method for preparing Ag nanoparticles is a reduction process using reducing agents such as hydrazine (H_2NNH_2), sodium borohydride ($NaBH_4$), and dimethyl formamide ($(CH_3)_2NCHO$, DMF). These chemicals are highly reactive and hence give rise to environmental and biological problems [6–9]. In recent years, a more environmentally friendly process has been developed that involves laser ablation of a solid metal target immersed in a solution [10–15]. This method has been used to fabricate Ag nanoparticles in solution with no chemicals except for a dispersant [15]. However, it produces large particles (known as debris) with a broad size distribution. Although a melting and fragmentation process applying additional laser irradiation was effective to reshape and resize the debris, this process was essentially a two-step synthesis.

As an alternative approach, we have reported a method for preparing stable gold [16] and platinum [17] nanoparticles with no reducing agent by highly intense laser irradiation of metal salt solutions containing a suitable dispersant. This method enables us to produce metal nanoparticles with both narrow size distribution and particle size down to 2 nm. While oxidation of metals is generally a problem in material processing in water, silver (like gold and platinum) is not oxidized in water since it has a higher free energy than water in the Ellingham diagram.

In this study, we fabricate Ag nanoparticles by highly intense laser irradiation of aqueous solutions of silver nitrate. The effects of the silver nitrate concentration and the addition of a dispersant on the production efficiency and Ag nanoparticle size are investigated.

2 Experimental

Silver aqueous solutions with concentrations of 0.3, 3, 30, and 300 mM were prepared by dissolving silver nitrate

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($AgNO_3$, Wako Pure Chemical Industries, Ltd., >99.9%) in ultra-pure water. All the solutions were transparent. Figure 1 shows UV-visible absorption spectra of these silver nitrate solutions obtained using a UV-visible spectrophotometer (Jasco Co., V630 iRM). The absorption peaks at around 310 nm are due to nitrate ions in the solution. Figure 2 shows a schematic representation of the experimental setup. A $10 \times 10 \times 45\ \mathrm{mm}^3$ quartz glass cuvette, which was optically transparent at the laser wavelength, was filled with 3 ml of the aqueous solutions. Highly intense femtosecond laser pulses (wavelength: 800 nm; pulse energy: 6 mJ; pulse width: 100 fs; repetition rate: 10 Hz) were generated by a chirped-pulse amplified Ti:sapphire laser. The laser beam was introduced normal to an aspherical lens (focal length: 8 mm; numerical aperture: 0.5), which is set just before the cuvette, and tightly focused inside the solution. The spot diameter was estimated to be 175 μm. The laser intensity was theoretically estimated to be $2.1 \times 10^{14}\ \mathrm{W/cm}^2$. The irradiation time was 45 min in all experiments. The optical characteristics of the solutions after irradiation were evaluated using the UV-visible spectrometer. Transmission electron microscopy (TEM; JEOL, JEM2000EXII) micrographs of the products were obtained after laser irradiation. TEM samples were prepared by dropping the solution on a carbon-coated copper grid (Okenshoji Co., Ltd., microgrid B) immediately after irradiation and then drying them in air. The particle size and size distribution were obtained by measuring the particle diameter in the TEM micrographs.

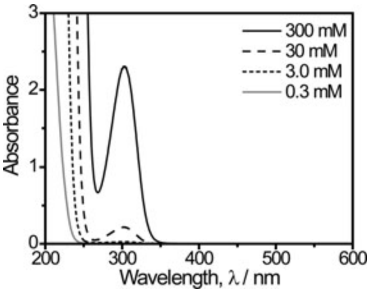
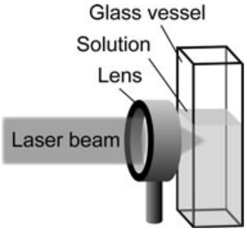


Fig. 1 UV-visible absorbance spectra of aqueous solutions of silver nitrate with concentrations of 0.3, 3.0, 30, and 300 mM

Fig. 2 Schematic representation of the experimental setup

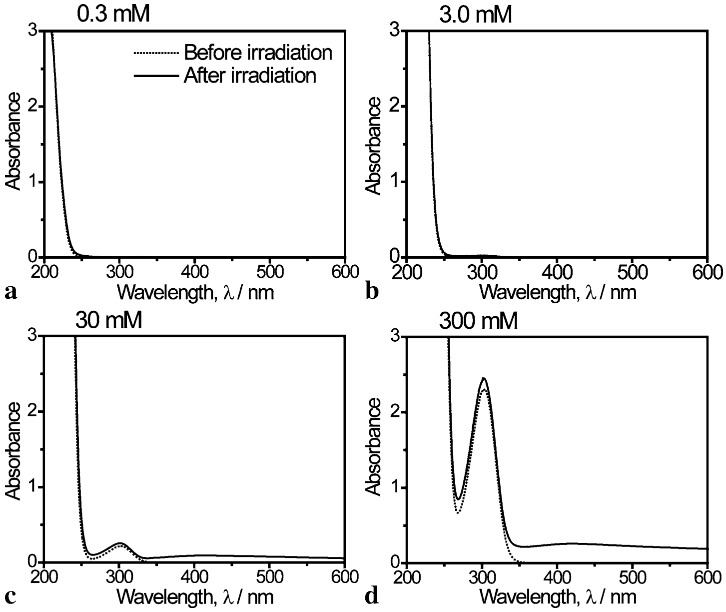


3 Results and discussion

When the solutions were irradiated by femtosecond laser pulses, a tiny plasma flash was observed and fine bubbles were generated near the focus. The bubbles were identified as hydrogen and oxygen by chromatographic analysis (Shimadzu Co., GC-8A), indicating the decomposition of water molecules by the highly intense laser field [18]. No visible changes were observed during the irradiation except for the 300 mM solution, which turned light gray after irradiation. In the 300 mM solution, a black precipitate appeared on the bottom of the cuvette one day after the laser irradiation. This precipitate seemed to be formed by the agglutination of silver particles fabricated by the laser irradiation.

Figure 3 shows the UV-visible absorption spectra of the $AgNO_3$ aqueous solutions before (dotted lines) and after

Fig. 3 UV-visible absorbance spectra of aqueous solutions of silver nitrate salt with concentrations of (**a**) 0.3, (**b**) 3.0, (**c**) 30, and 300 mM after laser irradiation (*solid curves*). Spectra of the solutions before irradiation (*dotted curves*) are also indicated in each figure for comparison



(solid lines) irradiation for 45 min. The spectra of the 0.3 and 3.0 mM $AgNO_3$ solutions are the same before and after irradiation. In contrast, a weak but broad absorption peak near 420 nm is visible in the spectra of the 30 and 300 mM solutions. This peak wavelength indicates the surface plasmon resonance (SPR) of Ag nanoparticles and its broadness implies that the scattering is caused by a small number of large particles simultaneously formed in the solution (see discussion below).

To ensure that the silver particles remain dispersed, 0.01 wt% polyvinylpyrrolidone (PVP, Merck), which is a commonly used dispersant for metal colloids, was added to the 300 mM $AgNO_3$ aqueous solution. This PVP concentration was found to give good dispersibility for both gold and platinum nanoparticles in our previous studies [16, 17]. After a certain irradiation time, the $AgNO_3$ solution containing PVP changed from transparent to yellow. The solid curve in Fig. 4 shows the UV-visible absorption spectrum of the 300 mM $AgNO_3$ solution containing 0.01 wt% PVP after irradiation, while the broken curve shows the spectrum of the $AgNO_3$ solution without PVP after irradiation. The absorption peak at around 420 nm due to the SPR of Ag nanoparticles [19, 20] became sharp and the tail in the longer-wavelength region was suppressed. This result strongly indicates that the addition of PVP reduces the particle size and makes the size distribution narrower.

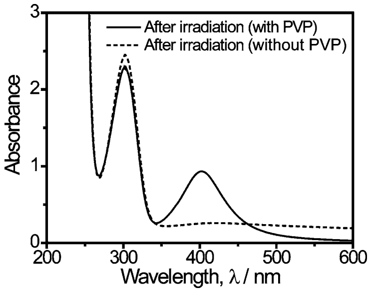


Fig. 4 UV-visible absorption spectrum of aqueous solution of 300 mM silver nitrate with 0.01 wt% PVP after irradiation (with PVP, *solid curve*). The absorption spectrum of the solution without PVP after irradiation (no additives, *broken curve*) is also shown for comparison

Figure 5 shows TEM micrographs and corresponding particle size distributions obtained by estimating the particle diameters from the TEM images. It also shows the mean sizes and standard deviations of the particles. These micrographs and profiles were obtained for $AgNO_3$ solutions without PVP (Fig. 5a) and with 0.01 wt% PVP (Fig. 5b). Selected-area electron diffraction (not shown) revealed that the particles in the bright-field images are silver. The silver particles formed in the solution without PVP (Fig. 5a) had a relatively broad size distribution. The particles may agglomerate during and/or after irradiation. In contrast, the mean particle size was small and the size distribution of the particles was narrow in the solution with 0.01 wt% PVP (Fig. 5b). This result is consistent with the UV-visible spectra of the solutions shown in Fig. 4. Namely, the increase in the number of small silver particles is attributed to the sharp peak of SPR. Moreover, the spectral broadening due to scattering by large particles is diminished. Silver nanoparticles stabilized with PVP have an average particle size of nearly 2 nm, which is similar to those of gold and platinum nanoparticles [16, 17].

The formation of Ag nanoparticles in the absence of any reducing agent can be attributed to the strong reducing species (i.e. solvated electrons and free radicals) generated by highly intense laser irradiation of the solution,

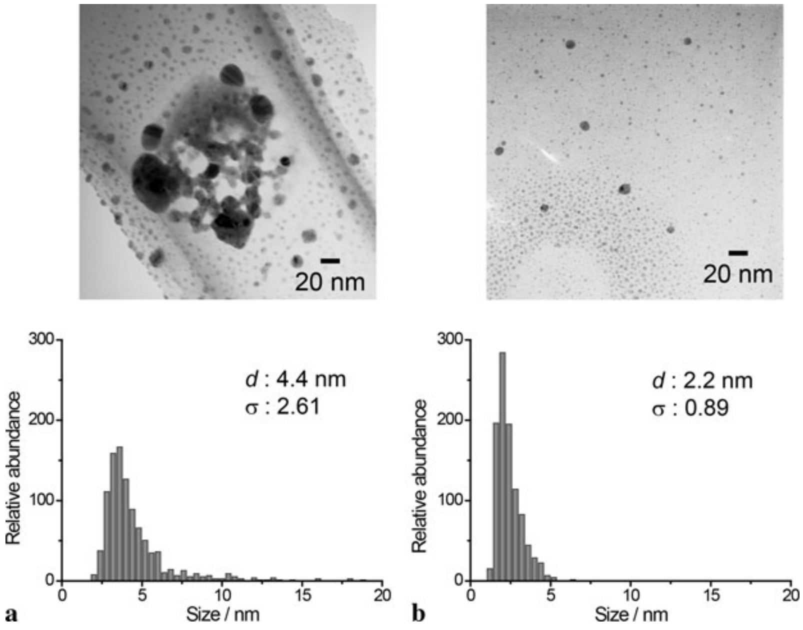


Fig. 5 TEM images obtained from samples prepared by a drop of a solution (**a**) without PVP and (**b**) with 0.01 wt% PVP (*upside*), and the corresponding size distribution profiles of particles obtained by measuring the diameter of particles in the micrographs (*downside*)

as proposed for radiolytic reduction [21, 22] and the solution plasma method [23]. Solvated electrons (e^-_{aq}) and hydrogen radicals ($\mathrm{H}^{\bullet}$), which are strong reducing agents ($E^{\mathrm{o}}(\mathrm{H_2O}/e^-_{\mathrm{aq}}) = -2.87$ V and $E^{\mathrm{o}}(\mathrm{H^+/H}) = -2.87$ V), are produced from water molecules:

$$\mathrm{H_2O} \rightarrow e^-_{\mathrm{aq}}, \mathrm{H}^{\bullet}, \mathrm{OH}^{\bullet}, \text{etc.} \tag{1}$$

The strong absorption at around 300 nm in Fig. 2 is caused by nitrate ions. The intense optical field generated in the experiment may be strong enough to induce photolysis of water and hence the production of solvated electrons and hydrogen radicals in the solution. The generation of oxygen and hydrogen near the focus during the laser irradiation by optical decomposition of water [18] indicates the presence of hydrogen and hydroxyl radicals ($\mathrm{OH}^{\bullet}$) in the solution. The solvated electrons and hydrogen radicals act as strong reducing agents in the solution. Therefore, silver ions in the solution are readily reduced to Ag^0:

$$\mathrm{Ag}^+ + e^-_{\mathrm{aq}} \rightarrow \mathrm{Ag}^0, \tag{2}$$

$$\mathrm{Ag}^+ + \mathrm{H}^{\bullet} \rightarrow \mathrm{Ag}^0 + \mathrm{H}^+. \tag{3}$$

When the silver particles become several nanometers in size, most of the atoms generated by the laser irradiation have been expended, so that particle growth terminates. PVP suppressed crystal growth and agglomeration during this process.

4 Conclusion

We fabricated Ag nanoparticles using a highly intense optical field produced by tightly focused femtosecond laser pulses in a solution of silver nitrate. This technique is simple and environmentally friendly because it does not use any chemicals except for a metal salt and a dispersing agent. This technique differs from other laser processes such as the formation of Ag nanoparticles by pulsed laser ablation of a solid-state silver target immersed in a liquid. Furthermore, it can be applied to binary and ternary component systems in solution in addition to a single-component system. In other words, laser irradiation of a liquid has the potential to synthesize metallic alloy nanoparticles with controllable size and size distribution.

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