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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.

Keywords: Metal colloids; Nanoparticles; Shape control; Laser; Laser ablation

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 price control of shape conversions.

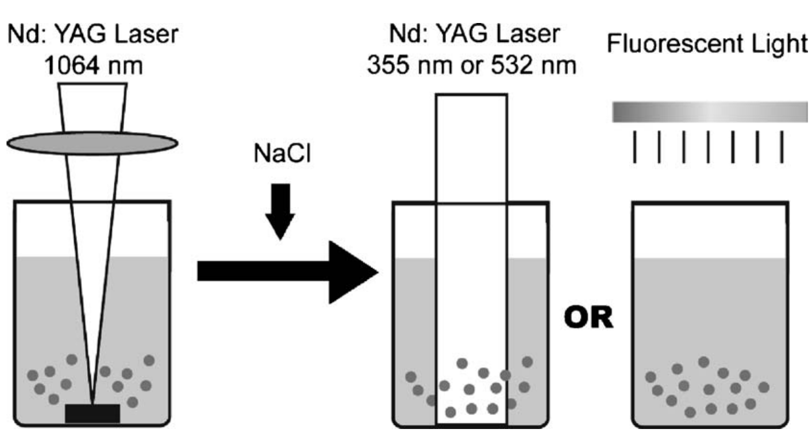
In this paper, we report effects of chloride ions. We have found that NaCl enhanced formation of crystal-shaped particles under laser irradiation. We have also found that nanoparticles with crystal-shaped particles were formed under fluorescent light irradiation with NaCl.

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 5.4×10^{-2} 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.