

Laser-induced morphology changes of silver colloids prepared by laser ablation in water

Enhancement of anisotropic shape conversions by chloride ions

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Abstract

Laser-induced morphology changes of silver nanoparticles were investigated by using silver colloids prepared by laser ablation in water. In the previous study, we have reported that nanoprisms and nanorods were formed by laser irradiation onto spherical silver nanoparticles. In the present study, we have revealed that shape conversions producing crystal-shaped particles including nanoprisms and nanorods were enhanced when NaCl was added into silver colloidal solution. In addition, it was found that formation of crystal-shaped particles was observed under fluorescent light irradiation onto silver colloidal solution containing NaCl. The effect of NaCl on the shape conversions of silver nanoparticles was explained in terms of the oxidative etching of silver nanoparticles by chloride ions followed by photo-reduction of the silver ions.

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1. Introduction

Since various properties of metal nanoparticles strongly depend on their morphology (size and shape) [1,2], significant effort have been made to control morphology in colloid synthesis. Particularly, recent researches on colloid synthesis are strongly aiming at producing anisotropic shapes because of their further characteristic optical and electronic properties differing from spherical particles. By a chemical reduction method using metal salts, it has recently been reported that various species of nanoparticles with anisotropic shapes such as nanoprisms, nanorods, and nanocubes has been successfully prepared by using as a capping agents such as poly(vinylpyrrolidone) [3–5].

Photo-irradiation onto already-prepared metal nanoparticles has been interested as an alternative approach to control morphology of nanoparticles using a simple procedure. At the first time, laser has been used as the irradiation light source due to its high photon-flux. It has been demonstrated that laser irradiation onto gold or silver nanoparticles dispersed in aqueous solution induced fragmentation or fusion of the colloidal nanoparticles

[6–10]. The photo-thermal dynamics involved in these processes has been also extensively investigated [11–14]. However, the shape of the produced nanoparticles was almost spherical whatever the shape of the original nanoparticles.

Recently, Jin et al. [15,16] and Callegari et al. [17] reported another type of the photo-induced morphology changes. They demonstrated that irradiation of fluorescent light induced the shape conversion of spherical silver nanoparticles into nanoprisms [16,17]. They also showed that size of the nanoprisms could be controlled by wavelength of irradiation light. These findings indicate that anisotropic shape control is also possible by using the photo-irradiation method. On the other hand, the mechanism of the morphology changes has not been clarified. Jin et al. [15] proposed that nanoprisms were produced from silver clusters formed by photo-fragmentation of spherical nanoparticles, and Callegari et al. [17] proposed that the shape conversion was caused by photo-induced aggregation of spherical nanoparticles.

It must be noted that the source colloids used in above researches were chemically synthesized and containing various reagents which must be attached on the surface of particles. Thus, the shape of the products could be affected by these reagents. On the other hand, we have very recently carried out laser irradiation onto silver colloids which were prepared by

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laser ablation in pure water [18,19]. Since the pioneering work by Fojtik and Henglein [20], it has been demonstrated that colloidal particles obtained by using laser ablation in pure water possess pure surface [21–30]. Various new phenomena of the morphology changes were observed as a result of irradiation of laser light at 355 nm onto silver colloids in pure water. At laser intensity larger than 150 mJ/cm^2 , particles with wire- and sheet-structures were produced [18]. These structures must be produced via fusion of spherical particles, because their shapes were irregular and their formation efficiency increased with laser intensity. Mafuné et al. also reported similar results [31]. On the other hand, at laser intensity from 50 to 100 mJ/cm^2 , we have found that crystal-shaped particles such as nanoprisms and nanorods were produced [19], while the formation efficiency was low. The latter phenomenon must be related with those reported by Jin et al. [15,16] and Callegari et al. [17], and indicates that further morphology control will be possible by using the photo-irradiation method. Thus, we have carried out further investigation of the photo-induced shape conversions producing crystal-shaped silver particles including nanoprisms and nanorods to clarify its mechanism and to make more precise control of shape conversions.

In this paper, we report effects of chloride ions. We have found that NaCl enhanced formation of crystal-shaped particles under laser irradiation. We have also found that nanoparticles with crystal-shaped particles were formed under fluorescent light irradiation with NaCl.

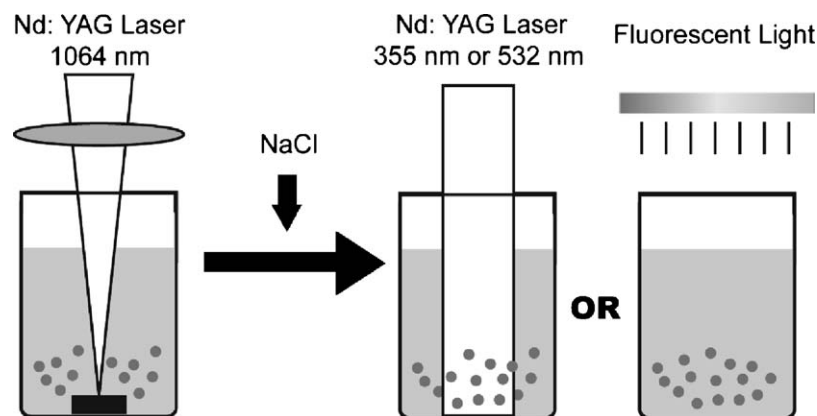
2. Experiment

Experimental procedure is illustrated in Scheme 1. Preparation of source silver nanoparticles dispersed in pure water was carried out by using the laser ablation technique. A silver plate (Nirako 99.99%) immersed in deionized water (5 mL) was ablated by focused 1064 nm light of a pulsed Nd:YAG laser (Spectra Physics GCR100) operated at 10 Hz. The laser intensity and irradiation time was 36 J/cm^2 and 10 min, respectively. Spherical particles with 10–100 nm of diameter were prepared by using laser ablation in pure water (Fig. 1a and b). After preparation of silver colloidal solution, the silver plate was removed and secondary irradiation of laser or fluorescent light onto the

colloidal solution was carried out. For laser irradiation, non-focused 355 or 532 nm light of the Nd:YAG laser was used. The intensity of the second irradiation laser light was adjusted at 50 mJ/cm^2 (10 mJ/pulse). The pulse duration and the repetition rate were 6 ns and 10 Hz, respectively. On the other hand, a convenient fluorescent tube (NEC FLR40S EX-N/M-HG) was used for fluorescent light (FL) irradiation. The light intensity at irradiation position was $5.4 \times 10^{-2} \text{ mW/cm}^2$ (546 nm). The spectrum of the FL is shown in Appendix A. In order to investigate influences of NaCl, a small amount of NaCl solution was added into silver colloidal solution just before the secondary irradiation. No significant changes were observed in the size and shape of silver colloids by NaCl when colloidal solution was settled in dark (Fig. 1c). Observations of morphology of colloidal particles were carried out by using a TEM (JEOL JEM2010EX) operated at 200 kV. TEM samples were prepared by dropping a small amount of colloidal solution onto a microgrid under dark conditions.

3. Results and discussions

Fig. 2a and b show changes in UV–vis spectra by laser irradiation at 355 nm onto silver colloids in pure water and containing 0.2 mM NaCl, respectively. By addition of 0.2 mM of NaCl in dark, no significant changes in the plasmon bands were observed, indicating that aggregation of colloidal particles caused by ions is not prominent at this concentration of NaCl. On the other hand, broadening and decreasing of plasmon bands were observed for both solutions after laser irradiation. The spectral changes were more prominent colloids in NaCl solution than those in pure water and increased with irradiation time. Although these spectral changes suggest that laser irradiation caused morphology changes and/or coalition of colloidal particles, they are not evidence for formation of significant number of nanoprisms and nanorods, because these products would show prominent plasmon peak at wavelength longer than 400 nm depending on their size [1,2]. Fig. 3 shows TEM images of silver nanoparticles in pure water and those in 0.2 mM NaCl solution after laser irradiation at 355 nm for 10 and 20 min. In colloids in pure water, changes in shape of nanoparticles by laser irradiation were not evident. Few numbers of crystal-shaped particles were observed



Scheme 1.

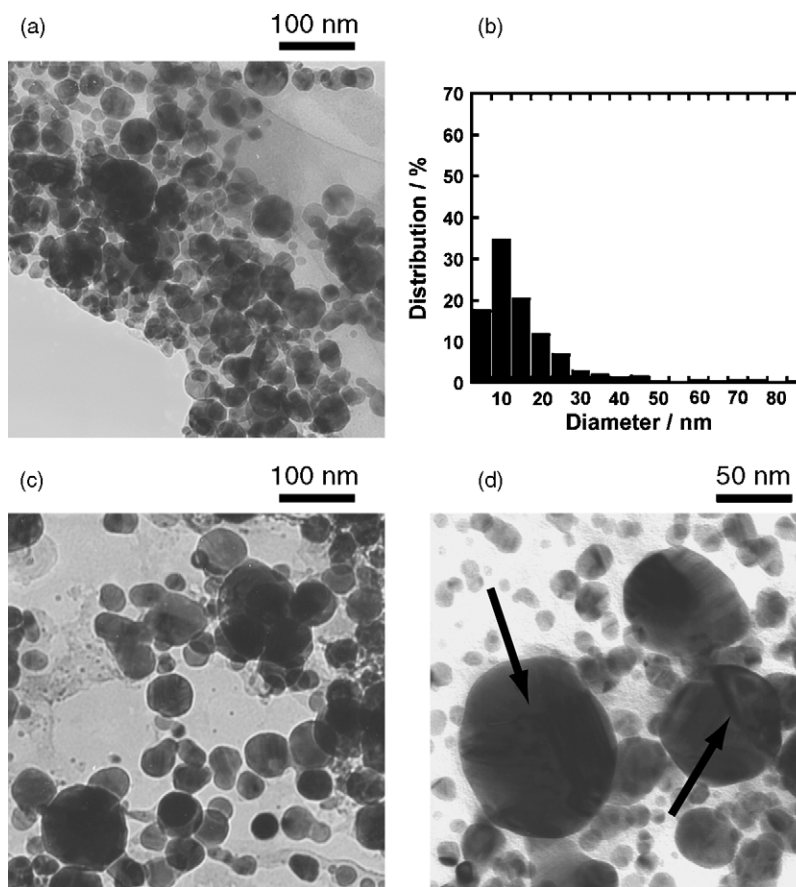


Fig. 1. TEM images of silver nanoparticles obtained by using laser ablation in water. (a) As prepared. (b) Size distribution of particles in (a). (c) After addition of 0.2 mM NaCl in dark. (d) Expand view of the source particles with non-single crystal structure. Arrows show borders of crystal surfaces (twin plane).

(Fig. 3a). In colloids containing 0.2 mM of NaCl, number of crystal-shaped particles significantly increased with irradiation time, while quantitative analysis was difficult because of the limited observation area of TEM. Nanorods (Fig. 3b), nanoprisms (Fig. 3c), and other non-spherical particles with rather irregular crystal-like shapes (Fig. 3d) could be observed. The selected area electron diffraction (SAED) patterns confirm that the crystal-shaped particles were composed of Ag (Fig. 3e). It must be noted, however, that the conversion efficiency to the crystal-shaped particles seemed much lower than that expected from the changes in the UV–vis spectra. The significant spectral changes must be mainly due to photo-induced dipole–dipole attraction

between colloidal particles [32], which should be investigated in the future.

Fig. 4 shows changes in UV–vis spectra of silver colloids containing 0.2 mM of NaCl caused by irradiation of FL light. Remarkably, significant broadening and decreasing of the plasmon bands were observed by FL irradiation, while no changes were observed in the case of colloids in pure water. By analogy with the result of laser irradiation at 355 nm, these spectral changes must be mainly due to photo-induced aggregation of nanoparticles. Fig. 5 shows TEM images of silver nanoparticles after FL irradiation for 10–30 min. No changes in the size and the shape of nanoparticles were observed for colloids in

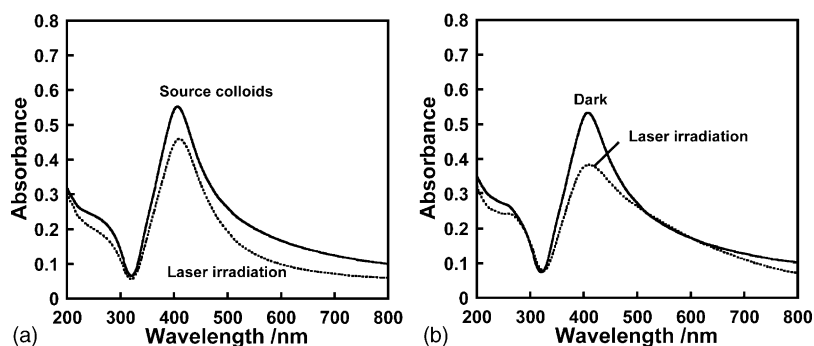


Fig. 2. Changes in UV–vis spectra of silver colloids by laser irradiation at 355 nm. (a) Colloids in pure water and (b) colloids in 0.2 mM NaCl solution. Laser intensity: 50 mJ/cm²; irradiation time: 10 min.

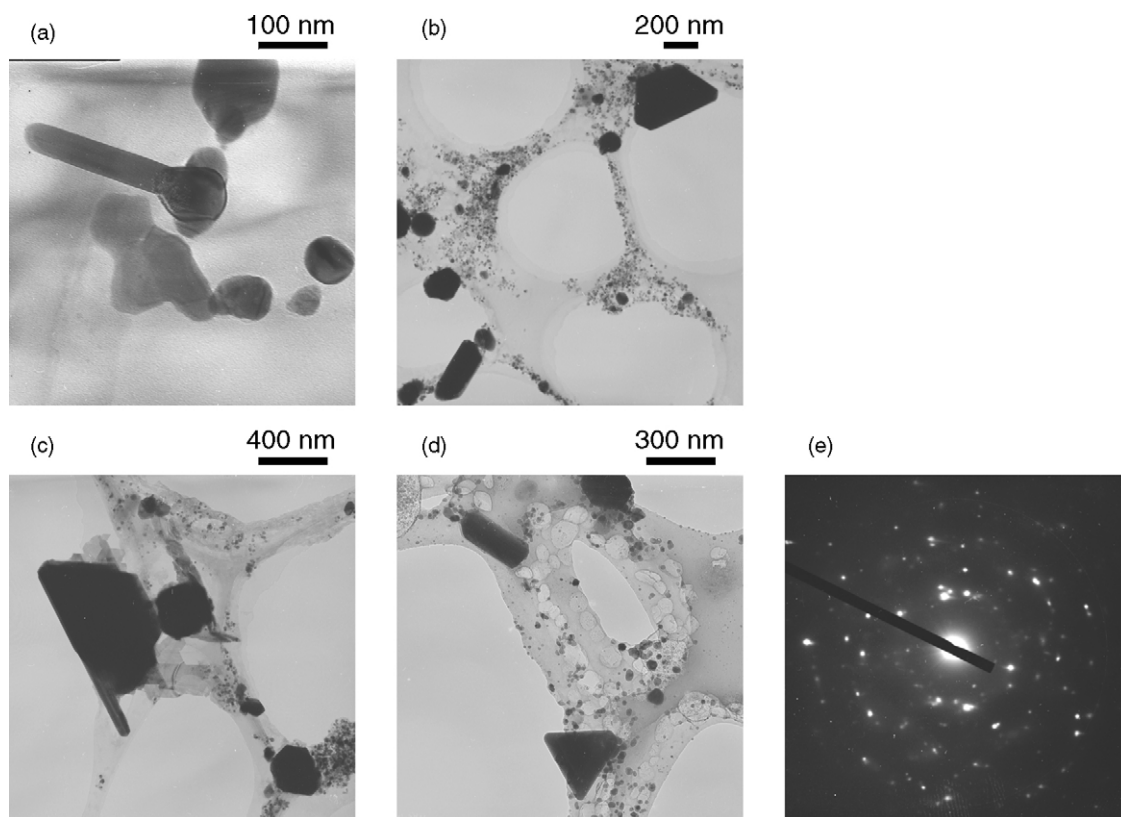


Fig. 3. TEM images of silver nanoparticles after laser irradiation at 355 nm. (a) Nanoparticles in pure water after laser irradiation for 10 min. Nanoparticles in 0.2 mM NaCl solutions after laser irradiation for (b), (c) 10 min and (d) 20 min. (e) An electron diffraction pattern of a crystal-like shape particle in Fig. 2c.

pure water, consistent with the fact that no shape conversions have been observed in colloids in pure water yet after they were placed under room light for much longer time. On the other hand, crystal-shaped particles were observed in colloids containing NaCl (Fig. 5a–d). The hexagonal SAED patterns indicates that Ag crystals are fcc single crystal (Fig. 5e).

Results of FL irradiation partially reproduced the result reported by Jin et al. [15,16] and Callegari et al. [17]. It must be notable that weak FL induces the shape conversions. Considering the fact that FL possesses spectral peak at 546 nm (see

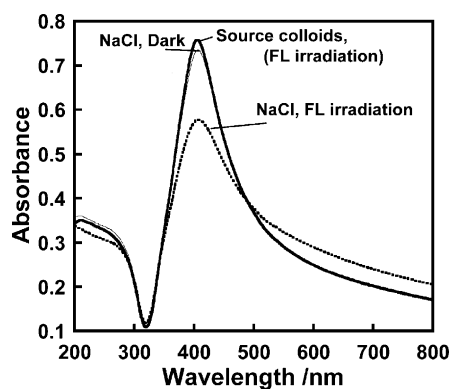


Fig. 4. Changes in UV-vis spectra of silver colloids by FL irradiation. The spectra of the source colloids and colloids after FL irradiation were identical. Light intensity: 5.4×10^{-2} mW/cm² (at 546 nm). Irradiation time: 10 min.

Appendix A), we have carried out irradiation onto silver colloids with 532 nm laser light. Few numbers of crystal-shaped particles were observed in colloids in pure water. On the other hand, number of crystal-shaped particles significantly increased (Fig. 6) in colloids with NaCl. These findings indicate that shape conversions could be occurred by laser irradiation at 532 nm. However, a quantitative comparison of the conversion efficiency between 532 and 355 nm irradiations is still difficult due to the limitations of the number of colloidal particles observed by TEM. At present, we conclude that the shape conversion efficiency was comparable for all irradiation methods examined here.

Above results of laser and FL irradiation onto silver nanoparticles clearly show that NaCl enhances shape conversions of spherical silver nanoparticles to crystal-shaped particles including nanoprisms and nanorods. Since we have used source silver colloids prepared by using laser ablation in pure water, influences of other substances such as protective reagents can be excluded. It can be ruled out that crystal-shaped particles were formed via fusion of spherical particles because of their well-ordered shapes. Furthermore, a rough estimation of temperature raised by light irradiation indicates that FL irradiation could not cause melting of silver nanoparticles. It can be also ruled out that photo-thermal heating (annealing) cause the shape transformations, because, in that case, the enhancement of shape conversion efficiency by addition of NaCl cannot be explained. At present, we assume that for the shape conversions of silver particles producing crystal-shaped particles, a series of reactions involving

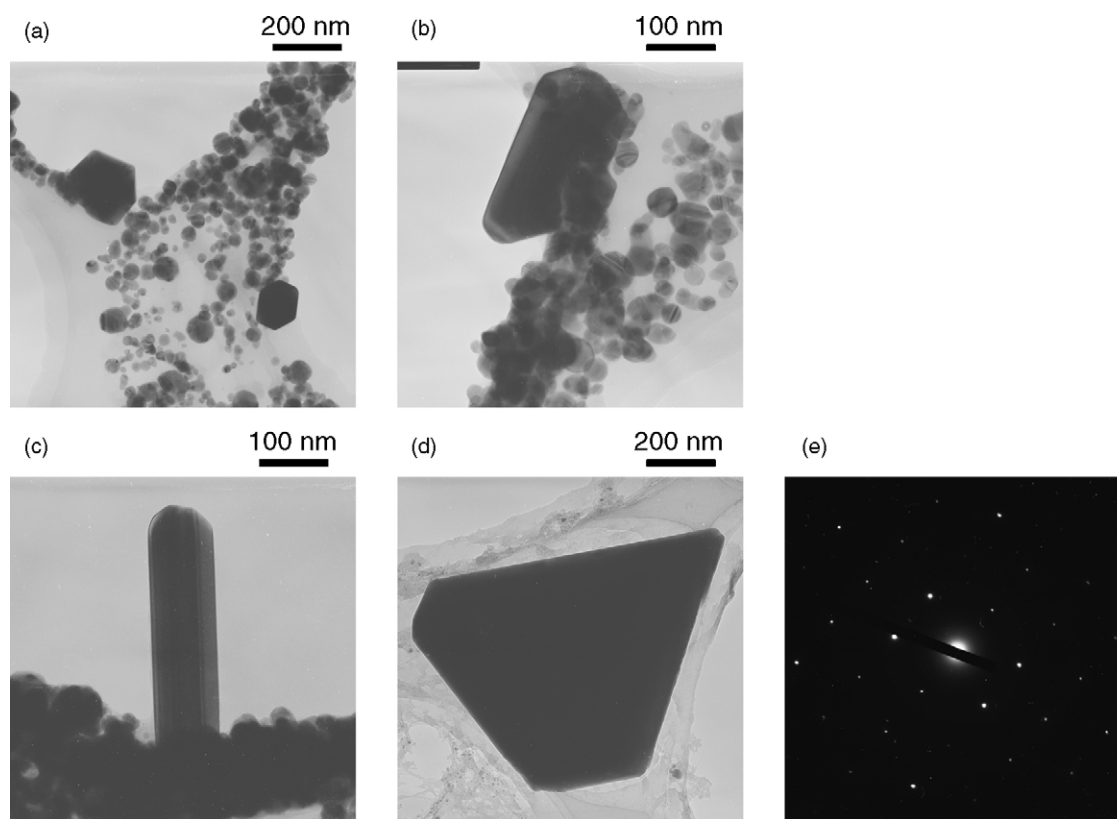


Fig. 5. TEM images of silver nanoparticles after fluorescent light irradiation. Nanoparticles in 0.2 mM NaCl solutions after laser irradiation for (a and b) 10 min and (c and d) 20 min. (e) An SAED pattern of a crystal-like shape particle in Fig. 4b.

oxidation of silver particles producing silver ions and reduction of those silver ions resulting in crystallization of silver atoms will be necessary. Thus, we propose a mechanism that is based on oxidative etching of silver nanoparticles by chloride ions followed by photo-reduction (Scheme 2).

Recently, Wiley et al. [33] demonstrated that addition of small amount of NaCl into silver colloidal solution induced dissolution of silver nanoparticles. They explained that if silver nanoparticles are composed of the twin plane, defects in the twin plane could receive oxidative etching from chloride ions in the presence of oxygen. In this context, some of silver nanoparticles

prepared by using laser ablation in water can be etched by chloride ions if they possess twin planes. Regarding to the presence of twin planes in our source silver nanoparticles, some borders of crystal structures which must involve twin planes are observed in the source nanoparticles (Fig. 1d). Such borders of crystal structures in silver nanoparticles must be created during their formation process, i.e., laser ablation in water, in which abrupt melting and cooling must occur. It is also suggested that photo-thermal heating of nanoparticles in laser irradiation must also induce transformation of a single crystal to a twinned crystal as was observed under electron beam irradiation [34]. As a result of

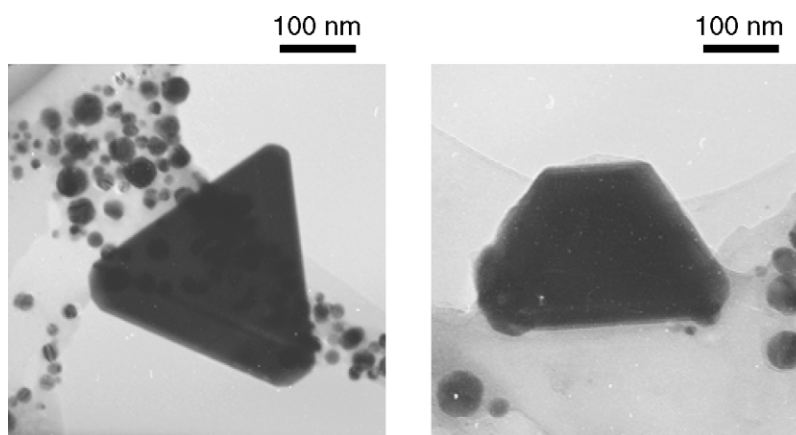


Fig. 6. TEM images of silver nanoparticles in 0.2 mM NaCl solutions after laser irradiation at 532 nm for 10 min.

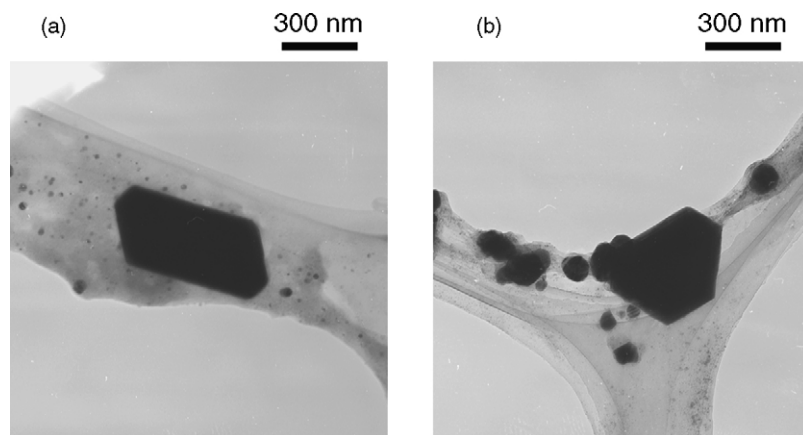
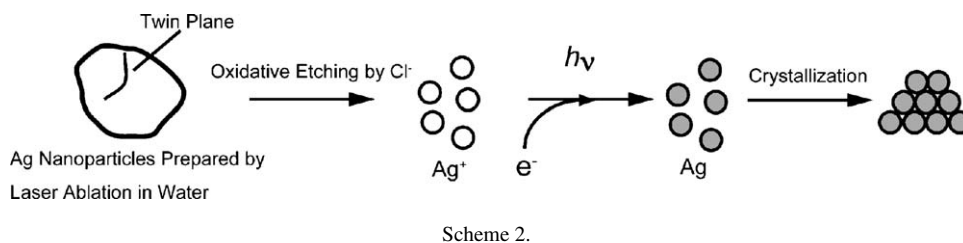


Fig. 7. TEM images of silver nanoparticles after FL irradiation onto (a) 0.2 mM KCl and (b) 0.2 mM MgCl₂ solutions.

the oxidative etching of silver particles, silver ions are produced. If those silver ions are illuminated by laser or FL light, photo-reduction of silver ions will occur and silver crystals will be formed. The main electron source of the photo-reduction process in this system must be water [35]. To confirm the roles of chloride ions, we have carried out laser and FL irradiation onto silver colloids containing 0.2 mM of KCl or MgCl₂. As shown in Fig. 7, crystal-shaped particles were formed by light irradiation in both solutions involving chloride ions, supporting the proposed mechanism. Furthermore, our preliminary result of measuring atomic absorption spectra indicates that amount of silver ions in colloidal solutions was increased by addition of NaCl. On the other hand, it must be noted that small amount of crystal-shaped particles were formed under laser irradiation even in pure water, which is inconsistent with the proposed mechanism. At present, we ascribe this phenomenon to ions containing as contamination. For example, it can be considered that Fe ions diluted from some parts of the sample holder composed of stainless steel might also induce the shape conversions of silver nanoparticles, because it has been reported that Fe(III) also causes oxidative etching of silver nanoparticles [36,37]. It must be also considered that silver oxides in the surface layer of nanoparticles [38] can be photo-oxidized resulting in formation of silver ions [39]. These reactions must be also investigated by future studies. In addition, above considerations of the effect of etching might provide some insights for the shape conversions from spherical particles to nanoprisms shown by Jin et al. [15,16] and Callegari et al. [17], where nanoprisms were more efficiently produced. While they added no chlorides into their colloids, they prepared the original silver colloids by using borohydrate reduction of AgNO₃. Thus, it can be suggested that some of sub-products may cause etching or

oxidation of unstable crystal surfaces of silver spherical particles, although we have no evidence for such a mechanism at present.

In addition to the consideration about the source of the crystal-shaped particles, we should also consider what factors control growth direction of silver crystals. No reagents which can arrange growth direction of silver atoms as polymers and surfactants do so are contained in our system. A possible mechanism is effect of surface plasmon excitation. Jin et al. [15,16] and Callegari et al. [17] proposed that excitation of surface plasmon activates or deactivate specific surfaces of silver nanoprisms. Maillard et al. [40] reported that shape of silver nanoparticles produced by photo-reduction of silver ions with citrates and seed silver nanoparticles strongly depended on excitation wavelength. They proposed that excitation of specific plasmon excitation determines growth direction. In order to clarify roles of plasmon excitation, further precise examinations using various wavelengths and analysis of the crystal structures of these particles must be necessary. For such investigation, colloids obtained by laser ablation in liquids must be a proper system because of their simple composition.

4. Conclusions

We have carried out laser and FL irradiation onto silver colloids prepared by using laser ablation in water. We have found that formation of crystal-shaped particles such as nanoprisms and nanorods were enhanced by addition of NaCl. This phenomenon was explained in terms of the oxidative etching of silver nanoparticles by chloride ions followed by photo-reduction. This procedure must be a new technique to control structures of nanoparticles using minimum chemical reagents. In order to

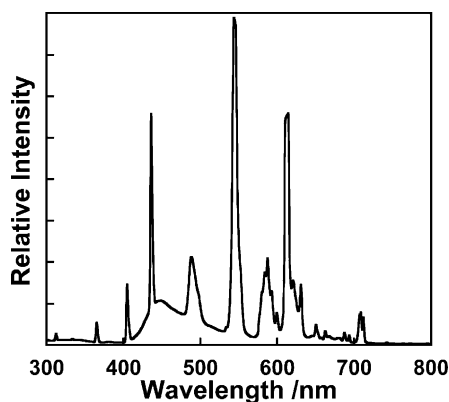


Fig. A.1. Spectrum of the FL used for irradiation.

utilize this technique, further studies for more precise and more efficient shape controls must be performed.

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Appendix A

See Fig. A.1.

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