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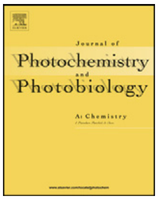

Utilization of laser ablation in aqueous solution for observation of photoinduced shape conversion of silver nanoparticles in citrate solutions

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ABSTRACT

Photoinduced shape conversion of silver nanoparticles in citrate solutions was examined using silver nanoparticles prepared by laser ablation. Nowadays, photoinduced shape conversion of silver nanoparticles in citrate solution attracts much attention as a novel technique to produce anisotropic-shaped nanocrystals in a simple manner. So far, the observations of the shape conversion have been carried out using source silver nanoparticles prepared by chemical synthesis. In this work, we demonstrate that silver nanoparticles prepared by laser ablation in liquids are an appropriate system to investigate the photoinduced shape conversion due to the simple preparation method and absence of unnecessary components in colloidal solution. Using this system, we have confirmed that particle size plays a critical role in the shape conversion. In addition, some novel information was obtained: the adsorption conditions of citrate are also important, and polyvinylpyrrolidone promote the conversion rate.

1. Introduction

The much effort is made on fabrication of nano-sized materials today, to discover novel functions which are different from those of bulk-sized materials, and to improve the efficiency of energy and natural resource consumption. Laser ablation (LA) is one of the most important fabrication techniques of nano-sized materials such as thin films and nanoparticles (NPs). In 1993, Henglein's group revealed that laser ablation is applicable for not only targets in evacuated circumstances but also those set in liquids [1]. They also revealed that colloidal NPs were formed from ejected materials. Therefore, nowadays this procedure, referred to as laser ablation in liquids (LAL), attract much attention as a novel technique to obtain colloidal NPs [2–11]. As a synthesis technique of NPs, the distinctive advantages of LAL toward the other synthesis techniques are (1) simplicity of the procedure and (2) absence of chemical reagents. Because of the simplicity of the preparation procedure, in principle, LAL is applicable for any materials. The absence of unnecessary reagents such as stabilizers and byproducts becomes useful when NPs are used for various applications such as biocompatible materials. Comprehensive reviews by Yang [12] and Amendola and Meneghetti [13] provides information about the fundamental and size-control method of LAL.

The advantages of NPs prepared by LAL are also useful when chemical and physical properties of NPs are investigated, because NPs of various materials can be prepared by one procedure and influences of byproducts can be excluded. In this article, we demonstrate that NPs prepared by LAL are applicable to investigate photoinduced shape conversion of silver NPs in citrate solutions. Recently, photoinduced shape conversion of silver NPs attracts much attention as a conventional method of shape control of metal NPs. The most remarkable example is the shape conversion of silver NPs in citrate solutions. As first reported by Jin et al. [14], irradiation of weak light for spherical silver NPs engenders the formation of nanoprisms. Furthermore, it has been demonstrated that the size of the resultant nanoprisms can be controlled by adjusting the wavelength of the irradiating light [15,16]. From the results of the following works, it was suggested that dissolved oxygen, citrate used in the synthesis of silver NPs, and localized surface plasmon resonance (LSPR) caused by photoirradiation are critical factors. First, LSPR of silver NPs on which citrate are absorbed will bring about electron transfer from the citrate to the NPs [17–21]. Next, the supplemental electrons injected into the silver NP will reduce silver ions around the silver NPs [19–21]. Here those silver ions are suggested to be formed by oxidative etching of the other silver NPs by oxygen dissolved in the solution through following scheme [20,21]:

$$2\mathrm{Ag} + \frac{1}{2}\mathrm{O_2} + \mathrm{H_2O} \rightarrow 2\mathrm{Ag^+} + 2\mathrm{OH^-} \quad (1)$$

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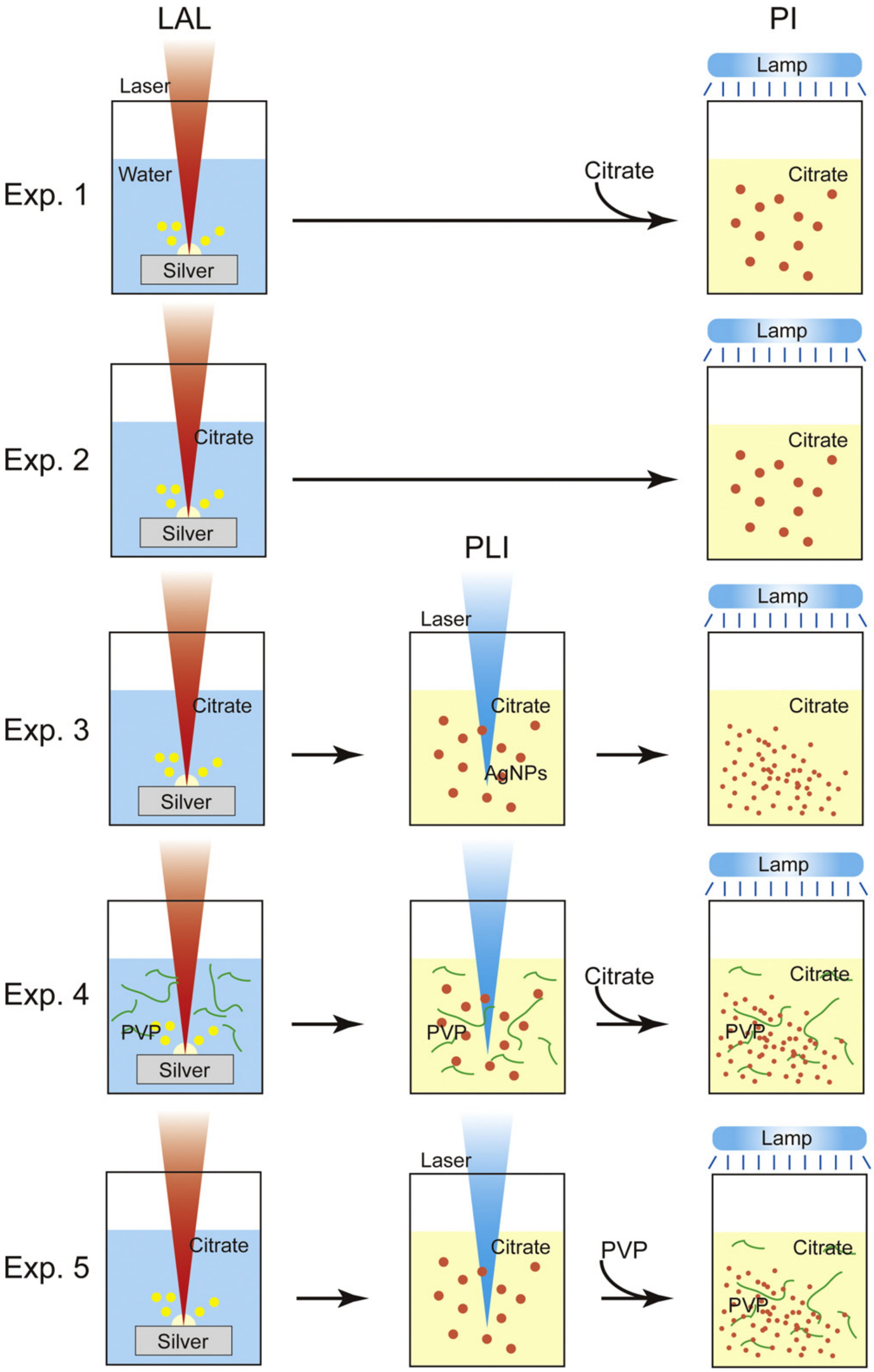

Fig. 1. Schematic diagrams of preparation procedure of the source silver colloids and photoirradiation. LAL, PLI, and PI stands for laser ablation in liquids for preparation of silver NPs, post laser irradiation to reduce particle size, and photoirradiation to induce the shape conversion. The experimental conditions are shown in text. The order of adding of citrate and PVP was different among the experiments.

As a result of these reactions, silver NPs subjected to LSPR can grow and NPs not subjected to LSPR will be reduced (this difference is determined by the size of NPs and the wavelength of irradiation light). Furthermore, if the heterogeneous electric field is induced on an NP, then the above reactions will occur in a limited portion of an NP, resulting in the formation of the anisotropic shaped nanocrystals (nanoprisms).

Although above mechanism explains the photoinduced shape conversion process appropriately, so far observation of the shape conversion have been limited in colloids prepared by chemical synthesis methods used by Jin et al. [14]. For example, Sun et al. claimed that the photoinduced shape conversion did not occur efficiently without polyvinylpyrrolidone (PVP) [22]. In addition, it is possible that counter ions and/or source reagents remained in

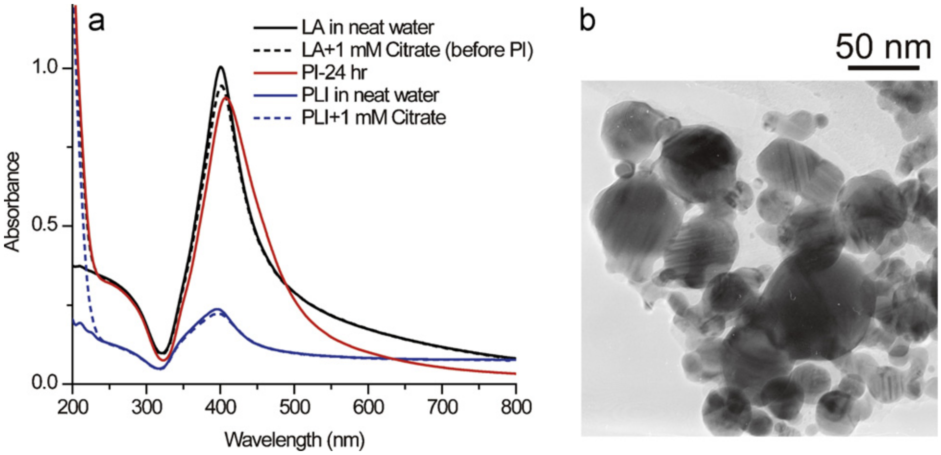

Fig. 2. (a) UV–Vis spectrum of silver colloids prepared by LA in neat water and its changes caused by adding of 1 mM sodium citrate, PI for 24 h, and PLI (see Exp. 1 in Fig. 1). (b) TEM image of silver colloids prepared using LA in neat water (before PI).

solution might influence the conversion processes in colloids prepared by chemical methods. Therefore, to confirm the mechanism proposed and the roles of the substances involved, observation of the photoinduced shape conversion using simpler systems is necessary. For that purpose, silver NPs prepared by LAL should be a proper system due to the simplicity of the preparation method and composition of the colloidal solutions. In our previous work, we used silver NPs prepared by LAL to investigate photoinduced shape conversion of silver NPs in halide solutions [23,24]. We prepared silver NPs using laser ablation in water. After addition of a small amount of halides, photoirradiation for the silver colloids was carried out, resulting in the formation of silver nanocrystals including nanoprisms and nanorods. For the shape conversion in halide solutions, we could attribute the shape conversion to halide etching. A similar simple protocol can be applied to investigate the shape conversion in citrate solutions. We carried out LAL to produce silver colloids containing citrate. In this paper, the necessary conditions for the photoinduced shape conversion were examined.

2. Experimental

LAL of silver plate in aqueous solutions to prepare silver NPs was carried out as described elsewhere [25,26]. Laser ablation of a piece of silver plate (99.99%, Nilako) set in 5 mL of aqueous solution was carried out using focused 1064 nm light of a nanosecond pulsed Nd:YAG laser (GDR-200; Spectra Physics) for 10 min. The pulse width and the repetition rate were, respectively, 8 ns and 10 Hz. The intensity of laser light was adjusted at 12 mJ/pulse. To obtain smaller sized silver NPs, we conducted additional laser irradiation for colloids prepared using LAL. Hereafter, we refer to this method as post laser irradiation (PLI). PLI was carried out using focused 355 nm light of another nanosecond pulsed Nd:YAG laser (GDR-100; Spectra Physics) for 10 min. The pulse width and the repetition rate were, respectively, 6 ns and 10 Hz. The intensity of laser light was adjusted at 12 mJ/pulse. It is notable that the total time of LAL and PLI to obtain source silver colloids was less than 30 min, which will be an advantage of this protocol toward chemical synthesis methods. Solutions were stirred during LA and PLI. In the present study, the preparation of silver NPs were carried out using neat water (spectrum grade, Kishida), or aqueous solutions containing 1 mM trisodium citrate (99.9%, Kishida), or 6 mM polyvinylpyrrolidone (M.W. = 40,000; Kishida). A several experimental procedures of addition of trisodium citrate and PVP were employed as summarized in Fig. 1. After the preparation of silver colloids by LA and PLI, photoirradiation (PI) for the colloidal NPs was carried out. Light from Xenon lamp (UXL500SX; Ushio Inc.) filtered by a UV- and IR-cut filter was used as irradiation light. The spectrum of the irradiation light was shown in Appendix A. The intensity of the irradiation light was ca. 4 mW/cm^2. Oxygen gas bubbling into the colloidal solutions was carried out during PI. The typical flow rate of oxygen gas was adjusted at 0.25 mL/min. Oxygen is a critical factor for the shape conversion as shown in Scheme (1). Actually, no significant change in the color of silver colloids was observed when nitrogen bubbling was conducted during PI. The solutions were cooled by airflow during PI to prevent the increase in the solution temperature. The absorption spectra of silver colloids were observed using a UV–Vis spectrometer (UV-2450; Shimadzu Corp.). Time evolution of the color change of the colloidal solutions was observed by monitoring a portion of the transparent light by means of a multichannel UV–Vis spectrometer (PMA10; Hamamatsu Photonics). The morphology of the silver NPs was observed by means of a TEM (JEM2100FX; JEOL).

3. Results and discussion

3.1. PI for silver colloids containing citrate

First, PI was carried out for silver colloids that were prepared by laser ablation in distilled water and 1 mM citrate were added after the preparation (Exp. 1 in Fig. 1). Fig. 2a shows UV–Vis spectra of silver colloids before and after PI for 24 h. Small red shift of the plasmon bands were observed after PI in the UV–Vis spectra and a few amount of nanocrystals were observed in the TEM images. Possibly, the low conversion efficiency will be due to the large size of the silver NPs. As shown in Fig. 2b, the average diameter of silver NPs prepared by LA in neat water was ca. 20 nm. It was reported that the conversion rate of particles larger than 10 nm was low [21], which is due to the redox potential of a silver NP decreasing with the decrease in the particle size [27]. To confirm the influence of particle size, we prepared smaller silver NPs using the PLI technique. Unfortunately, as shown in Fig. 2a, when PLI was carried out for silver colloids in deionized water, significant aggregation and sedimentation of the colloidal particles were brought about. In addition, adding of citrate into the solution brought about salting out of the colloidal particles, leading that PI experiments became difficult.

To obtain enough amounts of stable silver colloidal particles with smaller size, we conducted LAL and PLI in citrate aqueous solutions (Exps. 2 and 3 in Fig. 1). Fig. 3 shows UV–Vis spectra of silver colloids prepared by LA and PLI in a solution containing 1 mM citrate. From the comparison between Figs. 2a and 3, it is remark-

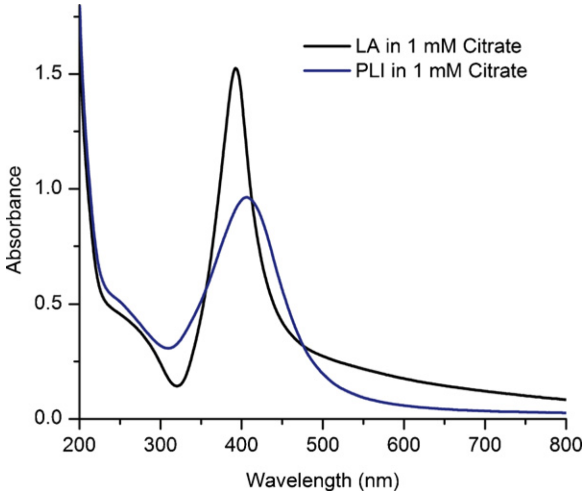

Fig. 3. UV–Vis spectra of silver colloids prepared by LA in 1 mM sodium citrate solution and its changes caused by PLI.

able that the amount of silver NPs obtained by laser ablation was higher in citrate solution than in neat water, and sedimentation of NPs during PLI in citrate solution was suppressed. This result indicates that silver NPs is efficiently stabilized when citrate is involved in solution during laser ablation. The enhanced stabilization effect of citrate can be explained in terms of efficient adsorption of citrate on the surface of NPs during laser ablation process as observed in gold NPs prepared by laser ablation in NaCl aqueous solution [28,29]. As illustrated in Fig. 4, when citrate anions are involved during laser ablation, citrates are attached on the pure surface of silver NPs efficiently. The counter sodium cations are dispersed in the entire part of the solution to lower free energy. Therefore, silver NPs are negatively charged and stabilized. On the other hand,

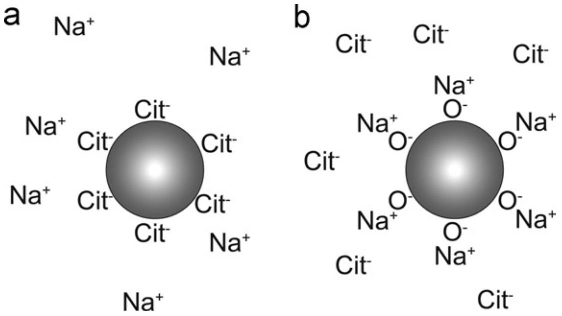

Fig. 4. Adsorption conditions of citrate on the surface of a silver NP prepared by LAL. (a) LA is conducted in a 1 mM sodium citrate solution. (b) LA is conducted in neat water and 1 mM sodium citrate is added after the preparation of NPs.

silver NPs formed in neat water have weak negative charges provided by oxygen [29]. When citrate was added into the colloids, citrate anions and sodium cations are dispersed in the entire part of the solution equivalently, and thus neutralization of the negative charge of silver NPs by sodium cations can occur. Fig. 5a and 5b, respectively, shows TEM image of silver NPs prepared by LAL in a 1 mM citrate solution and that of silver NPs after PLI. Most of the NPs were reduced to less than 10 nm (the average size of the smaller NPs were ca. 6 nm) by PLI. We carried out PI for those silver NPs with and without PLI to confirm the size dependence of the photoinduced shape conversion. It must be noted that the critical particle size which induces the shape conversion has not been determined by the present work, because the precise size control method using the PLI technique has not been accomplished.

As shown in Fig. 6a, for silver colloids without PLI (Exp. 2), the change in the UV–Vis spectrum after PI for 24 h was almost same as that observed in Fig. 2a, indicating that no significant formation of nanocrystals occurred. On the other hand, as shown in

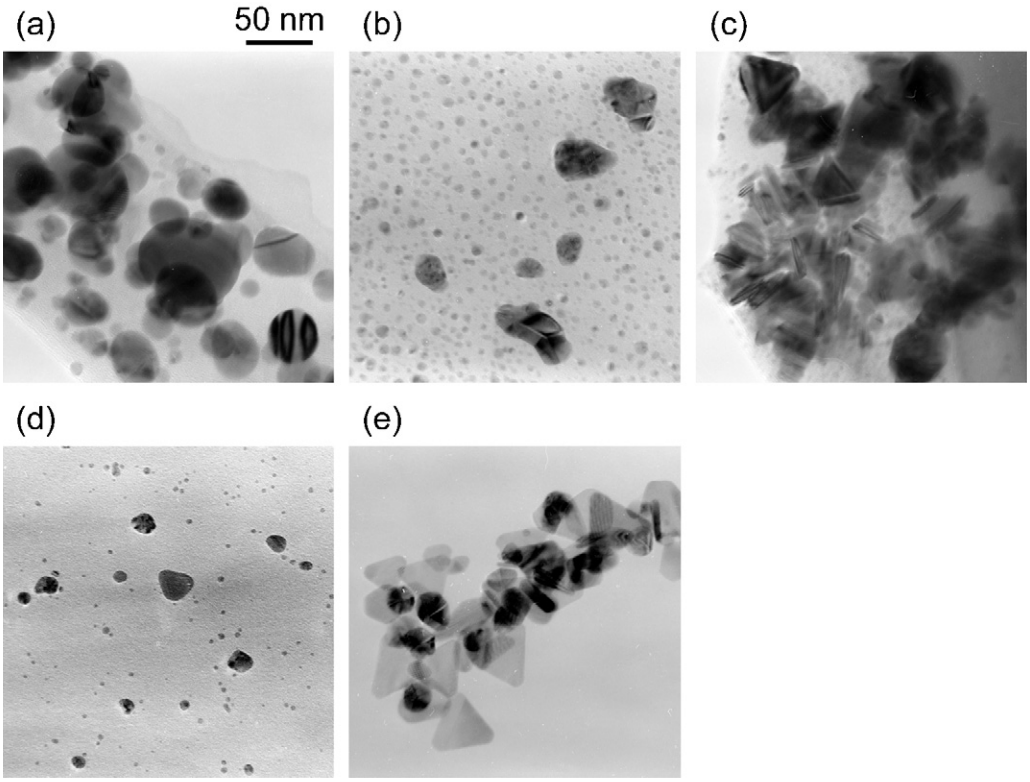

Fig. 5. TEM images of silver colloids (a) prepared using LA in a 1 mM sodium citrate solution, (b) after PLI, (c) after PI for 24 h, (d) after PI for 90 min, and (e) after PI for 12 h (Exp. 3 in Fig. 1).

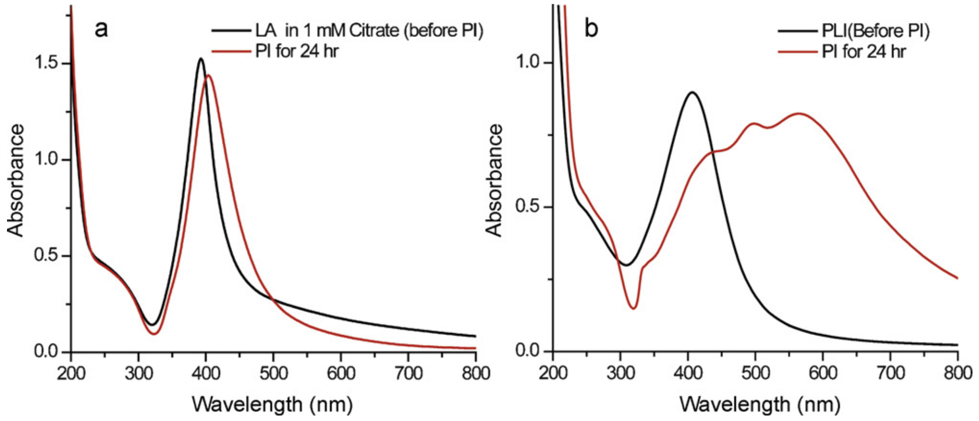

Fig. 6. Changes in UV–Vis spectra silver colloids caused by PI for 24 h. The source colloids (a) without and (b) with PLI after preparation by LA in a 1 mM sodium citrate solution (see Exps. 2 and 3 in Fig. 1).

Fig. 6b, for silver colloids with PLI (Exp. 3), the color of the colloidal solution changed from yellow to dark violet after PI for 24 h. In Fig. 6b, the band at 400 nm due to spherical particles was diminished and new bands are observed at 335, 435, 495, and 565 nm. The band at 335 nm is due to the out-of-plane quadrupole plasmon mode characteristic to planar nanoparticles [14]. Other bands can be assignable to non-spherical nanoparticles including nanoprism [30]. In the TEM images of the colloids after PI (Fig. 5c), nanoprisms as well as nanocrystals with various shapes were formed, consistent with the UV–Vis spectrum. From these results, it was confirmed that particle size is a critical factor for the photoinduced shape conversion of silver NPs in citrate solution. However, it must be noted that the critical particle size for the shape conversion has not been determined in the present work. To determine the critical particle size, more precise control of the particle size using the PLI technique is necessary. Such a study should be carried out in the following work.

The time evolution of UV–Vis spectrum was also observed (Fig. 7). It was found that the shape conversion process of the silver NPs is composed of three stages. In the first stage (<2 h), the band at 400 nm narrowed and became higher. Though the similar spectral change was reported by Wu et al. [20], no interpretation has been provided. Therefore, we carried out a TEM observation of silver NPs in the first stage. Fig. 5d shows a TEM image of silver NPs after PI for 90 min. The most remarkable change in the first stage was the reduction of the particle size. The most of the NPs were reduced to less than 5 nm. On the other hand, the amount of prisms was low. This result of the TEM observation indicates that the oxidative etching of silver NPs is the dominant process of the first stage. The rise and narrowing of the 400 nm band in the UV–Vis spectrum would be due to the dispersion of NPs, which are aggregated in the PLI process, as a result of the etching of the surface. The presence of the first stage indicates that formation of prisms begins after the concentration of silver ions is increased. Furthermore, it was found that no such spectral change was observed when silver NPs were set in dark (with oxygen bubbling), indicating that PI promotes the oxidative etching. These findings indicate that the first stage plays an important role in the photo-induced shape conversion process. Further investigation of the first stage will be carried out in the future.

In the second stage (3–13 h), a new band was rising at 585 nm, and its relative intensity to that of the 400 nm band increased. The spectrum observed at 13 h is very similar to the spectrum of colloidal solution containing prisms [14,21,22]. In the TEM images of the colloids in the second stage (Fig. 5e, sampled at 12 h), nanoprisms, of which relative amount in the particles seems to be higher than that of nanoprisms observed in Fig. 5c, were observed, confirming that the 585 nm band is assignable to nanoprisms. These

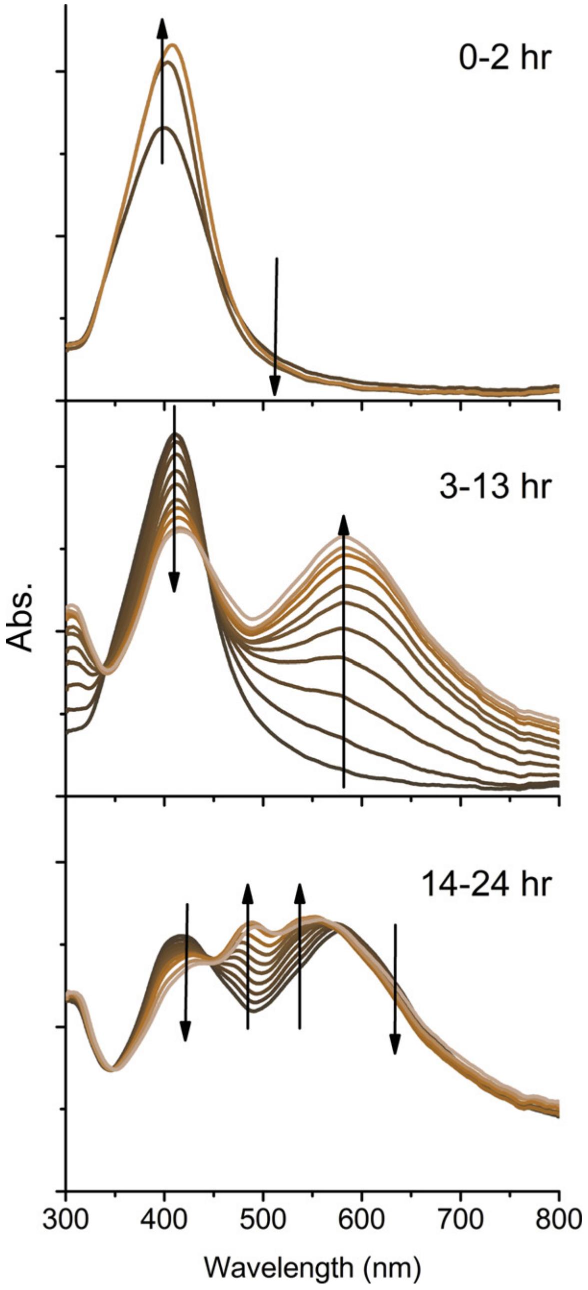

Fig. 7. Time-evolution of UV–Vis spectra during PI for silver colloids prepared by LA and PLI in a 1 mM sodium citrate solution (Exp. 3 in Fig. 1).

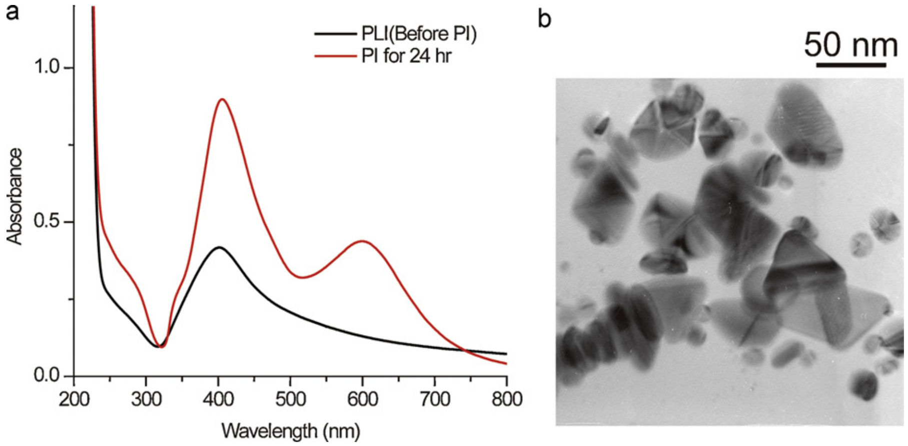

Fig. 8. (a) Change in UV–Vis spectra of silver colloids caused by PI for 24 h. The source silver colloids were prepared by LA and PLI in 6 mM PVP (M.W. = 40,000) solution and 1 mM sodium citrate was added before PI. (b) TEM image of nanoprisms formed by PI (see Exp. 4 in Fig. 1).

results indicate that prisms are the dominant product in the second stage.

In the third stage (≥13 h), the intensity of the 585 nm band slightly decreased and new band appeared at 495 and 565 nm. The change in the UV–Vis spectrum indicates that the shape conversion from spherical NPs to nanoprisms occurred in 13 h, and after 13 h, other non-spherical nanocrystals were formed from not only spherical NPs but also the nanoprisms. Such a process of the photoinduced shape conversion following the formation of prisms has not been reported previously.

3.2. PI for silver colloids containing citrate and PVP

We also conducted PI experiments using silver colloids prepared in PVP aqueous solutions for the further confirmation of the size dependence of the shape conversion. It has been found that stable colloids of silver NPs of which the diameter is smaller than 5 nm are formed by LAL and PLI in PVP solution [25,26]. In this experiment, silver NPs were prepared by means of LAL and PLI in PVP solutions, and then 1 mM citrate was added after the preparation (Exp. 4).

The color of the solution turned to green after 24 h PI. In the UV–Vis spectra of the solution (Fig. 8a) prominent bands are observed at 400 and 585 nm, which is very similar to the spectrum of colloidal solution containing prisms [14,21,22] and the spectrum of the second stage of silver colloids containing citrate (Fig. 7), indicating that prisms are the dominant product. The formation of prisms was confirmed by TEM observation (Fig. 8b).

From the time evolution of UV–Vis spectra (Fig. 9), it is clear that the conversion process composed of two stages and each stage is corresponding to the first and second stages of the shape conversion process in citrate solution (Fig. 7). In the first stage (0–6 h), the band at 400 nm was sharpened. In the second stage (7–24 h), the band assignable to nanoprisms appeared at 585 nm which is same as the position at which the band assigned to nanoprisms appeared in Fig. 7.These results indicate that the photoinduced shape conversion processes in Exps. 3 and 4 are essentially same, while it proceeded more slowly in Exp. 4 than in Exp. 3. The lowering of the conversion rate in Exp. 4 can be explained in terms of hindering effect of PVP adsorbed on the surface of silver NPs. As observed in LAL and PLI in citrate solution, the surface of silver NPs generated by LAL can efficiently adsorb substances which have a high affinity with silver NPs. It is well known that PVP has a high affinity with silver NPs [31,32]. Therefore, the surface of silver NPs generated in PVP solution will be covered with PVP and collision of oxygen and citrate to the silver NPs will be suppressed.

From this observation, it is suggested that adsorption conditions of citrate on the surface of silver NPs will be also an important factor for photoinduced shape conversion. To confirm this assumption, we carried out additional experiment in which silver NPs were prepared using LA and PLI in 1 mM citrate solutions and 6 mM PVP was added before PI (Exp. 5). After PI for 24 h, the color of the colloidal solution changed to dark violet which was the same color as that of colloidal solution after PI without PVP (Exp. 3). The time evolution of UV–Vis spectra (Fig. 10) shows that shape conversion process

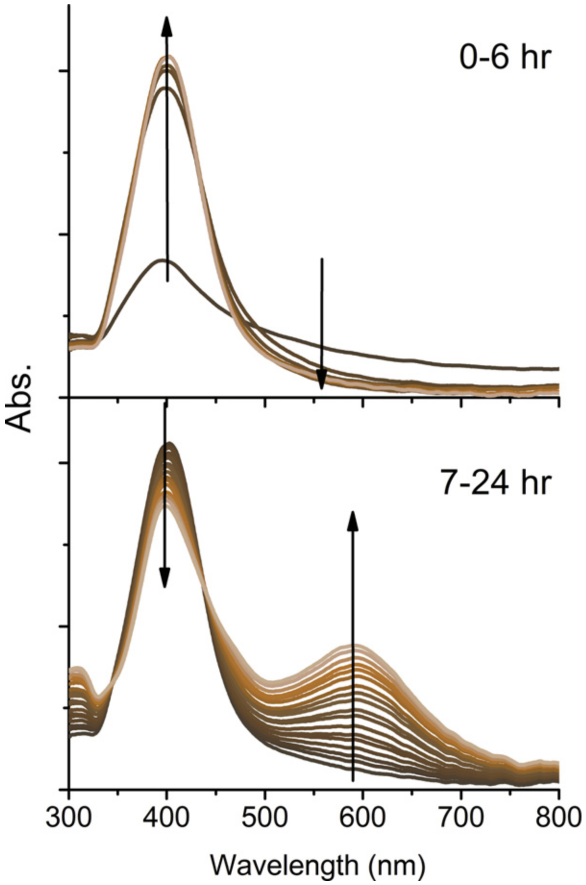

Fig. 9. Time-evolution of UV–Vis spectra during PI for silver colloids prepared by LA and PLI in a6 mM PVP solution and 1 mM sodium citrate was added before PI.

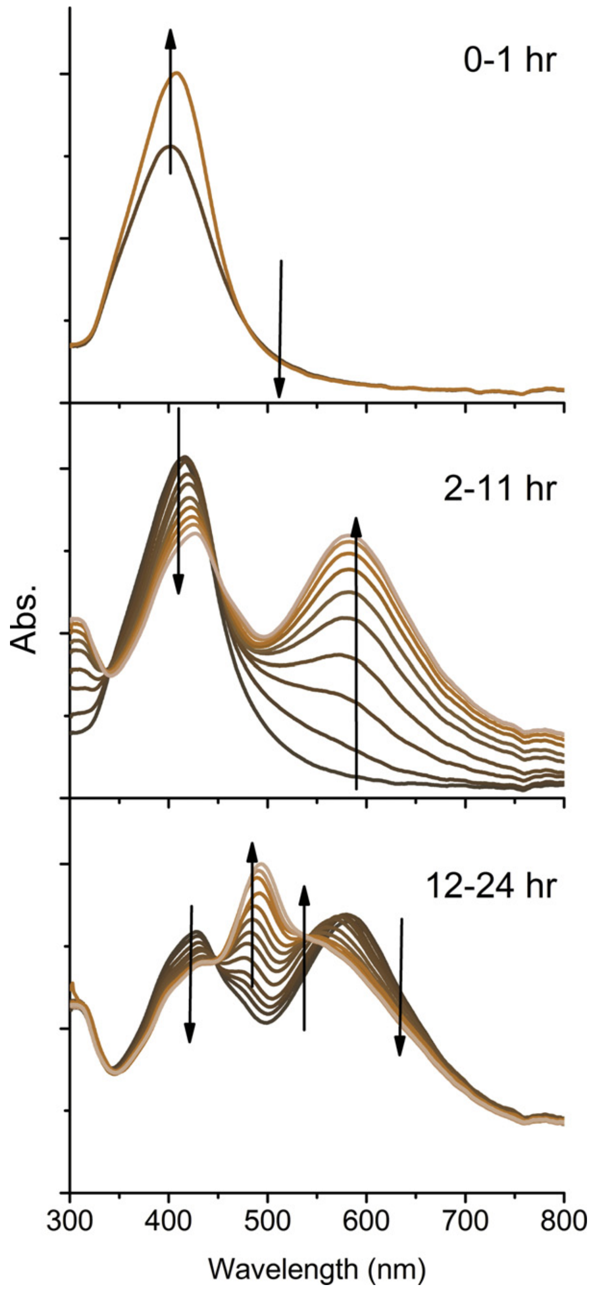

Fig. 10. Time-evolution of UV–Vis spectra during PI for silver colloids prepared by LA and PLI in a 1 mM sodium citrate solution and 6 mM PVP was added before PI (see Exp. 5 in Fig. 1).

is almost same as that observed for PI without PVP and is different from the result of Exp. 4. It can be assumed that the surface of silver NPs obtained by Exp. 5 will adsorb citrate and PVP dispersed around the NPs bring about no significant hindering effect, resulting in the efficient shape conversion induced by citrate. As mentioned in the former part, it has been suggested that photoinduced shape conversion of silver NPs in citrate solution would be initiated by electron transfer from citrate to silver NPs [17–21]. The fact that efficient adsorption of citrate promotes the photoinduced shape conversion supports this mechanism.

In addition, the comparison between Figs. 9 and 10 shows that the conversion rate in Exp. 5 (Fig. 10) was rather higher than that in PI without PVP (Exp. 3, Fig. 9). The promotion of the conversion by PVP will be essentially the same as that observed by Sun et al. [22] in which photoinduced conversion could not be observed without PVP, and can be explained in terms of stabilization of silver ions by PVP as suggested for promotion of silver ions by bis(*p*-sulfonatophenyl)phenylphosphine (BSPP). As reported previously [20,21], the conversion rate increases with BSPP. It was suggested that BSPP coordinate and stabilize silver ions generated by oxidative etching [Scheme (1)], resulting in the increase in the concentration of silver ions in solution [21]. For PVP, it is suggested that PVP can also coordinate metal ions at nitrogen in the pyrrolidyl group [33]. Therefore, PVP can also stabilize silver ions and can promote the conversion rate.

4. Conclusion

The photoinduced shape conversion of silver NPs in citrate solution was investigated using silver NPs prepared by LAL. The results essentially support the mechanism of the photoinduced shape conversion suggested by previous works. That is, oxygen and particle size are critical factors of the photoinduced shape conversion. On the other hand, novel information was also obtained. (1) There is an additional shape conversion process following the formation of nanoprisms. (2) The efficient adsorption of citrate promotes the shape conversion. (3) PVP can also promote the shape conversion which may be due to the stabilization of silver ions by PVP. In addition, (4) it was suggested that the oxidative etching process should be investigated more precisely.

It must be noted that this study was proceeded utilizing characteristic points of LAL. (1) The source silver colloids can be prepared efficiently. (2) The surface of NPs adsorbs substances efficiently during the generation process of NPs in LAL. We are continuing this work to confirm the roles of plasmon excitation by investigating the influences of wavelength and intensity of irradiation light.

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Appendix A.

See Fig. A1.

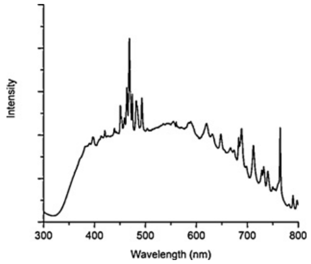

Fig. A1. Spectrum of irradiation light obtained by a Xenon lamp and a UV- and IR-cut filter.

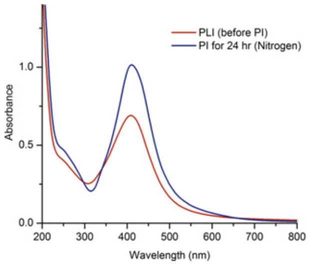

Fig. A2. UV–Vis spectra of silver colloids prepared by LAL and PLI in 1 mM citrate solution before and after PI for 24 h with nitrogen bubbling.

Appendix B.

See Fig. A2.

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