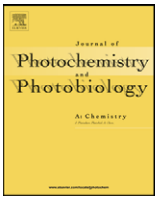
Journal of Photochemistry and Photobiology A: Chemistry 206 (2009) 134–139

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Laser-induced silver nanocrystal formation in polyvinylpyrrolidone solutions

Takeshi Tsuji[a,*], Takeshi Mizuki[b], Shogo Ozono[b], Masaharu Tsuji[a]

[a] *Institute of Advanced Materials Chemistry, Kyushu University, 6-1 Kasuga-Koen, Kasuga, Fukuoka 816-8580, Japan*
[b] *Department of Applied Science for Electronics and Materials, Graduate School of Engineering Science, Kyushu University, 6-1 Kasuga-Koen, Kasuga, Fukuoka 816-8580, Japan*

ARTICLE INFO

Article history:
Received 16 March 2009
Received in revised form 18 May 2009
Accepted 3 June 2009
Available online 11 June 2009

Keywords:
Laser irradiation
Laser ablation
Silver
Nanoparticles
Nanocrystals
Polyvinylpyrrolidone

ABSTRACT

We report unusual laser-induced shape conversions of silver nanoparticles dispersed in polyvinylpyrrolidone (PVP) aqueous solutions. Silver nanocrystals such as nanoplates and nanorods were formed using laser irradiation for colloidal silver nanoparticles prepared using laser ablation in aqueous solutions of PVP. Differing from the nanocrystal formation observed in neat water and halide solutions, which were induced by weak laser or fluorescent-light irradiation, the nanocrystal formation in PVP solutions was induced by strong laser irradiation. On the other hand, nanocrystal formation was not observed in polyvinylalcohol (PVA) solutions, in which fusion of nanoparticles were prominent. It is proposed that the nanocrystals were formed from fragmented nanoparticles protected by PVP via a ripening process.

1. Introduction

During metal nanoparticle synthesis, shape control is strongly required to provide characteristic optical properties differing from those of bulk metals. Syntheses of anisotropic-shaped particles such as nanorods and nanoprisms are of particular interest because their optical properties are more sensitive to changes in their size or aspect ratio than those of spherical particles. Moreover, the electronic field induced by plasmon excitation is more concentrated at corners of anisotropic-shaped nanoparticles than on spherical surfaces of isotropic-shaped nanoparticles, which will be useful to design strong photon-molecule coupling field such as SERS substrates. The synthesis of anisotropic-shaped metal nanoparticles is typically performed using chemical reduction methods in which various synthesis parameters such as the concentration of reagents, temperatures (increasing rate), and addition of oxidants are controlled precisely [1,2].

On the other hand, photo-irradiation is recently interested as an alternative shape control technique. Shape control of metal nanoparticles using photo-irradiation has been firstly presented by Jin et al., revealing that fluorescent-light irradiation for spherical silver nanoparticles led to the formation of silver nanoprisms [3]. They also demonstrated that the nanoprism size is controllable according to the irradiation light wavelength [4]. Differing from strong laser irradiation for metal nanoparticles, which cause nanoparticles' fragmentation or fusion [5], their findings suggest that complex shape control of metal nanoparticles, such as that performed using chemical synthesis, is possible using photo-irradiation techniques. Therefore, further investigations of photo-induced shape changes of metal nanoparticles should be conducted.

The laser ablation technique in a liquid produces proper metal nanoparticle samples to facilitate investigation of their photophysical and photochemical properties. As Fojtik and Henglein first demonstrated [6], laser ablation of a metal plate immersed in water or organic solvents causes formation of colloidal metal nanoparticles. A remarkable and advantageous feature of nanoparticles prepared using this technique in contrast to those prepared using chemical synthesis is their absence of uncontrolled byproducts, such as ions and protective reagents, in the solutions. Consequently, it was possible to investigate chemical properties of nanoparticles without the influence of those substances [7,8]. If we add a reagent to a solution, then we can clarify the influences of that additive [9–11].

In former studies, we revealed that weak intensity (non-focused) laser irradiation for silver colloids prepared using laser ablation in neat water caused the formation of well-faceted silver nanocrystals such as nanoprisms and nanorods [12]. In addition, photo-induced formation of nanocrystals was enhanced by halides (NaCl, KCl, $MgCl_2$, NaI, KI): nanocrystal formation resulted from fluorescent- or xenon-light irradiation in the halide solutions [13,14]. As the formation mechanism of nanocrystals in the halide solutions, we propose that the shape conversions occur via silver

---

* Corresponding author. Tel.: +81 92 583 7816; fax: +81 92 583 7816.
E-mail address: ta-tsuji@cm.kyushu-u.ac.jp (T. Tsuji).

1010-6030/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2009.06.001

ions produced by halogen etching, because AgX_2^- (X = Cl, I) was detected in the solutions after the addition of the halides. In neat water, we assumed that silver ions generated by etching using impurities and those generated from the oxidized layer on the surface of nanoparticles played an identical role.

In this article, we report photo-induced nanocrystal formation of a different type observed in silver nanoparticles prepared using laser ablation in a liquid. In a previous work, we conducted laser ablation of silver plates immersed in polyvinylpyrrolidone (PVP) aqueous solutions to elucidate effects of PVP on the size, formation efficiency, and stability of produced nanoparticles [11]. In that work, to reduce the size of prepared silver nanoparticles, we also conducted additional laser irradiation for the colloids at intensities that was much stronger than the moderate laser or fluorescent-light irradiation conducted in neat water and halide solutions. The results revealed that PVP enhanced fragmentation because of its protective effects. For this study, we conducted more extensive and precise examinations of additional laser irradiation effects on the shape of silver colloids in PVP solutions. Results show that nanocrystal formation had been caused by laser irradiation in addition to the fragmentation.

2. Experiments

The preparation of silver colloids and laser irradiation for the produced colloids were conducted using the same procedure as that reported elsewhere [12–14]. It has been revealed that the formation efficiency of silver colloids by laser ablation in water was higher using 1064-nm laser light than using 355-nm laser light [15,16]. On the other hand, silver colloids absorb 355-nm laser light more efficiently than 1064-nm laser light. For that reason, silver colloids were prepared using laser ablation of a silver plate using 1064-nm laser light, and then the silver plate was removed and laser irradiation for the colloids was conducted using 355-nm laser light.

A silver plate (99.99%; The Nilaco Corp.) was set in a quartz cell containing 5 mL neat water or PVP solution at various concentrations. The molecular weights of PVP used for this study were 10,000, 40,000, and 360,000, which are designated respectively hereinafter as PVP-10K, PVP-40K, and PVP-360K. The PVP concentration was 0.5–18 mM; typical experiments were conducted at around 6 mM for all PVPs because the stability of colloids and the viscosity of samples, which affect TEM sample preparation, were well balanced.

Laser ablation was conducted using 1064-nm laser light of a Nd:YAG laser (GCR-100; Spectra-Physics) at 12 mJ/pulse for 10 min. The pulse duration and the repetition rate of the laser pulses were, respectively, 8 ns and 10 Hz. Spherical nanoparticles with the diameter from 5 to 80 nm were obtained (Fig. 1).

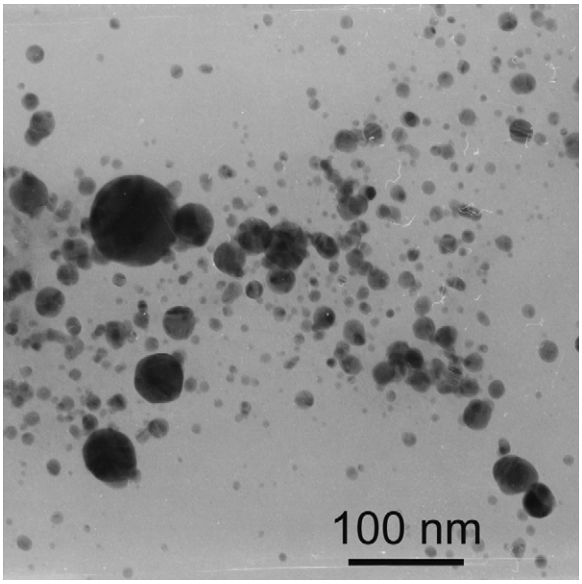


Fig. 1. The source silver nanoparticles prepared by laser ablation of a silver plate in a 6 mM PVP-40K aqueous solution. The average diameter and the standard deviation of the produced silver nanoparticles were, respectively, 18 and 10 nm.

Laser irradiation of the produced colloids was conducted using focused 355-nm laser light at 12 mJ/pulse for 10 min. The laser beam was focused just below the air–water interface of the solutions. During laser irradiation weak optical emissions were observed at the laser-irradiated spot. The laser fluence at the focal spot was ca. 36 J/cm^2. The typical experiments were conducted in the air atmosphere. When laser irradiation was conducted in N_2 or O_2 atmosphere, bubbling of N_2 or O_2 gas into the colloidal solutions was started 15 min before the laser irradiation and it was continued during the laser irradiation. The solutions were stirred during the laser irradiation. The nanoparticles were analyzed using a UV–vis spectrometer (UV-2450; Shimadzu Corp.) and TEM (JEM2100FX; JEOL).

3. Results

Fig. 2 depicts UV–vis spectra of silver colloids in a solution of PVP-40K at 6 mM before and after laser irradiation. A sharp plasmon band attributable to silver nanoparticles was observed around 400 nm. Strong absorption in less than 220 nm results from PVP. After laser irradiation, the plasmon band intensity was decreased. The decrease in the absorption by laser irradiation must be attributable to photo-induced coagulation of colloidal particles [17]. On the other hand, shape changes of the plasmon bands such as new peaks and shoulders were not observed.

In TEM images of the nanoparticles after laser irradiation, we detected remarkable products. As shown in Fig. 3 for 6 mM PVP-40K solution, various shapes and sizes of nanocrystals, such as prism (a), cube (b), rod (c), hexagonal plate (d), and large plate (e) were observed in addition to fragmented nanoparticles. The ED patterns (f) showed that the nanocrystals were composed of silver. Such nanocrystal formation was detected in PVP-40K solution at the concentrations of 1 mM and higher, although the exact lower limit of the PVP concentration above which nanocrystal formation occurs was uncertain. In 0.5 mM PVP solution, it was significantly difficult to find nanocrystals. On the other hand, fusion of sil-

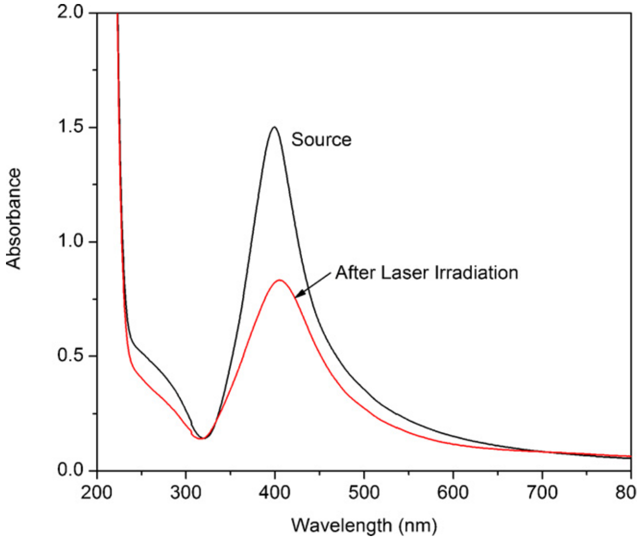


Fig. 2. UV–vis spectra of silver colloids in a 6 mM PVP-40K solution before and after laser irradiation at 355 nm.

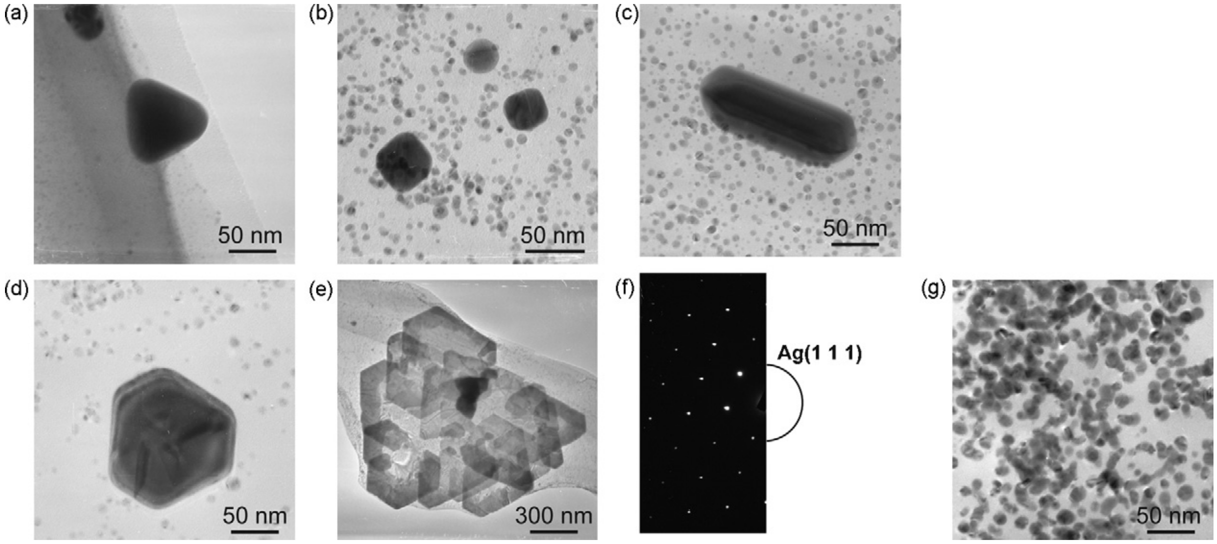


Fig. 3. (a)–(e) TEM images of silver nanocrystals with various shapes generated using laser irradiation for spherical silver nanoparticles prepared using laser ablation in 6 mM PVP-40K solution. (f) An SAED pattern of (e). (h) Fused silver nanoparticles observed in a 0.5 mM PVP-40K solution.

ver nanoparticles (Fig. 4g) was more prominent at 0.5 mM than that at 1 mM and higher, consistent with the result of the former study [11]. While the formation efficiency of nanocrystals could not be quantitatively estimated, because of the low concentrations of the silver colloids and TEM limitations, the amounts of the nanocrystal formed in PVP-40K solutions at the concentrations of 1 mM and higher were almost identical with those observed in halide solutions [14]. It must be noted that no indications of the formation of the anisotropic-shaped nanocrystals were observed in the UV–vis spectra. This discrepancy must be attributable to low concentration of the nanocrystals and multiplicity of their shape.

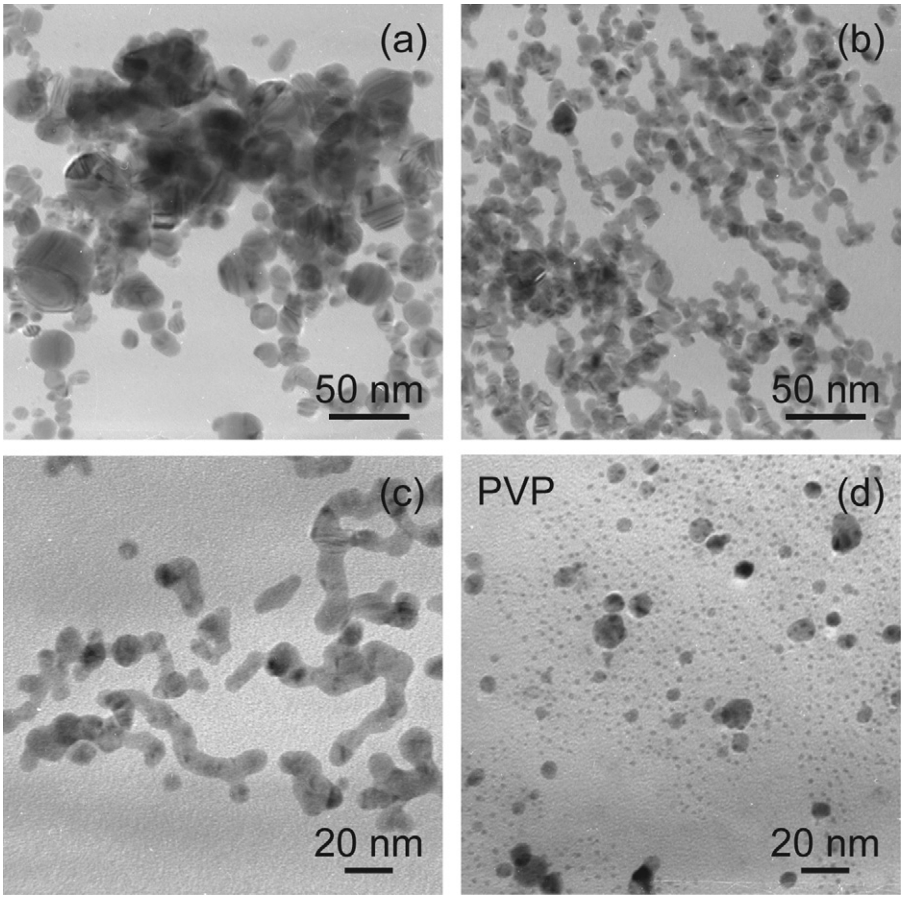


Fig. 4. TEM images of silver nanoparticles dispersed in PVA solutions. (a) Source particles prepared by laser ablation in a 6 mM PVA-2K solution, and (b) particles after laser irradiation at 355 nm for 10 min. (c) A magnified image of particles in a 6 mM PVA-2K solution after laser irradiation to compare the morphology of the particles with (d) those formed in a 6 mM PVP-40K solution.

The nanocrystal formation in the PVP solutions has been unexpected. Differing from halides which can etch silver nanoparticles, PVP is an inert protective polymer for silver nanoparticles. Furthermore, the laser irradiation conditions used in the present study are quite different from those used in the previous study. In the present experiments, photo-irradiation was conducted using strong focused laser irradiation (36 J/cm^2, focused). On the other hand, for colloids in water and halide solutions, photo-irradiation was conducted using lower intensity laser (50 mJ/cm^2, non-focused), fluorescent tube (5×10^{-2} mW/cm^2), or xenon lamp (6×10^{-2} mW/cm^2) irradiation [12]. Using strong laser intensity (36 J/cm^2, at the focal point), only fragmentation and fusion of nanoparticles were observed in water and halide solutions [12,18]. Therefore, to reveal the role of photo-irradiation in the present system, we conducted weak laser irradiation (50 mJ/cm^2, non-focused) for silver colloids in PVP solutions. Remarkably, no crystal formation was observed in PVP solutions that had been irradiated at the lower intensity. This finding suggests that the mechanism of photo-induced formation of nanocrystals in PVP solutions differed from that in water and halide solutions, and must be attributed to processes that are caused by strong laser irradiation for silver colloids.

The same experiments were also conducted for silver colloids in PVP-10K and PVP-360K and polyvinylalcohol (PVA; M.W. 2000, (PVA-2K)) solutions. The nanocrystal formation was observed in those PVPs, and no molecular weight dependencies of the formation efficiency and the morphology were observed. On the other hand, no crystals were observed in PVA-2K solutions. Alternatively, as shown in Fig. 4a and b, although the particle size was decreased by laser irradiation, the nanoparticles in PVA solutions were fused with each other and formed network structures. In addition, the comparison of the morphology of nanoparticles in 6 mM PVA-2K solution (Fig. 4c) and that of nanoparticles in 6 mM PVP-40K solution (Fig. 4d) revealed that small fragmented nanoparticles less than ca. 5 nm, observed in the PVP-40K solutions, were not observed in the PVA-2K solutions. Such differences in the morphology of colloidal particles after laser irradiation were also observed in the UV–vis spectra. As shown in Fig. 5, the shape of the plasmon band of silver colloids prepared in PVP-2K became more broader than that of colloids prepared in PVP-40K after laser irradiation. The more remarked fusion of nanoparticles in the PVA-2K solutions than that in the PVA-40K solutions can be explained on the basis of the lower protective effect of PVA-2K than that of PVA-40K. Upon laser irradiation for colloidal particles, both fragmentation and fusion of nanoparticles occur. It is also possible that a particle fragmented or fused by a laser pulse are repeatedly fragmented and fused by following laser pulses [19]. If a protective reagent was added into colloidal solutions, the fragments are protected by the reagent and the fusion is reduced, resulting in the formation of smaller nanoparticles [5,11]. In other words, if protective efficiency of the reagent decreases, then the fusion increases. We have compared the stability of colloids prepared in PVA-2K with that prepared in PVP-40K and confirmed that colloids in PVA-2K showed coagulation more rapidly than colloids in PVP-40K. It is notable that the result of laser irradiation for PVA-2K solutions and that for thin (0.5 mM) PVP solutions indicate that the crystal formation was suppressed when fusion of nanoparticles is prominent.

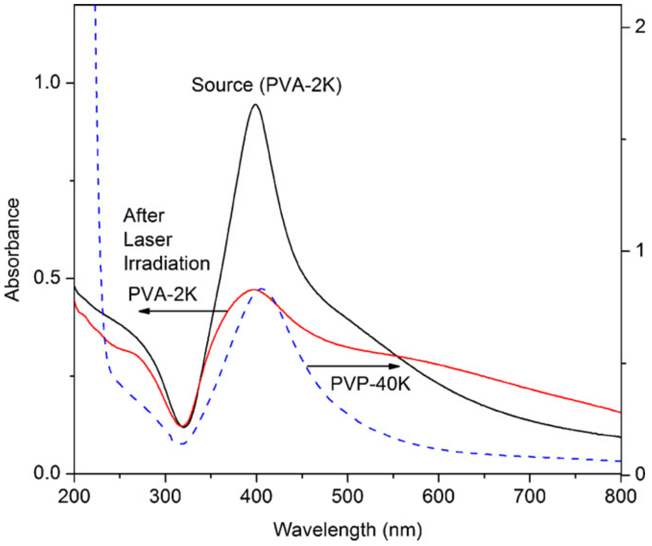


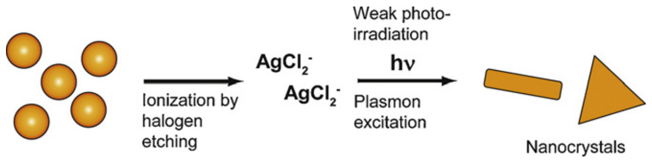
Fig. 5. UV–vis spectra of silver colloids in a 6 mM PVA-2K solution before and after laser irradiation (solid lines), and that in a 6 mM PVP-40K solution after laser irradiation (dashed line).

It must be noted that nanocrystals were formed when PVP was added after silver colloids had been prepared in neat water, indicating that PVP affects the nanocrystal formation at only the laser irradiation stage. On the other hand, one can expect that 355-nm laser ablation directly induces nanocrystal formation, because 355-m laser light can illuminate both silver plate and generate nanoparticles at the same time. In fact, nanocrystal formation was observed in the colloidal solution prepared using 355-nm laser ablation without the secondary laser irradiation. However, the lower formation efficiency of colloidal particles by 355-nm laser ablation than that by 1064-nm laser ablation made the observation of the products significantly difficult.

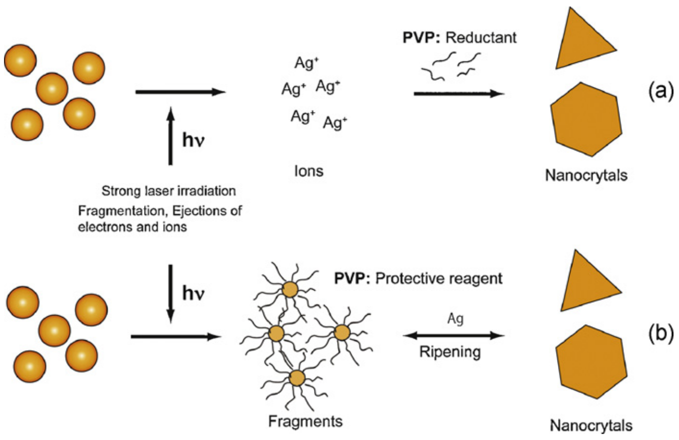
4. Discussion

As described previously, we observed photo-induced crystal formations of silver nanoparticles in water (containing oxidants) and in halide solutions [14]. For silver colloids in water and in halide solutions, it was revealed that photo-induced nanocrystal formation occurred via the intermediate silver ion state (Scheme 1) generated by chemical oxidization. Ordered shaped nanocrystals must be formed via thermal reduction of the silver ions, along with plasmon excitation; while influences of the plasmon excitation are still under investigation [14]. While the shapes and sizes of the nanocrystals in the PVP solutions resembled those observed in halide solutions, their formation mechanism will be different from that in the halide solutions, because PVP must not oxidize silver nanoparticles as halides do, and the nanocrystals in the PVP solutions were formed only under strong laser irradiation conditions in which only fragmentation and fusion were observed in the halide solutions.

Based on the fact that the nanocrystal formation in the PVP solutions was induced by strong laser irradiation for silver nanoparticles, several mechanisms of the shape conversions can be proposed. First, one can consider the case where the nanocrystals were constructed directly from silver atoms, clusters, and ions ejected from silver nanoparticles by strong laser irradiation. The role of PVP is a masking agent that covers some specific surfaces of a silver cluster and control orientation of crystal growth, as proposed for crystal formation by chemical syntheses [1,2]. However, from the fact that nanocrystals were formed in the halide solutions in which



Scheme 1. Proposed mechanism of the photo-induced nanocrystal formation in halide solutions.



Scheme 2. Proposed mechanism of the nanocrystal formation in PVP solutions induced by strong laser irradiation. (a) Reduction of mechanism and (b) ripening mechanism.

no masking agents were contained [12–14], it is strongly suggested that masking agents were not a necessary factor for nanocrystal formation of silver.

Second, it can be proposed that the nanocrystals were formed by chemical reduction of silver ions ejected by laser irradiation (Scheme 2a). Recently, Washio et al. reported that triangular silver nanoplates were produced by heating an aqueous solution of $AgNO_3$ and PVP [20]. They suggested that the slow reduction reactivity of PVP was a key condition to obtain triangular plates. It has been revealed that laser-induced fragmentation process of metal nanoparticles involves Coulomb explosion accompanying ejections of cationic clusters and metal ions along with electrons [21–23]. Therefore, it is suggested that silver ions are generated by laser irradiation for silver nanoparticles, and these ions would interact with PVP, then the weak reduction reaction brought by PVP will lead to nanocrystal formation. In fact, the zeta potential of the silver nanoparticles in PVP solutions was raised from −6 to −1 mV by laser irradiation, as was observed for gold nanoparticles [21]. To make further confirmation of this mechanism, we have investigated influences of scavengers on the crystal formation. The reaction of silver ions ejected by laser irradiation will be affected by the presence of scavengers such as oxygen molecules. As Werner et al. proposed [24], oxygen molecules solved in colloidal solution quench electrons ejected by laser irradiation to form oxygen anions which subsequently neutralize cationic clusters and metal ions. Therefore, it is expected that the formation efficiency of nanocrystals in a PVP solution saturated with oxygen will be lower than that in a PVP solution saturated with nitrogen, because oxygen anions neutralize the silver ions. To confirm this assumption, we have conducted laser irradiation for silver colloids which were settled in a N_2 or O_2 atmosphere. From TEM observations, no significant differences in the formation efficiency of the nanocrystals were detected between colloids in N_2 or O_2 atmosphere, suggesting that silver ions are not involved in the nanocrystal formation process.

The third possible mechanism of the nanocrystal formation was based on the fact that the formation of nanocrystals was prominent when fusion of nanoparticles was suppressed. It is well-known that stability of atoms in a nanoparticle decreases with the decrease in the particle size. Such unstable atoms can leave from a nanoparticle and move to the other nanoparticles. The repeating of the transportation of silver atoms results in the formation of nanoparticles with stable size and shapes. Such transformation processes observed in nano-sized colloids are known as “ripening”. As a result of a ripening process, it will be possible that nanocrystals are formed as stable shaped products. In fact, Stoeva et al. have shown that gold nanocrystals were formed from mono-dispersed gold nanoparticles of ca. 5 nm [25] via a ripening process. Consequently, it will be possible that the nanocrystals in the PVP solutions were formed from the small nanoparticles, which were generated by laser irradiation cooperated by the protective effect of PVP, via a ripening process (Scheme 2b). The fact that the size of the nanocrystals was larger (stable size) than the fragmented nanoparticles also supports this ripening mechanism. On the other hand, in the PVA solutions and in the thin PVP solutions, the nanocrystal formation would be suppressed because of the lowering of the amount of the fragmented particles. At present we conclude that this ripening mechanism is the preferable mechanism of the laser-induced nanocrystal formation. From our results, the critical size which determine whether the ripening process occurs in silver nanoparticles or not will be ca. 5 nm.

On the other hand, high protective effects will not be the sufficient factor of the nanocrystal formation. For example, no crystal formation has been observed in silver colloids dispersed in surfactants such as sodium dodecyl sulfate (SDS), although the surfactants suppressed the laser-induced fusion [9,19]. These facts suggest that the interaction between protective reagents and silver nanoparticles and/or silver atoms released from them should be an important factor of promotion of the ripening process. To confirm these assumptions, quantitative and theoretical analyses of binding energy (and its size-dependence) of metal atoms in a nanoparticles, and protective effect of reagents for metal nanoparticles should be performed in the future works.

Finally, it must be noted that the results of the present study also provide some insights for the formation mechanism of nanocrystal in halide solutions. For the nanocrystal formation in halide solutions, we have assumed that plasmon excitation controls the orientation of crystal growth and produces the well-faceted nanocrystals [14]. On the other hand, for the nanocrystal formation in PVP solutions, it is suggested that well-faceted nanoparticles would be formed via the spontaneous transformation (ripening) process which is a characteristic of nano-sized metal particle. In other words, plasmon excitation will not be a necessary factor of the crystal formation in PVP solutions. Consequently, it will be possible that halides produce small nanoparticles via oxidative etching and that those small nanoparticles will be transformed to the nanocrystals via a ripening process. In that case, a possible role of photo-irradiation will be the promotion of the halide etching. The confirmation of such mechanism is in progress. Through those works using metal nanoparticles prepared by laser ablation with controlled adducts, intrinsic properties of metal nanoparticles will be revealed.

5. Conclusion

Strong laser irradiation for silver colloids dispersed in PVP aqueous solutions induced the formation of well-faceted nanocrystals. Differing from that in halide solutions, nanocrystal formation was not promoted by weak laser irradiation. On the other hand, in the thin PVP solutions and in the PVA solutions, in which nanocrystals were not observed, fusion of nanoparticles was prominent. We proposed that the nanocrystals will be formed via a ripening process from the fragmented small silver nanoparticles protected by PVP.

Acknowledgments

The authors thank Prof. Fumitaka Mafuné for providing useful experimental information related to the laser-induced ejections of electrons and ions from metal nanoparticles. We also thank Prof. Naoki Toshima for providing useful information about chemical properties of PVP. KAKENHI (Grant-in-Aid for Scientific Research) on Priority Area “Strong Photon-Molecule Coupling Fields (No. 470)” and KAKENHI B (No. 19310064) from the Ministry of Education, Culture, Sports, Science and Technology of Japan, and by the Joint Project of Chemical Synthesis Core Research Institutions.

References

[1] C.J. Murphy, T.K. San, A.M. Gole, C.J. Orendorff, J.X. Gao, L. Gou, S.E. Hunyadi, T. Li, J. Phys. Chem. B 109 (2005) 13857.

[2] Y.N. Xia, N.J. Halas, MRS Bull. 30 (2005) 338.

[3] R.C. Jin, Y.W. Cao, C.A. Mirkin, K.L. Kelly, G.C. Schatz, J.G. Zheng, Science 294 (2001) 1901.

[4] R.C. Jin, Y.C. Cao, E.C. Hao, G.S. Metraux, G.C. Schatz, C.A. Mirkin, Nature 425 (2003) 487.

[5] H. Fujiwara, S. Yanagida, P.V. Kamat, J. Phys. Chem. B 103 (1999) 2589.

[6] A. Fojtik, A. Henglein, Ber. Bunsen-Ges. Phys. Chem. Chem. Phys. 97 (1993) 252.

[7] M. Prochazka, J. Stepanek, B. Vlckova, I. Srnova, P. Maly, J. Mol. Struct. 410 (1997) 213.

[8] J.P. Sylvestre, S. Poulin, A.V. Kabashin, E. Sacher, M. Meunier, J.H.T. Luong, J. Phys. Chem. B 108 (2004) 16864.

[9] F. Mafune, J. Kohno, Y. Takeda, T. Kondow, H. Sawabe, J. Phys. Chem. B 104 (2000) 9111.

[10] J.P. Sylvestre, A.V. Kabashin, E. Sacher, M. Meunier, J.H.T. Luong, J. Am. Chem. Soc. 126 (2004) 7176.

[11] T. Tsuji, D.H. Thang, Y. Okazaki, M. Nakanishi, Y. Tsuboi, M. Tsuji, Appl. Surf. Sci. 254 (2008) 5224.

[12] T. Tsuji, T. Higuchi, M. Tsuji, Chem. Lett. 34 (2005) 476.

[13] T. Tsuji, Y. Okazaki, T. Higuchi, M. Tsuji, J. Photochem. Photobiol. A 183 (2006) 297.

[14] T. Tsuji, Y. Okazaki, M. Tsuji, J. Photochem. Photobiol. A: Chem. 194 (2008) 247.

[15] T. Tsuji, K. Iryo, N. Watanabe, M. Tsuji, Appl. Surf. Sci. 202 (2002) 80.

[16] T. Tsuji, K. Iryo, Y. Nishimura, M. Tsuji, J. Photochem. Photobiol. A: Chem. 145 (2001) 201.

[17] K. Kimura, J. Phys. Chem. 98 (1994) 11997.

[18] T. Tsuji, N. Watanabe, M. Tsuji, Appl. Surf. Sci. 211 (2003) 189.

[19] A. Takami, H. Kurita, S. Koda, J. Phys. Chem. B 103 (1999) 1226.

[20] I. Washio, Y.J. Xiong, Y.D. Yin, Y.N. Xia, Adv. Mater. 18 (2006) 1745.

[21] K. Yamada, Y. Tokumoto, T. Nagata, F. Mafune, J. Phys. Chem. B 110 (2006) 11751.

[22] A. Pyatenko, M. Yamaguchi, M. Suzuki, J. Phys. Chem. B 109 (2005) 21608.

[23] Y. Takeda, T. Kondow, F. Mafune, Nucleosides Nucleotides Nucleic Acids 24 (2005) 1215.

[24] D. Werner, S. Hashimoto, T. Tomita, S. Matsuo, Y. Makita, J. Phys. Chem. C 112 (2008) 1321.

[25] S.I. Stoeva, V. Zaikovski, B.L.V. Prasad, P.K. Stoimenov, C.M. Sorensen, K.J. Klabunde, Langmuir 21 (2005) 10280.