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Photo-induced morphological conversions of silver nanoparticles prepared using laser ablation in water—Enhanced morphological conversions using halogen etching

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Abstract

Our previous report showed that chloride ions enhanced photo(laser and fluorescent-light)-induced morphological conversions of silver nanoparticles prepared using laser ablation in pure water, in which spherical particles were converted to crystal-shaped nanoparticles such as nanoprisms or nanorods. In the present study, we investigated the morphological conversion of nanoparticles in iodide solutions and that of smaller nanoparticles in chloride solutions. In addition to the formation of crystal-shaped particles in photo-irradiated conditions, marked morphological changes in the dark conditions were observed in these solutions, which was different from the results of the previous study. Besides, the formation of AgI and $AgCl_2^-$ was also detected. These findings confirm that halogen etching of silver plays a critical role in the morphological conversions. Photoirradiation at various wavelengths was also carried out to investigate the role of the photoirradiation. The formation of the crystal-shaped particles that occurred even by long wavelength (700 nm) irradiation indicates that the photoirradiation might control the interaction between silver atoms and the nanoparticle surface via electronic field excitation rather than the reduction rate of silver ions.

Keywords: Nanoparticles; Silver; Laser ablation; Photoirradiation; Chlorides; Iodides; Morphological conversion

1. Introduction

Shape control of metal nanoparticles, particularly the synthesis of nonspherical particles, has received much attention because various properties of metal nanoparticles depend strongly on the particle shape. For example, gold nanorods exhibit two prominent absorption bands around 500 and 800 nm, which are the results of the transverse and longitudinal surface plasmon modes, respectively; and the position of the latter absorption band changes sensitively with their length [1,2]. Remarkable success in the shape control of nanoparticles has been demonstrated recently using chemical synthesis techniques [3,4]. Various interestingly shaped particles have been produced controlling experimental conditions such as temperature and using adducts such as polymers [5], surfactants [2], and oxidative reagents [6,7].

Photoirradiation for nanoparticles has also been used to control particle shape. Many studies have demonstrated that strong laser light irradiation for metal colloids causes fragmentation or fusion of the colloid particles, thereby increasing or decreasing the particle size [8–13]. Although this simple technique is useful to control the nanoparticle size, unfortunately, the shape of the nanoparticles obtained by laser irradiation is spherical, regardless of the source particle shape.

On the other hand, it was recently reported that silver nanoprisms were produced from spherical nanoparticles in aqueous solutions using weak fluorescent-light irradiation [14,15]. It was also shown that the nanoprism size increased with increased irradiation wavelength [16]. These findings showed that the photoirradiation technique has potential to become an alternative shape control method of nanoparticles, because if it is developed, this technique will show a great advantage over chemical synthesis methods due to its simple procedure. However, the

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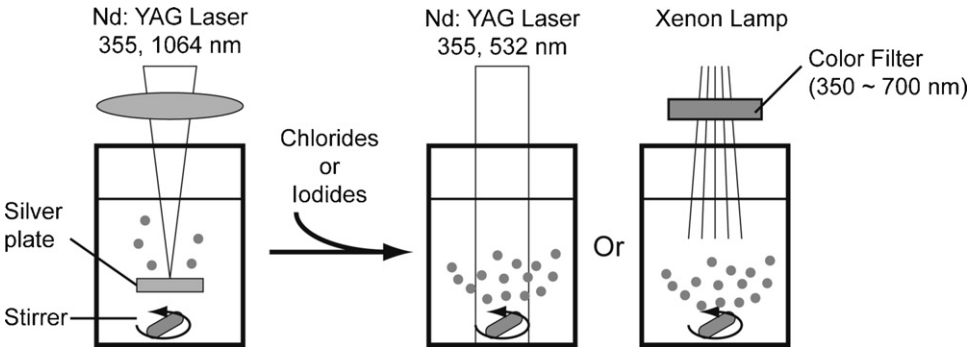


Scheme 1.

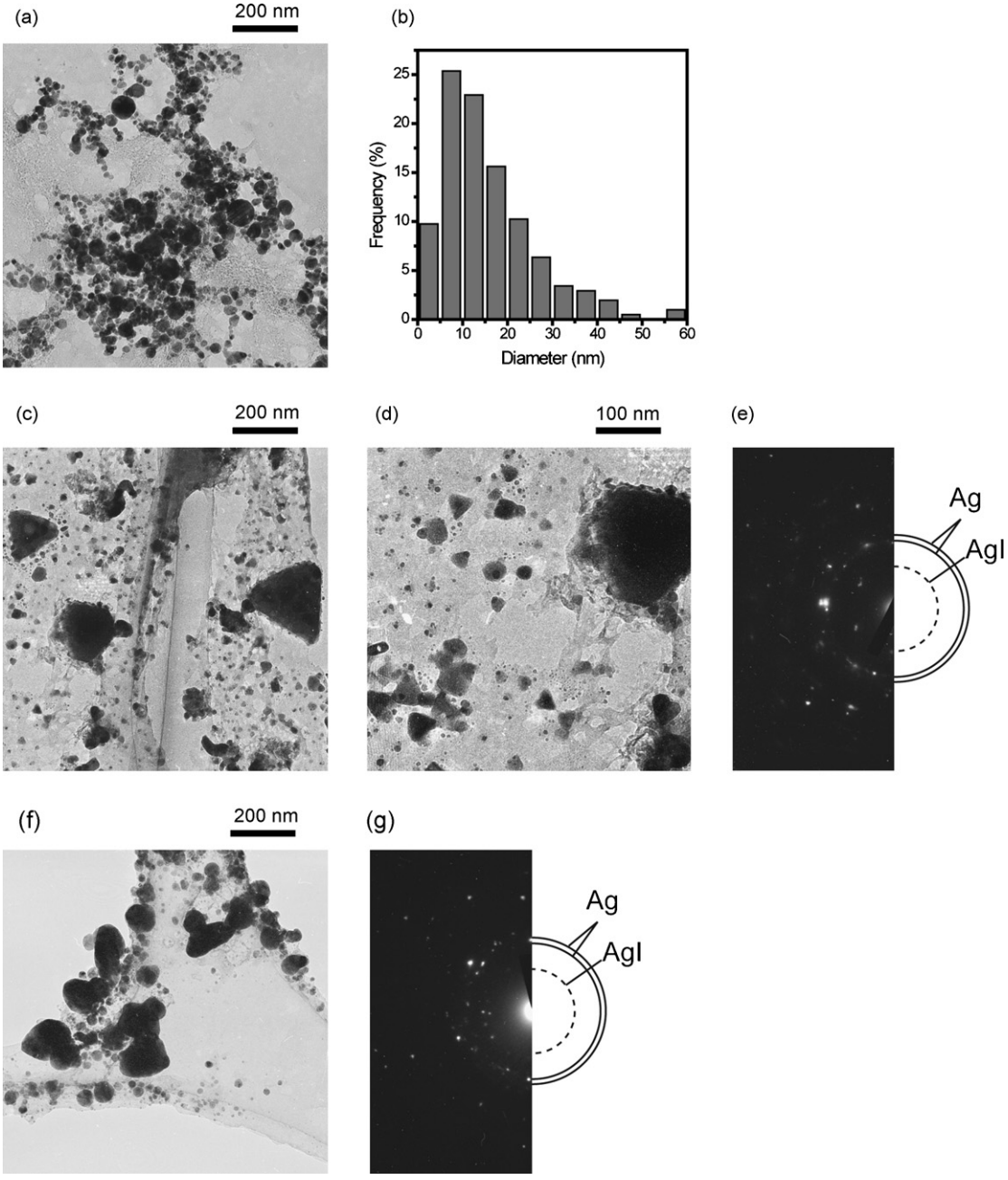


Fig. 1. Morphological changes of silver nanoparticles by iodides. (a) Source colloids prepared using 1064-nm laser ablation in neat water. (b) The size distribution of the source colloids. The average diameter and the standard deviation were 16 and 13 nm, respectively. (c) Crystal-shaped particles obtained by laser irradiation at 355 nm at 500 mW/cm^2 for 10 min with 0.2 mM NaI. Note that the similar results were obtained by laser irradiation at 532 nm. (d) An expanded view of (c). (e) The ED pattern of the nanoparticles in (c). (f) After settling in the dark conditions for 10 min in 0.2 mM NaI. (g) The ED pattern of the nanoparticles in (f).

mechanism of the photo-induced morphological conversions remains ambiguous at present. In particular, since the systems in which this type of morphological conversion was observed seem to be complex, it will be difficult to reveal the critical factor of the morphological conversions.

Recently, we found that similar morphological conversions of silver nanoparticles could be observed using much simpler systems. We prepared silver colloids using laser ablation of silver in water, differing from the previous study in which the colloids were prepared using chemical synthesis methods. Upon laser irradiation, morphological conversions from spherical nanoparticles to crystal-shaped nanoparticles including nanoprisms and nanorods were observed [17]. Very recently, we found that this photo-induced morphological conversion was enhanced by a small amount of NaCl added to the colloidal solution before laser irradiation [18]. In addition, we demonstrated that the morphological conversions occurred even by fluorescent-light irradiation when the colloidal solutions contained NaCl [18]. The latter result suggested that the morphological conversions were not caused by laser-induced fragmentation or fusion of nanoparticles, and confirmed that chlorides plays a critical role for the morphological conversions. Therefore, we have explained the mechanism of the morphological conversions based on etching of silver nanoparticles by chloride ions with subsequent photoreduction. First, silver nanoparticles undergo chloride etching, thereby forming silver ions. Next, those silver ions are reduced by photoirradiation, thereby forming silver atoms. Finally, these silver atoms aggregate with each other to form the crystal-shaped particles. However, the etching process and the role of the photoirradiation remain unclear.

In this study, we further investigated the mechanism of the photo-induced morphological conversions. We investigated the influences of iodides, which is a stronger etchant for noble metals than chlorides. We also examined morphological conversions of the smaller nanoparticles because the reactivity of metal nanoparticles increases with decreased size. Photoirradiation was carried out at various wavelengths to elucidate the role of photoirradiation.

2. Experimental

The experimental procedures were shown in Scheme 1. The experimental conditions and the apparatuses of this study were the same as those of the previous study [18], except for those of the irradiation-wavelength experiment. The source silver nanoparticles were prepared using laser ablation of a piece of silver plate (Nilako, 99.99%) in neat water for 10 min using 355 or 1064 nm light of a Nd:YAG laser (GCR-100; Spectra Physics). The intensity of the 1064-nm ablation laser light was adjusted to 12 mJ/pulse, whereas that of the 355-nm ablation laser light was increased to 24 mJ/pulse to obtain a sufficient amount of the source colloids. The concentration of silver atoms in the colloidal solutions obtained using 1064-nm laser ablation was determined to be ca. 6×10^{-2} mM by means of an atomic absorption meter (Z-5310, Hitachi). After the preparation of the source colloids, chlorides (NaCl, KCl) or iodides (NaI, KI) were added. These reagents were purchased from Kishida Co., Ltd., and were used without further purification. The final concentration of halogen ions was adjusted at 0.2 mM.

The photoirradiation was carried out using 355 or 532 nm laser light or wavelength-selected light of a Xenon lamp (UXL500SX; Ushio Inc.) for 10 min with stirring. The wavelength-selection of the Xenon lamp irradiation was carried out using band-pass color filters (10 nm fwhm). The intensities of the laser light and filtered Xenon lamp light were adjusted to 500 and 6×10^{-2} mW/cm^2, respectively. The morphology of the colloidal particles was analyzed using a TEM (JEM-2100XS; JEOL) and an ultraviolet spectrometer (UV-2450; Shimadzu Corp.). Small amounts of the colloidal solutions were dropped on carbon mesh microgrids in the dark conditions to prepare TEM samples.

3. Results and discussion

Fig. 1a shows a TEM image of silver nanoparticles prepared using 1064-nm laser ablation in neat water. Spherical particles with the average size of 16 nm were prepared (Fig. 1b). Then, 0.2 mM NaI was added to the colloidal solutions and the laser irradiation at 355 or 532 nm was carried out for 10 min. As shown in Fig. 1c and d, crystal-shaped particles were obtained after laser irradiation, as was observed in chloride solutions [18]. The ED patterns (Fig. 1e) showed that the crystal-shaped nanoparticles were composed of silver, although some amount of AgI was contained.

Fig. 1f shows that nanoparticles in a 0.2 mM NaI solution settled in the dark conditions for 10 min. Although the morphology of nanoparticles did not change in the dark conditions in NaCl solutions [18], the morphology of nanoparticles in iodide solutions changed markedly. A number of larger particles with

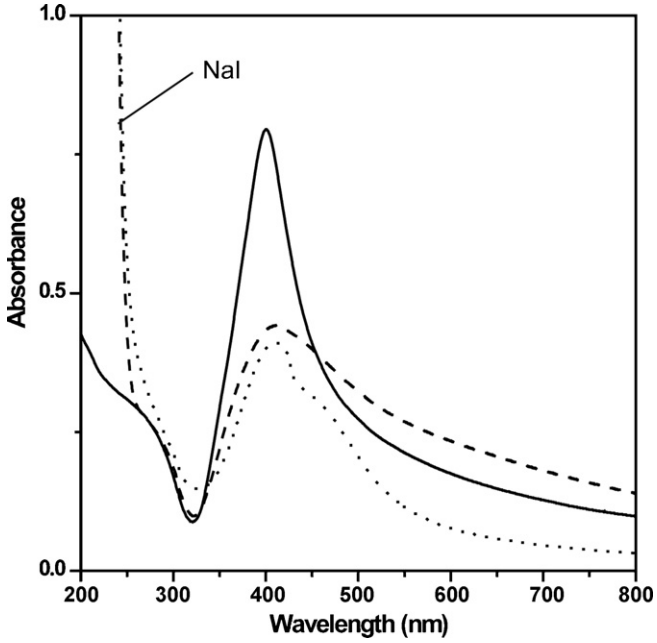


Fig. 2. UV–vis absorption spectra of silver colloids. Solid line: source colloids prepared by 1064-nm laser ablation in neat water. Dashed line: 0.2 mM NaI solution in the dark conditions. Dotted line: 0.2 mM NaI solution after laser irradiation at 355 nm. Laser irradiation was carried out for 10 min at 500 mW/cm^2.

irregular shapes were produced. The ED patterns showed that major components of these nanoparticles were silver, although a small amount of AgI was involved (Fig. 1g). These phenomena were also observed in KI solutions. Reportedly, similar morphological changes of nanoparticles induced by iodides were observed for Au nanoparticles [19]. Spherical particles of 3 nm changed to irregularly shaped particles of 50 nm after CH_3I was added. This morphological change was explainable as etching of gold by iodide ions. Iodide ions are known to be stronger etchant of noble metals than chloride ions. Therefore, the fact that the formation of crystal-shaped particles in the photo-irradiated conditions and the morphological changes in the dark conditions occurred more prominent in iodide solutions than in chloride solutions strongly suggest that halogen etching plays an important role in the photo-induced morphological conversions.

Fig. 2 shows absorption spectra of silver colloidal solutions. The shape of the plasmon bands around 400 nm was broadened by addition of 0.2 mM NaI, which was more drastic than that occurred by addition of NaCl [18]. Upon laser irradiation at 355 nm, the plasmon bands became broader and fewer, and a shoulder band at 440 nm appeared. Recently, Tan and Fan [20] reported that laser irradiation for silver colloids containing I_2,

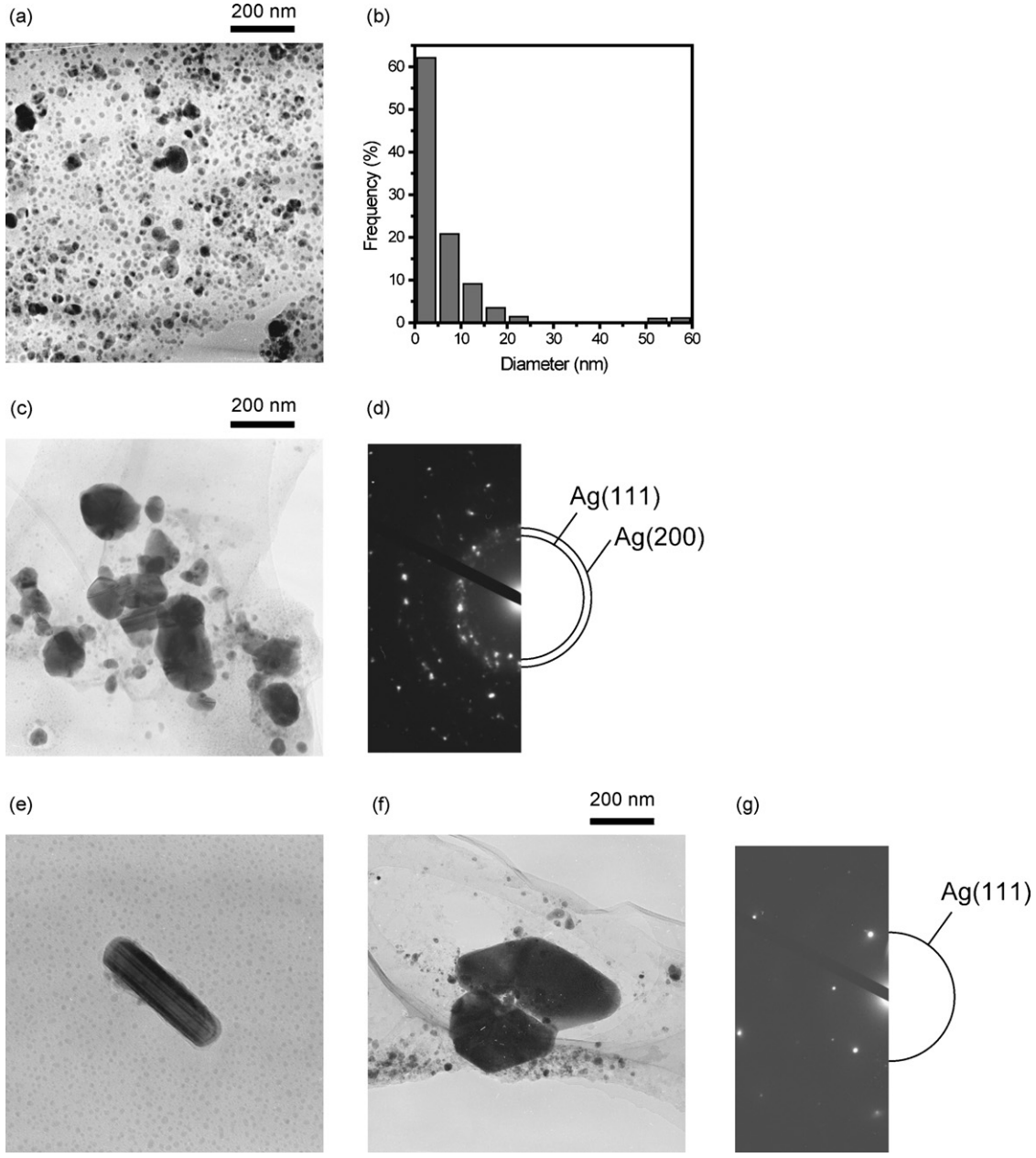


Fig. 3. Morphological changes of silver nanoparticles prepared using 355-nm laser ablation by chlorides. (a) Source colloids prepared using 355-nm laser ablation in neat water. (b) The size distribution of the source colloids. The average diameter and the standard deviation were 8 and 7 nm, respectively. (c) After settling in the dark conditions for 10 min in 0.2 mM NaCl. (d) The ED pattern of the nanoparticles observed in (c). (e) Crystal-shaped particles obtained by laser irradiation at 355 nm for 10 min at 500 mW/cm^2 with 0.2 mM NaCl. (f) The ED pattern of the nanoparticles in (c). (g) Crystal-shaped particles obtained by laser irradiation at 532 nm for 10 min at 500 mW/cm^2 with 0.2 mM NaCl.

which were prepared using laser ablation in SDS solution, produced Ag@AgI core-shell nanoparticles. While the formation of such core-shell nanoparticles are unclear in our TEM images in which only the formation of AgI was assigned by the ED patterns, the shoulder band at 440 nm in the absorption spectrum can be attributed to the Ag@AgI core-shell structure.

Fig. 3a shows a TEM image of the source silver colloids prepared using 355-nm laser ablation. As previously reported [21], silver nanoparticles prepared by 355 nm laser ablation were smaller than those produced by 1064-nm laser ablation (Figs. 1b and 2b). From the comparison of the absorption intensity of the interband transitions of silver at 250 nm (Fig. 4) with that of the colloids prepared using 1064-nm laser ablation (Fig. 2), the amount of silver atoms prepared using 355-nm laser ablation was estimated to be ca. 0.01 mM. After the addition of 0.2 mM of NaCl, morphological changes were observed in the dark conditions (Fig. 3c), different from nanoparticles prepared using 1064-nm laser ablation [18]. Irregularly shaped nanoparticles that were significantly larger than the source particles were produced. The ED patterns showed that these particles were composed of Ag (Fig. 3d). This phenomenon closely resembles that observed in the iodide solutions: it must be due to halogen etching. Because the stability of metal atoms on the surface of a nanoparticle decreases with decreased particle size, the reactivity of chloride ions with silver nanoparticles is higher for the smaller nanoparticles prepared using 355-nm laser ablation than for the larger nanoparticles prepared using 1064-nm laser ablation.

The laser irradiation onto those colloids produced crystal-shaped silver nanoparticles (Fig. 3e and f). Despite the limitation of the TEM observation area and the lower concentration of nanoparticles, qualitatively, the crystal-shaped nanoparticles became more numerous than nanoparticles prepared using 1064-nm laser ablation.

In the absorption spectra, the addition of NaCl caused considerable changes (Fig. 4). The plasmon bands were broader and fewer, even in the dark conditions, although no significant spectral changes were occurred by addition of NaCl for colloids prepared by 1064-nm laser ablation, which strongly implies that smaller particles are more sensitive for chloride ions. In addition, a new prominent absorption peak appeared at 260 nm after the addition of NaCl. This absorption band was assigned to $AgCl_2^-$, a typical product of etching of noble metals by halogens [22], because this band was observed for aqueous solution that obtained by solving AgCl powders by NaCl (the dash-dotted line in Fig. 4). Therefore, the detection of $AgCl_2^-$ strongly suggests that the halogen-etching process is involved in this system.

The halogen-etching process of silver is generally described as follows [22–24]:

Anodic reactions:

$$Ag \rightarrow Ag^+ + e^- \quad (1)$$

$$Ag^+ + 2X^- \rightarrow AgX_2^- (X = \text{halogen}) \quad (2)$$

Cathodic reactions:

$$X_2 + X^- \rightarrow X_3^- \quad (3)$$

$$X_3^- + 2e^- \rightarrow 3X^- \quad (4)$$

Total reaction:

$$2Ag + X^- + X_3^- \rightarrow 2AgX_2^- \quad (5)$$

Thus, the halogen-etching process of silver can be regarded as an electron transfer reaction from the silver to the halogens. In our system, taking account of the fact that halogen molecules (X_2) are not involved in our solutions, another electron acceptor should be involved. As Henglein [25] showed, silver colloidal particles can act as an electron storage medium. By introducing this idea, the etching process in our system can be described as

$$Ag_n + 2X^- \rightarrow Ag_{n-1}^- + AgX_2^- \quad (6)$$

Here, Ag_n represents a silver colloidal particle. In addition, the morphologically changed particles observed after addition of halogens must be produced via the following reduction process:

$$Ag_{n-1}^- + AgX_2^- \rightarrow Ag_n + 2X^- \quad (7)$$

Based on the fact that the morphological changes were observed in the dark conditions, Eq. (7) can occur as a thermal process. In a previous report [18], we assumed that water molecules were the electron donors [26] of the reduction process. However, Eq. (7) suggests that it is not necessary to involve water molecules in the reaction.

It must be noted that AgI was detected in the iodide solutions. The formation of AgI implies the formation of AgI_2^-, because AgI can be dissolved by I^- ions forming AgI_2^-, supporting that the above etching mechanism can be applied for iodide solutions. On the other hand, the role of AgI in the shape conversion process is unclear, at present.

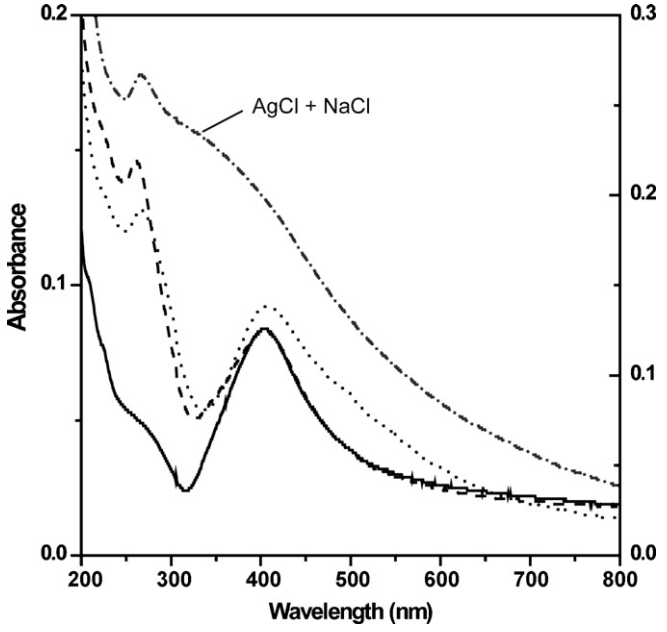


Fig. 4. UV–vis absorption spectra of silver colloids prepared by 355 nm laser ablation. Solid line: source colloids. Dashed line: after settling in the dark conditions for 10 min in 0.2 mM NaCl. Dotted line: after laser irradiation at 355 nm for 10 min at 500 mW/cm^2 with 0.2 mM NaCl. Dash-dotted line: a spectrum of an aqueous solution obtained by solving AgCl powders by NaCl.

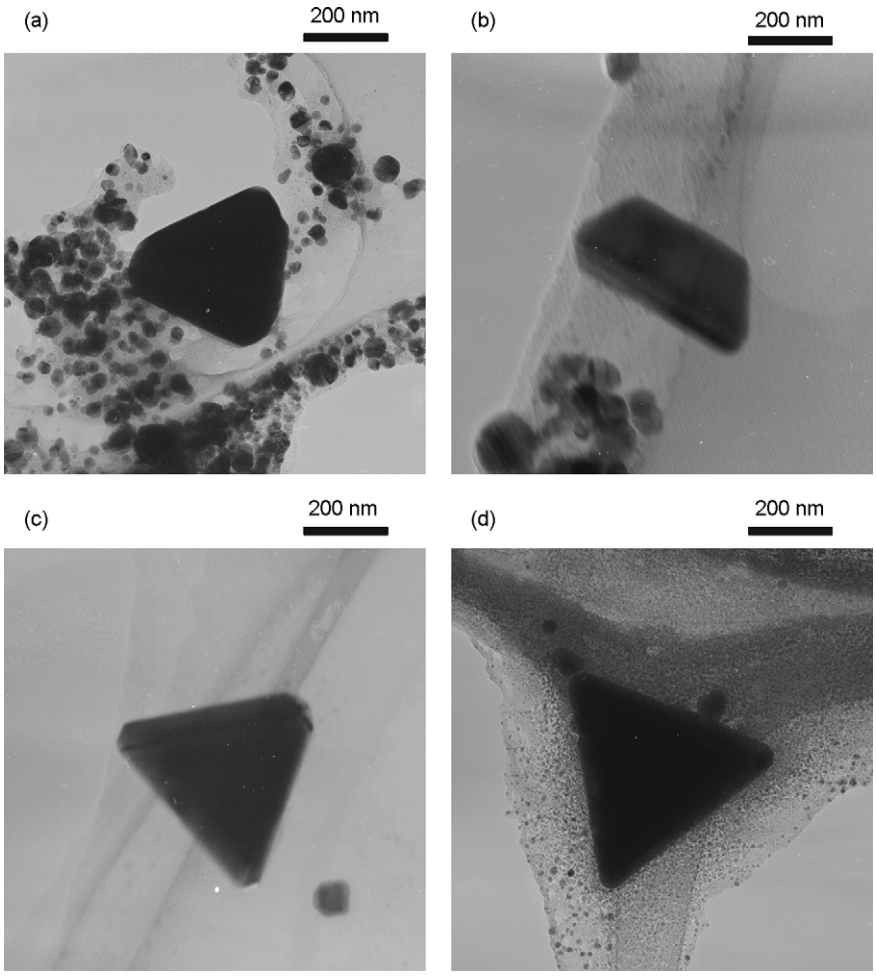


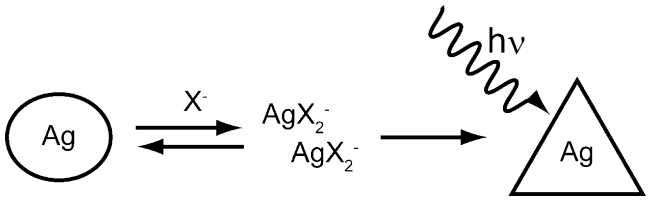
Fig. 5. Crystal-shaped silver nanoparticles prepared using photoirradiation for 10 min at various wavelengths onto silver colloids in 0.2 mM NaCl solution. The source colloids were prepared using 1064-nm laser ablation. Photoirradiation was carried out using Xenon lamp light filtered by band-pass color filters centered at (a) 350 nm, (b) 400 nm, (c) 550 nm, and (d) 700 nm with intensity of 6.0×10^{-2} mW/cm^2 and band width of 10 nm fwhm.

After laser irradiation at 355 nm, the peak intensity at 260 nm in Fig. 4 decreased and the intensity of the plasmon bands increased, indicating that the reduction of $AgCl_2^-$ can be promoted by photoirradiation. From the fact that the crystal-shaped particles were produced only under light irradiation, it can be inferred that the promotion of reduction of silver ions by the photoirradiation induces the formation of crystal-shaped particles because the Ag atom formation rate is a critical factor, which determines whether an ordered or non-ordered crystal-growth occurs. Therefore, to investigate roles of the photoirradiation in the formation of the crystal-shaped nanoparticles, photoirradiation was carried out at more various wavelengths for silver nanoparticles in NaCl solutions.

Based on the previous result that the crystal-shaped particles were produced by fluorescent-light irradiation, the experiments were carried out using Xenon lamp that had been filtered using band-pass color filters. As shown in Fig. 5, crystal-shaped nanoparticles were produced at all wavelengths. Unfortunately, it was difficult to analyze the wavelength dependence of their shape, size, and abundance quantitatively, because the abundances of the crystal-shaped particles produced by photoirradiation at these wavelengths were low. On the other hand, it is notable that the crystal-shaped particles were produced by 700-nm irradiation, which is far from the absorption band of $AgCl_2^-$. Although the multi-photon absorption process can be assumed for the laser irradiation at 532 nm, the possibility of the multi-photon process by the weak Xenon lamp irradiation is negligible. Actually, no marked changes were observed in the UV–vis spectra upon Xenon lamp irradiation at 700 nm. Therefore, although the photoreduction was observed for 355-nm laser irradiation, it is concluded that promotion of the reduction rate by the photoirradiation of silver ions was not a necessity factor for the formation of the crystal-shaped nanoparticles.

A possible role of the photoirradiation in producing the crystal-shaped particles must be the inducement of the electronic field on the surface of nanoparticles via plasmon excitation. Maillard et al. [27][1] reported that photoreduction of silver ions was enhanced by plasmon excitation of silver nanoparticles contained in the solutions. In addition, it was remarkable

[1] In that article, they also proposed that silver nanoparticles act as an electron transfer medium, which enhances the reduction of silver ions on the nanoparticle surface.



Scheme 2.

that nanoprisms were produced after the photoirradiation. They proposed that, upon the excitation of plasmon of a surface, the induced electronic field near the surface of the nanoparticles attracts silver atoms, leading that the surface-specific accumulation of silver atoms, which subsequently forms anisotropic shapes. Such effects of the induced electronic field of nanoparticles have also been proposed for the morphological conversion mechanism of silver nanoparticles to nanoprisms [14,16].

Considering the above idea, the photo-induced morphological conversion process in our system might be depicted as in Scheme 2. By addition of halogens into silver colloids, the equilibrium between silver nanoparticles and silver ions (AgX_2^-) (Eqs. (6) and (7)) will be formed. Photoirradiation will induce the electronic field on the surface of the nanoparticles, which affects the silver atoms or ions near the surface, thereby forming the ordered accumulation (crystal growth) of silver atoms. Those ordered surfaces must be more stable than the disordered surfaces that are generated by laser ablation. For that reason, the stable ordered surfaces predominantly remain after the repetition of the $Ag_n \leftrightharpoons AgX_2^-$ equilibrium, resulting in the formation of the crystal-shaped particles.

On the other hand, the wavelength dependence of the products' size or shape, which clarifies the influence of the plasmon excitation, was not clearly observed in this study because the amount of the crystal-shaped particles was low. To confirm these effects of the plasmon excitation on crystal growth, further investigations, which include theoretical analysis of the interaction between the induced electronic field and metal atoms or ions, are necessary.

4. Conclusions

Photo-induced morphological conversions of silver nanoparticles, in which spherical particles are converted to crystal-shaped particles, was investigated using nanoparticles prepared by laser ablation in water. Results showed that the morphological conversions were more enhanced by iodides than by chlorides. In addition, irregular morphological changes were observed in iodide solutions in the dark conditions, differing from those occurring in NaCl solutions. These findings strongly suggest that the morphological conversion process involves halogen etching of silver nanoparticles. This assumption was supported by the fact that the morphological changes in the dark conditions and the formation of $AgCl_2^-$ were observed in NaCl solutions that contain smaller silver particles. Results also showed that the morphological conversions occurred by light irradiation at 700 nm, suggesting that photoreduction is not a necessary factor for formation of the crystal-shaped particles. Photoirradiation will control the orientation of the accumulation of silver atoms via inducement of the electronic field on the nanoparticle surface. While the formation efficiency of crystal-shaped particles remained still insufficient for practical applications throughout the present study, the information obtained here will be useful for future works for developing the photoirradiation technique.

Finally, Maillard et al. [27] predicted that silver ions contained in the colloidal solution should act as an intermediate in the morphological conversion from nanoparticles to nanoprisms investigated by Jin et al. [15,16]. In this study, we revealed that silver–halogen complexes produced by halogen etching play an important role for morphological conversion, which strongly supports their assumption.

Acknowledgements

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