Rapid Synthesis and Characterization of Polyvinylpyrrolidone-Protected Silver Nanoparticles by Heating Method

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Silver nanoparticles were successfully synthesized by heating mixed solutions of silver nitrate, hexamethylenetetramine (HMTA), and polyvinylpyrrolidone (PVP) at 80°C for 7 min. The characterization of as-prepared silver nanoparticles were carried out by measuring ultraviolet-visible (UV-vis) and FTIR spectra, and images of transmission electron microscopy (TEM). The results of extinction spectra and TEM images indicated that the higher concentration of PVP and higher MW of PVP decrease the particle size of silver nanoparticles produced in the present systems. In addition, the interaction between silver atoms and oxygen atoms in the carbonyl group of PVP was also discussed by FTIR spectroscopy. It can be concluded that this heating method at 80°C is very useful for the preparation of stable and homogeneous silver nanoparticles in the present systems. [DOI: 10.1380/ejssnt.2015.431]

Keywords: Silver nanoparticle; Polyvinylpyrrolidone; Heating method; Extinction spectra; Transmission electron microscopy

I. INTRODUCTION

Metal nanoparticles have a characteristic surface plasmon absorption band in the visible region. In late years the development of new devices using phenomena unique to metal nanoparticles is pushed forward, and particularly it is expected that devices using surface plasmon resonance will find practical applications in various fields including information and communication, medical care, environment and energy. Since silver nanoparticles have good electric conductivity and optical properties, expected fields of applications include such as bio-sensing and surface-enhanced Raman scattering [1–4].

The most popular preparative method of metal nanoparticles would be the chemical reduction of metal ions [5–8]. The use of a stabilizer is a known technique to control metal colloidal flocculation. Polyvinylpyrrolidone (PVP) is popularly used as a polymer stabilizer. Zhu et al. have reported the synthesis of PVP-protected silver nanoparticles [9]. It is thought that PVP forms silver ions and complex compounds, and strongly adheres to silver nanoparticles. It has been well known that the polymer such as PVP causes dispersion and flocculation [10]. These two effects appear depending on the amount of polymer added in the colloidal dispersion systems. If the additive amount is small, bridging flocculation occurs and then this type of flocculation occurs when two particles with rough-surfaced adsorption layers come close to each other, whereby one adsorbed layer is adsorbed to the other particle. As the additive amount increases, repulsion occurs between the two particles when come close to each other and dispersion occurs. It has been known that crosslink of silver nanoparticles occurs more easily with a smaller addition as the molecular weight of polymer becomes greater.

This paper presents a heating method to synthesize silver nanoparticles rapidly within 7 min. The synthesis of silver nanoparticles are performed using hexamethylenetetramine (HMTA) as a reductant and PVP as a stabilizer, and the as-prepared silver nanoparticles are characterized using ultraviolet-visible (UV-vis) and FTIR spectroscopic methods, and transmission electron microscopy (TEM).

II. EXPERIMENTAL

Silver nitrate (Wako Pure Chemical Industries, Ltd.), polyvinylpyrrolidone (PVP) (MW: 10000 and 55000) from Sigma Aldrich and PVP (MW: 40000) from Wako Pure Chemical Industries Ltd., and hexamethylenetetramine (HMTA) from Merck were used without further purification. Distilled water of 50 mL was added in a 200 mL beaker, which was placed in a hot water bath at 80°C on a hot stirrer. PVP, AgNO3 (0.85 g), and HMTA (0.04 g) were added in the beaker and agitated at 80°C. At every 1 min, a solution of 500 mL was transferred to a test tube and diluted 10 times by adding distilled water of 4.5 mL. This operation was repeated for 7 min to prepare silver colloidal solutions. The silver colloidal products were separated by centrifugation and washed with distilled water twice.

In order to characterize as-prepared silver nanoparticles, extinction spectra were measured by using UV-vis spectrophotometer (Shimadzu, UV-1800) with a quartz cell of 1 cm. FTIR spectra were also measured to confirm the interaction between silver nanoparticles and PVP using an FTIR spectrometer (Perkin-Elmer Spectrum-One B). Transmission electron microscopy (TEM) was performed with a JEOL electron microscope (model JEM-3010 VII). Samples were prepared by dispersing a drop of dilute solution containing a suspension of as-prepared silver nanoparticles on a copper grid with a carbon foil, and the solvent was evaporated under reduced pressure at room temperature in an incubator. Approximately 200 particles were counted and then size distribution of silver nanoparticles was determined.

III. RESULTS AND DISCUSSIONS

Figure 1 shows extinction spectra at [PVP] = 1.0×10⁻⁴ M (MW: 40000, 0.2 g). After 1 min, an extinction maximum was observed at 421 nm. With increasing reaction time, the peak intensity of this band was increas-
FIG. 1. Extinction spectra of as-prepared silver nanoparticle solutions after 1, 2, 3, 4, 5, 6, and 7 min. \([\text{PVP}] = 1.0 \times 10^{-4}\text{ M (MW: 40000, 0.2 g)}\).

ing and then, this peak position shifted to longer wavelength region (425 nm after 3 min, 449 nm after 5 min, and finally to 472 nm for 7 min). The formation of silver nanoparticles is also supported by the fact that the peak assignable to the surface plasmon band of silver nanoparticles is appearing around 420 nm. As shown in Fig. 1, a small extinction peak around 300 nm was observed and its peak intensity was increasing with reaction time; this peak has been known to be an interband of silver [11]. The strong absorption below 250 nm comes from PVP [12]. Jin et al. have reported that triangular silver nanoparticles have a weak extinction peak at 335 nm [13]. Thus, the shoulder around 340 nm may suggest the formation of triangular silver nanoparticles. These facts correspond to the red-shift of extinction maximum assignable to the surface plasmon resonance band, and after 7 min various types of silver nanoparticles may form and agglomeration of particles may occur rapidly.

Figure 2 shows TEM images of PVP protected silver nanoparticles at \([\text{PVP}] = 1.0 \times 10^{-4}\text{ M (MW: 40000, 0.2 g)}\). The average particle diameter of silver nanoparticles after 1, 3, 5, and 7 min was 11±3, 13±3, 19±5, and 76±12 nm, respectively. It can be confirmed that the particle size is increasing with reaction time. After 7 min, not only spherical and polygonal but also triangular particles were observed in Fig. 2.

Moreover, the relationship of both extinction intensity and average particle size against reaction time is also shown in Fig. 3; this result shows that the red shift of the plasmon peak corresponds to the increase of particle size of silver nanoparticles with reaction time. This was mainly due to the fact that the particles grow with the reaction time and that longer reaction time can also promote the particle aggregation to form larger particles, leading to a red shift of the extinction peak [14].

Figure 4 shows the extinction spectra of silver nanoparticles produced under different of additive amounts of PVP (MW: 40000) at reaction time of 7 min. The extinction peak at 472 nm observed with the additive amount of PVP (MW: 40000, 0.2 g, \([\text{PVP}] = 1.0 \times 10^{-4}\text{ M}) shifted to the short wavelength region with the increase in the additive amount of PVP. The extinction peak was observed at 447 nm with 0.4 g \([\text{PVP}] = 2.0 \times 10^{-4}\text{ M})], at 435 nm with 0.6 g (\([\text{PVP}] = 3.0 \times 10^{-4}\text{ M}), and at 421 nm with 0.8 g \([\text{PVP}] = 4.0 \times 10^{-4}\text{ M})\), respectively. We can see that with the increasing PVP-concentration, there is a blue-shift in the extinction peak of the spectra. It has been well known that the maximum extinction peak shift to longer wavelength when the particle size becomes larger [14]. With this blue-shift of peak wavelength, it can be considered that the increasing of additive amounts of PVP (PVP concentration) prevent the growth of silver nanoparticles and lead to decreasing particle size [15–17]. Moreover, at the additive amount of PVP (0.2 g, \([\text{PVP}] = 1.0 \times 10^{-4}\text{ M})\), a broad and weak band around 800 nm was appearing as shown in Fig. 4 (d). Jin et al. [13] have also reported that the triangular silver nanoparticles produced by ultraviolet-irradiation have a strong peak at 670 nm in
FIG. 4. PVP-concentration dependence of extinction spectra of the colloidal silver nanoparticle solutions after 7 min. Additive amount of PVP (MW: 40000); (a) 0.8 g, [PVP] = 4.0×10^{-4} M, (b) 0.6 g, [PVP] = 3.0×10^{-4} M, (c) 0.4 g, [PVP] = 2.0×10^{-4} M, and (d) 0.2 g, [PVP] = 1.0×10^{-4} M.

FIG. 5. PVP-concentration dependence of TEM images of the colloidal silver nanoparticle solutions after 7 min. PVP (MW: 40000); (A) 0.4 g, [PVP] = 2.0×10^{-4} M, (B) 0.6 g, [PVP] = 3.0×10^{-4} M, and (C) 0.8 g, [PVP] = 4.0×10^{-4} M.

FIG. 6. TEM images of the colloidal silver nanoparticle solutions after 7 min; (A) PVP (MW: 10000, 0.2 g, [PVP] = 1×10^{-4} M) and (B) PVP (MW: 55000, 0.55 g, [PVP] = 1×10^{-4} M).

extinction spectra. Thus, this result suggests that various nanoparticles including triangular nanoparticles, nanorod or other shapes of particles are formed in case of present systems.

We also measured TEM images of silver nanoparticles after 7 min for PVP (MW: 40000) to investigate the effect of PVP-concentration on the size and shape of silver nanoparticle. The TEM images in Fig. 5 also indicated that the size of silver nanoparticles is dependent on the additive amount of PVP (PVP concentration). For the additive amount of PVP (MW: 40000) 0.4, 0.6, and 0.8 g, the average diameters of silver nanoparticles were 83±12, 76±9, and 48±8 nm, respectively; this result also indicates that with increasing the additive amount of PVP, the particle size of silver nanoparticles becomes smaller and exist as monodispersed state without aggregation and then corresponds to the behavior of extinction maximum peak shift in extinction spectra as discussed in Fig. 4. Based on the results of the relationship between extinction maximum and silver nanoparticle size, it can be shown that the peak wavelength shifts to shorter wavelength as the concentration of PVP increases and the size of silver nanoparticles decreases.

Furthermore, to investigate the effect of MW of PVP on the size and the shape of silver nanoparticles, we compared TEM images at [PVP]=1.0×10^{-4} M for PVP (MW: 10000, 0.2 g) and PVP (MW: 55000, 0.55 g); the results are shown in Fig. 6. When we used PVP (MW: 10000), the average particle size of silver nanoparticles synthesized was 114±15 nm and their shapes were spherical or polygonal. On the other hand, the particle size for PVP (MW: 55000) was 62±11 nm and the shapes of silver particles were polygonal and rod-shaped. As shown in Fig. 2(D), the particle size for PVP (MW: 10000, 0.2 g) was 76±12 nm. With increasing MW of PVP used in this work, the average particle size also decreased; this fact may suggest that the increase of MW is essentially the same with the increase of PVP concentration. In summary, based on the present results of extinction spectra and TEM images, the particle aggregation is suppressed at the higher concentration of PVP and the higher MW of PVP, so that smaller nanoparticles with a plasmon peak at shorter wavelength region are formed. These facts support that PVP molecules play an important role as capping and protecting agents.

In order to investigate interaction between silver nanoparticles and PVP, namely, to prove the formation of PVP-protected silver nanoparticles, we measured FTIR spectra of the present systems (Fig. 7). In Fig. 7, the comparison of FTIR spectra for only PVP system (Fig. 7(a)) and PVP-silver nanoparticle system (Fig. 7(b)) is very significant. As shown in Fig. 7(a) and (d), the IR band at 1170 cm^{-1} assignable to C-N vibrational mode of PVP showed no wavenumber shift at all, while the C=O
stretches mode of PVP observed at 1663 and 1733 cm$^{-1}$ showed drastic difference of IR band intensity. Upon addition of silver nanoparticles to PVP system, the band intensity at 1733 cm$^{-1}$ was strengthened as shown in Fig. 7(d); this spectrum change indicates that the reaction of silver and PVP occurs and the oxygen atoms in the C=O stretching of PVP strongly interacts with Ag atoms and then coordination bond is formed. Moreover, although a new band at 1250 cm$^{-1}$ for silver nanoparticle-PVP system in Fig. 7(d) was also observed in this work, detail assignment for this vibrational mode is now in progress.

IV. CONCLUSIONS

In this paper, we succeeded to prepare PVP-protected silver nanoparticles by short-time heating method at 80°C and for 7 min. The results of extinction spectra and TEM images indicated that the higher concentration of PVP and higher MW of PVP decrease the particle size of silver nanoparticles produced in the present systems and PVP can act as protecting agents. In addition, the interaction between silver atoms and oxygen atoms in the carbonyl group of PVP was also discussed by FTIR spectroscopy. It can be concluded that this heating method at 80°C is very useful for the preparation of stable and homogeneous silver nanoparticles in the present systems.

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