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Morphological changes from spherical silver nanoparticles to cubes after laser irradiation in acetone–water solutions via spontaneous atom transportation process

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ABSTRACT

Morphological changes were studied in spherical silver nanoparticles (NPs) prepared using laser ablation of silver plates in an acetone–water mixed solution after laser irradiation. When reagent solutions were left for 1–14 days after laser irradiation, Ag nanocrystals (NCs) involving cubes formed spontaneously. Results show that laser irradiation and acetone are unnecessary for cube formation, but they enhance the cube formation efficiency because of the spherical NP size reduction. These findings suggest that cube formation occurs via an atom transportation process resembling that which occurs in the ripening process of NPs prepared using chemical reduction methods.

1. Introduction

Morphological changes of colloidal nanoparticles (NPs) caused by laser irradiation (LI) attract a great amount of attention because of LI's potential for use as a convenient morphology control technique for NPs. Typical morphological changes by LI are NP fragmentation caused by LI at high intensity [1–4], and NP fusion caused by LI at moderate intensity [5,6]. As an example of the latter case, the formation of submicrometer-sized spherical particles via NP fusion was identified very recently [7–9]. Fundamentally, these morphological changes result in the formation of only size-increased or size-decreased spherical particles, and their mechanism is explainable in terms of laser heating of NPs, causing phenomena such as melting and vaporization.

On the other hand, we have found another type of laser-induced morphological change that results in the formation of non-spherical particles and has a mechanism that is difficult to be explained by laser heating of NPs. Results of our previous studies showed that Ag NPs with crystalline shapes such as nanoplates (hereinafter, we designate an NP with a crystalline shape as an NC) were formed after LI for Ag NPs in pure water [10] and in Ag NPs in polyvinylpyrrolidone (PVP) aqueous solutions [11]. It is difficult to assume that the NCs would be formed during LI because the laser intensity used to conduct those studies was sufficiently high to decompose the well-faceted structures of the NCs [12]. In one earlier report [11], we proposed that the Ag NC formation would occur after LI. In that study, however, further investigation of the transformation of Ag NPs after LI was insufficient.

Metallic NCs such as nanoprisms, nanocubes, and nanorods are interesting because of their characteristic optical properties arising from the multiple localized plasmon modes. In general, NCs are prepared using chemical reduction methods with complex crystal-growth-control techniques such as the use of seed NPs for epitaxial crystal growth, and the use of capping agents that restrict crystal growth orientation [13–18]. If the NC formation induced by LI would become more controllable, then a more convenient NC preparation method might be developed. In addition, when NPs prepared using laser ablation in liquids technique (LAL) are used as a source of NCs, one can investigate the influences of minimum substances (NPs, solvent, and one species of stabilizing reagent) in the solution on the NC formation. The absence of unnecessary substances enables us to clarify the role of each factor in the NC formation, which is also expected to be useful for shape control when using chemical methods. For these reasons, investigating NC formation induced by LI is important.

This study investigated shape changes of spherical Ag NPs in acetone–water mixed solutions after they were laser-irradiated and left for 1–14 days. Results showed that monodispersed Ag nanocubes were formed in high yields. Effects of laser irradiation, solvents, and leaving times were examined to obtain information related to the roles of these experimental parameters. The possible spontaneous growth mechanism of Ag cubes after laser irradiation in acetone–water mixed solutions is

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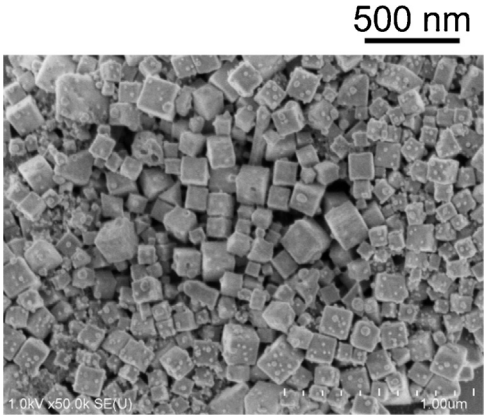

Fig. 1. SEM image of Ag nanocubes formed in Ag NPs in a 25% acetone–water solution. The Ag NPs were prepared using a combination of laser ablation of an Ag plate in an aqueous solution of 25% acetone and supplemental laser irradiation for colloids generated by laser ablation followed by leaving the solution as it is for 10 days.

discussed.

2. Experimental

Ag NP colloids used for this study were prepared using a procedure similar to that used to prepare Ag NPs and to modify their size [11,19]. As the first step, LAL was conducted for a piece of silver plate (10 × 10 × 0.5 mm, 99.9%; The Nilaco Corp.) set in 10 mL of 25% acetone aqueous solution using a focused laser beam of a nanosecond pulse Nd:YAG laser (GCR-200; Spectra Physics) at 1064 nm to generate Ag NPs. The laser pulse width, the laser pulse repetition rate, laser fluence, and LAL duration were, respectively, 10 ns, 10 Hz, 90 J/cm^2, and 10 min. Acetone was used to stabilize Ag NP colloids. The largest amounts of Ag NPs were obtained in 25% acetone aqueous solutions among 25%, 50%, 75%, and 100% acetone solutions (see Fig. S1 in Supporting Information (SI)). In addition, the amount of Ag NPs in a 25% acetone aqueous solution was greater than those contained in the colloidal solutions used in the previous study [11] (see Fig. S1 in SI). As the second step, the silver plate was removed from the colloidal solution after LAL. Then LI for the colloidal solution was applied using a non-focused laser beam of a nanosecond pulse Nd:YAG laser (GCR-100; Spectra Physics) at 355 nm. The laser pulse width, the laser pulse repetition rate, laser fluence, and LI duration were, respectively, 6 ns, 10 Hz, 80 mJ/cm^2, and 30 min. To observe the morphological changes of Ag NPs after preparation, a 50 mL of Ag NP colloidal solution was prepared using the procedure described above and was settled in a dark condition at room temperature. Then 5 mL of the colloidal solution was sampled at each sampling time and was centrifuged (3000g × 30 min) to condense the Ag NPs. The Ag NP shape was observed using a scanning electron microscope (SEM, SU8000; Hitachi Ltd.) and a transmitted electron microscope (TEM, EM-02B; JEOL). The UV–vis spectra of the Ag NPs were obtained using a UV–vis spectrometer (UV-2450; Shimadzu Corp.).

3. Results and discussion

Fig. 1 portrays an SEM image of products obtained from our first experiment in which LI was carried out for Ag NPs prepared using laser ablation in a 25% acetone–water mixed solution and the colloidal solution was left for 10 days after LI. It is noteworthy that cubic Ag NCs with edge lengths of 50–200 nm were formed. Although this phenomenon resembles the Ag NC formation observed in earlier studies [10,11], the amount of cubic Ag NCs observed here was apparently significantly larger than that in the previous studies, probably because this colloidal solution contained a larger amount of Ag NPs than that used in earlier studies. Because of the larger Ag NC amount, we can investigate morphological changes of Ag NPs more precisely to obtain information related to the Ag NC formation mechanism.

Fig. 2a and b respectively portray TEM images of the source Ag NPs in a 25% acetone–water solution obtained using LAL (within 1 h) and (b) after LI (within 1 h). The average diameter of Ag NPs (Fig. 2a) prepared using LAL was 25 nm. After LI at 80 mJ/cm^2 for 30 min (Fig. 2b), the average diameter of Ag NPs was reduced to 11 nm, indicating that Ag NP fragmentation was brought about by LI in these conditions. Only spherical Ag NPs were obtained. No NC with well-defined facets was formed with these timings.

The fact that no NC was observed in Ag NPs sampled within 1 h after LAL and LI indicates that Ag NCs presented in Fig. 1 were formed after LI. Because Ag nanocubes presented in Fig. 1 were found in Ag NPs sampled at 10 days after LI, we monitored the morphological changes of the Ag NPs after LI between 1 and 14 days. Fig. 3 presents SEM images of Ag NPs in 25% acetone–water solutions sampled at 1, 3, 7, and 14 days after LI. As depicted in Fig. 3a, a small amount of Ag NPs with flat facets was found in Ag NPs sampled in 1 day (ca. 6 h). In Ag NPs sampled at or after 3 days (Fig. 3b–e), more distinctive Ag NCs with various shapes were observed. Ag nanocubes with {100} facets were also contained in the samples (e.g., Fig. 3e), although the Ag nanocube

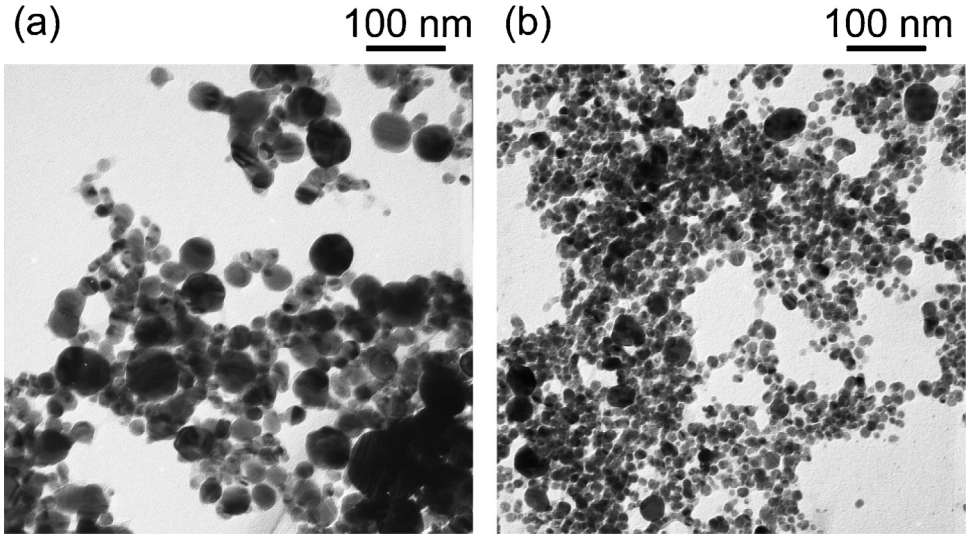

Fig. 2. TEM images of Ag NPs in a 25% acetone–water solution (a) after preparation using laser ablation (within 1 h) and (b) after supplemental laser irradiation (within 1 h). The average diameters of the Ag NPs are (a) 25 and (b) 11 nm.