

Effect of sodium carbonate on the formation of colloidal silver particles by a reduction reaction of silver ions with PVP

Chang Young Kim, Byung Moo Kim, Sung Hoon Jeong^a and Sung-Chul Yi*

Department of Chemical Engineering, Hanyang University, Seoul 133-791, Korea

^aDepartment of Fiber & Polymer Engineering, Hanyang University, Seoul 133-791, Korea

Silver nanoparticles were prepared by a polyol process of silver nitrate in the presence of Polyvinylpyrrolidone (PVP) with sodium carbonate as a reducing agent. The effect of the $\text{Na}_2\text{CO}_3/\text{AgNO}_3$ molar ratio and the PVP concentrations on the reduction rate of the silver ions and the particle size of the silver particles were investigated. The mean particle size decreases with increasing PVP in the solution, but increases with increasing molar ratio between Na_2CO_3 and AgNO_3 . To understand the silver particle formation mechanism, the evolution of particle size during the reaction was monitored by TEM and UV-visible absorbance techniques.

Key words: Silver, Nanoparticles, Polyol process, Sodium carbonate, PVP.

Introduction

Recently, chemical synthesis of silver nanoparticles has attracted much attention because of their potential applications in catalysis, surface-enhanced Raman spectroscopy, transparent conductive coatings, staining pigment for glasses and ceramics, electronic and antimicrobial materials [1-6]. For example, silver coated Al_2O_3 has been used to prepare a protective coating against corrosion and wear, as well as to improve the wetting of ceramics with metal melts [4]. Also, silica spheres coated with silver or gold nanoparticles have merited particular attention because silver or gold have intense plasmon responses and large scattering cross sections [5, 6]. Currently, there is a lot of interest in finding ways to produce dispersions of silver nanoparticles with respect to an industrial scale.

It is well known that the property of metal nanoparticles greatly depends on their size and shape. A great deal of study has been devoted to develop a simple and economical preparation strategy to create metal nanoparticles with well-controlled sizes and shapes [7, 8]. A number of methods such as the solution phase method [9, 10], hydrothermal synthesis [11], electrochemical synthesis [12], γ -irradiation [13, 14], and a sonochemical method [15] have been suggested to prepare metal nanoparticles. However, most preparation methods have a limitation in the preparation of highly concentrated metal nanoparticles having well-controlled size and shape with simple equipment. As a conse-

quence, these preparation methods are not suitable for large-scale manufacturing.

The polyol process was developed by Fiévet and co-workers as a simple and versatile route to preparing colloidal metal particles [16]. This process has been used widely to produce monodispersed fine metal particles. Generally, the primary reaction of this process involves the reduction of the precursor by a polymeric solvent at the boiling point. At the boiling temperature, metal ions can be transformed into metal atoms. Subsequent nucleation and growth of reduced metal species in the solution phase gives metal particles. In the majority of cases, to control the size of particles, a polymeric stabilizer was used. In a typical process, ethylene glycol and PVP are used as the solvent and polymer stabilizer. However, PVP can act not only as a stabilizer but also as a reducing agent [17]. Silvert et al. employed PVP to synthesize silver nanoparticles with 20 nm in diameter by reducing silver nitrate with a hot polyol solution [18]. In addition, the temperature-dependent reducing potential of polyol makes it ideal for the synthesis of colloidal particles over a broad range of sizes. Despite a number of publications in this area of research, the preparation of aqueous colloidal silver nanoparticles has not yet been reported.

In this study, in order to obtain a high concentration of silver colloidal dispersion in water, silver nanoparticles were prepared in the presence of the PVP as a stabilizing agent. To enhance the reduction of silver ions, sodium carbonate was used as a reducing agent. The resulting colloidal particles were characterized using TEM and a UV-visible spectrophotometer. On the basis of the experimental results, the effect of the reaction parameters such as PVP concentration and $\text{Na}_2\text{CO}_3/$

*Corresponding author:
Tel : +82-2-2220-0481
Fax: +82-2-2298-5147
E-mail: scyi@hanyang.ac.kr

AgNO₃ molar ratio on the evolution of silver particles size is explained. The formation process and reduction mechanism for the silver nanoparticles is also briefly discussed.

Experimental Procedure

Materials

All chemicals used in this investigation were reagents grade materials. Silver nitrate (99.8%, AgNO₃, Junsei chemical Co.) was used as a silver ion source. Polyvinylpyrrolidone (PVP K-15, MW 10,000, Junsei Chemical Co.) was used as a nucleation-prompting agent and stabilizer for silver nanoparticles. Sodium carbonate (99.0%, Na₂CO₃, Samchun Pure Chemical Co.) was used to reduce the silver ions. The water used in this study was de-ionized by Eco-RO&UP (Mirae Scientific Technology Co.), having 18.2 MΩ electrical resistivity.

Preparation of silver colloidal dispersion in water

The quasi-spherical colloidal silver particles were synthesized in a 250 ml three-neck round flask by the polyol process. The composition for each experimental condition is indicated in Table 1. 33.15 ml of AgNO₃ aqueous solution (0.62 M) was mixed with an ethanol/de-ionized water mixed solution containing PVP under mild stirring. After 30 minutes, the Na₂CO₃ was added into this solution. Finally, silver particles were formed by reduction of the silver ions by PVP under a nitrogen atmosphere as the solution was heated to a given temperature. In a typical process, the reaction was conducted at 100 for 300 minutes. After the reaction, a dark brown solution was obtained and contained at room temperature to prevent any structural change of the silver nanoparticles.

Characterization

To investigate the formation and the morphological properties of silver nanoparticles, transmission electron microscopy (TEM, Jeol-model JEM-2000EX II) was used. Silver particles for observation under the microscope were prepared by placing a drop of the colloidal

silver dispersion onto a standard microscope grid coated with a carbon film. The size distribution and mean particle size of the colloidal silver and the standard deviation of the particle population were determined from image analyses of the micrographs of these particles.

UV-visible absorption spectra of the colloidal silver dispersions in water were measured using a Shimadzu UV-1650PC double beam spectrophotometer. All the samples for the measurements of UV-visible spectra were diluted except for the samples used to investigate the changes of the UV-visible spectra during the nanoparticle formation.

Results

The reduction of silver ions was monitored by checking the time to complete the color evolution of the solution using UV-visible absorbance measurements. In the case of samples 2 and 6 in Table 1, the color of the precursor solution changed to a light brown color as reduction agent was added and then gradually became a dark brown color as the reaction proceeded. Figure 1 shows the evolution of the UV-visible absorption spectra of the colloidal silver during the reaction. Before the injection of the reducing agent, a very broad UV-visible spectrum band appeared. This spectrum showed that the particles were not formed at that time. The reduction of silver ions immediately started after addition of the reducing agent, and continued throughout the investigated reaction period, as indicated by the progressive increase in the intensity of the well-defined plasmon band at 398 nm.

The reduction mechanism of silver ions by Na₂CO₃ can be represented by the following steps [19]. First, Ag₂CO₃ is formed by combining of a carbonate ion and silver ions. Second, silver ions were reduced to metal because the carbonate ion was hydrolyzed and transformed into hydroxyl ions. As a result, the suspension would gradually become dark in color.

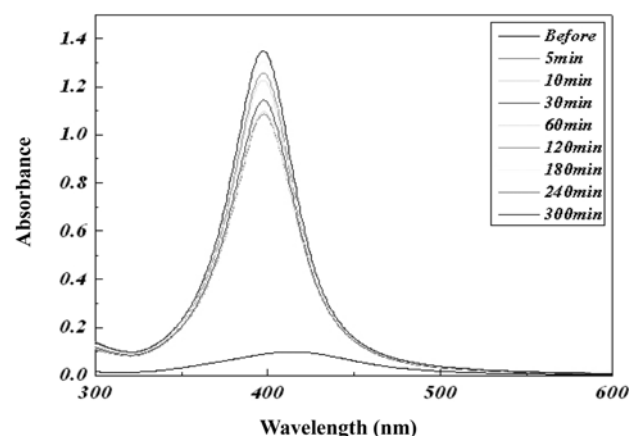


Fig. 1. UV-visible spectra of the colloidal silver at various times during the reaction.

Table 1. Experimental conditions and characteristics for colloidal silver. (S : stable, U : unstable)

Sample number	Molar ratio (Na ₂ CO ₃ /AgNO ₃)	Molar ratio (PVP/AgNO ₃)	Average diameter (nm)	Stability
# 1	0.6	0.16 × 10 ⁻² M	6.47	S
# 2	0.8	0.16 × 10 ⁻² M	7.87	S
# 3	1.0	0.16 × 10 ⁻² M	10.51	S
# 4	1.2	0.16 × 10 ⁻² M	25.83	U
# 5	0.6	0.32 × 10 ⁻² M	4.81	S
# 6	0.8	0.32 × 10 ⁻² M	5.72	S
# 7	1.0	0.32 × 10 ⁻² M	8.14	S
# 8	1.2	0.32 × 10 ⁻² M	24.76	U

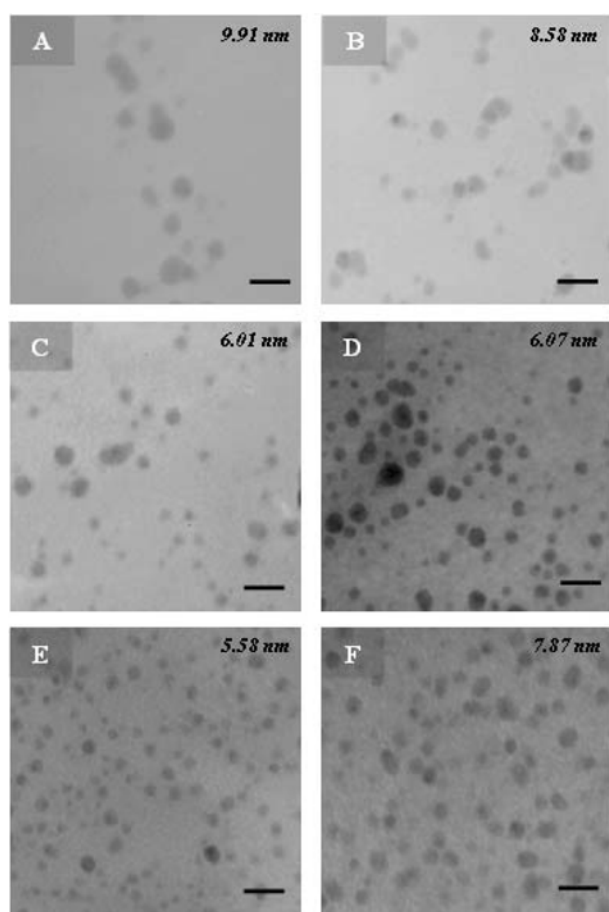


Fig. 2. TEM photographs of silver particles at different reaction times. (A: absence of Na_2CO_3 , B: 10 minutes, C: 60 minutes, D: 90 minutes, E: 180 minutes, F: 300 minutes, Scale bar: 20 nm)

Morphological evolution of silver particles was investigated by TEM. Figure 2-A shows a TEM photograph of the silver particles obtained in the absence of Na_2CO_3 under the conditions of sample 2 in Table 1. To investigate the effect of Na_2CO_3 on the formation of silver particles, samples were periodically taken after the addition of Na_2CO_3 and observed by TEM as shown in Fig. 2 B-F. In the absence of Na_2CO_3 , silver nanoparticles with a mean particle size of 9.91 nm were obtained. After the addition of Na_2CO_3 , smaller particles were obtained and the size of silver particles then increased with an increase in reaction time. The final product obtained, shown in Fig. 2 F, is composed of silver particles with a narrow size distribution and mean particle size of 7.87 nm. According to Mie's theory for the optical properties of metal colloids, the surface plasmon resonance band shifts to a longer wavelength when the particles size increases; however, at particles sizes between about 3 and 20 nm, there is not a strong dependence of the absorption spectra on particle size [20, 21].

To investigate the effect of Na_2CO_3 on the formation of silver particles, the molar ratio between Na_2CO_3 and AgNO_3 was varied from 0.6 to 1.2. With a higher

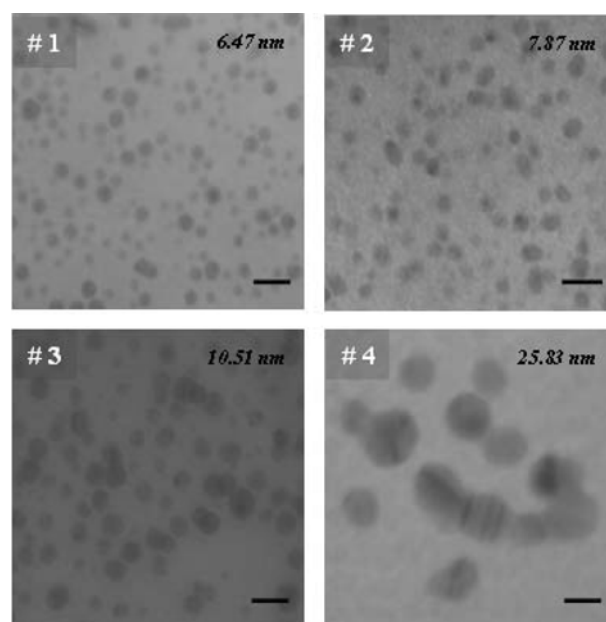


Fig. 3. TEM photographs of silver particles obtained using different molar ratio between Na_2CO_3 and AgNO_3 . (Scale bar: 20 nm)

molar ratio of $\text{Na}_2\text{CO}_3/\text{AgNO}_3$ under the conditions of samples 3, 4, 7 and 8 in Table 1, the precursor solution would quickly turn to a dark color and then gradually agglomerate. Because the reduction rate is very fast, PVP molecules did not have sufficient time to coat these newly formed silver colloids, and were thus unable to prevent the agglomeration. The effect of Na_2CO_3 on the size and size distribution was investigated by TEM. Figure 3 indicates that the effect of the quantity of Na_2CO_3 on the particle size under the conditions of samples 1-4 in Table 1. It can be seen that the mean particle size increased with an increase in the $\text{Na}_2\text{CO}_3/\text{AgNO}_3$ molar ratio. When the molar ratio between Na_2CO_3 and AgNO_3 was above 1.2, the protection was not sufficient to prevent silver colloids agglomerating into large particles. By contrast, well-dispersed quasi-spherical shaped silver particles with a narrow particle size distribution were obtained in the case of samples 2 and 3.

PVP plays an important role in the protection of the synthesized silver particles, but it has also been found to act as a reducing agent. The PVP protective mechanism of silver reduced by a reducing agent can be interpreted in three steps [22]. The first step is the formation of coordinative bonding between PVP and Ag ions. PVP is a homopolymer whose individual unit contains an imide group. The N and O atoms of this polar group probably have a strong affinity for silver ions and metallic silver. The second step involves PVP-promoted Ag nucleation, which tends to produce small silver particles. Thirdly, the steric effect of PVP covering the silver surface via physical and chemical bonding inhibits particle-particle contact, and thus the

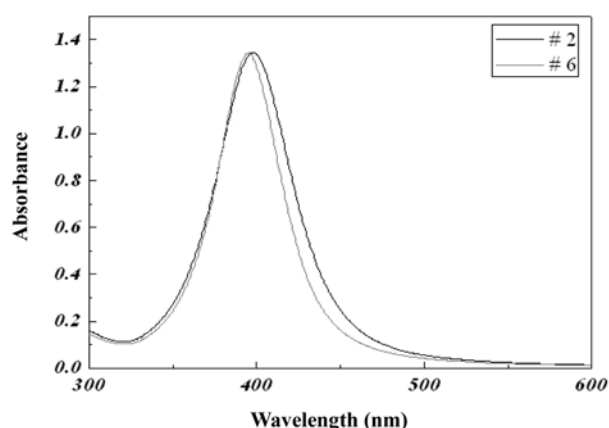


Fig. 4. UV-visible spectra of colloidal silver using different amounts of PVP.

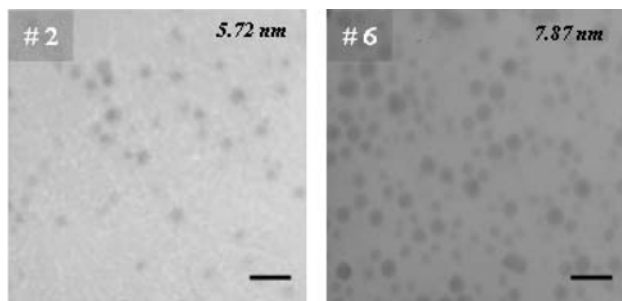


Fig. 5. TEM photographs of silver particles obtained using different PVP concentration. (Scale bar: 20 nm)

agglomeration of particles.

The influence of PVP concentration on silver particle formation was investigated with different PVP/AgNO₃ molar ratios additions: 0.16×10^{-2} M and 0.32×10^{-2} M. The effect of PVP concentration on mean particle size and absorbance is presented in Fig. 4 and Fig. 5. Usually, the narrow peak indicates a narrow particle size distribution and the maximum absorbance band shifts to a longer wavelength with an increase in particle size. UV-visible spectra (Fig. 4) show that the maximum absorbance band shifted to a longer wavelength. This observation shows that an increase in the concentration of PVP leads to the suppression of the growth of silver particles and an increase in the reduction rate. This phenomenon can also be seen in the following TEM result. TEM photographs in Fig. 5 show that the size of silver particles decreases with an increase in the PVP concentration. These results can be explained as follow: PVP plays an important role in the determination of the reduction rate, and an increase in the PVP concentration adjusts the reduction rate of silver ions leading to the formation of a smaller silver particle.

Conclusions

Silver nanoparticles were prepared by a polyol pro-

cess of a silver precursor in the presence of Na₂CO₃ and PVP. It is confirmed that both the Na₂CO₃/AgNO₃ molar ratio and the concentration of PVP affect the reduction rate of Ag ions, which determines the particle size. At a higher molar ratio of Na₂CO₃/AgNO₃, Na₂CO₃ determines the reduction rate of silver ions. In addition, at a fixed molar ratio of Na₂CO₃/AgNO₃, the PVP concentration determines the size of silver particles and stability of the silver colloid.

Acknowledgements

This research was supported by Hanyang Fusion Materials Program and authors gratefully appreciate the financial support.

References

1. P.K. Stoimenov, R.L. Klinger, G.L. Marchin, and K.J. Klabunde, *Langmuir* 18[17] (2002) 6679-6686.
2. K. Yoshida, M. Tanagawa, and M. Atsuta, *Journal of Biomedical Materials Research* 47[4] (1999) 516-522.
3. H.J. Son, M. Cho, H.M. Chung, S.G. Choi, and J.Y. Yoon, *J. Ind. Eng. Chem.* 10[5] (2004) 705-709.
4. G.-M. Shi, J.-K. Han, Z.-D. Zang, H.-Y. Song, and B.-T. Lee, *Surface & Coatings Tech.* 195 (2005) 333-337.
5. B. Sadler, and A. Wei, *Chem. Commun.* (2002) 1604-1605.
6. J. Kobayashi, V. Salgueirino-Maceira, and L.M. Liz-Marzan, *Chem. Mater.* 13 (2001) 1630-1635.
7. T.H. Hyeon, S.S. Lee, J. Park, Y. Chung, and H.B. Na, *J. Am. Chem. Soc.* 123[51] (2001) 12798-12801.
8. E. Leontidis, K. Kleitou, T. K-Leonidou, V. Bekiari, and P. Lianos, *Langmuir* 18[9] (2002) 3659-3668.
9. I. Pastoriza-Santos, and L.M. L-Marzan, *Langmuir* 18[7] (2002) 2888-2894.
10. J.C. Ray, D.-W. Park, and W.-S. Ahn, *J. Ind. Eng. Chem.* 12[1] (2006) 142-148.
11. J.S. Park, J.S. Kim, J.H. Han, S.-W. Nam, and T.-H. Lim, *J. Ind. Eng. Chem.* 11[6] (2005) 897-901.
12. K. Okitsu, A. Yue, S. Tanabe, and H. Matsumoto, *Chem. Mater.* 12[10] (2000) 3006-3011.
13. S. Kapoor, S. Adhikari, C. Gopinathan, and J.P. Mittal, *Mater. Res. Bull.* 34 (1999) 1333.
14. J.-K. Kim, H.-D. Lee, and S.-C. Kim, *J. Ind. Eng. Chem.* 10[5] (2004) 850-855.
15. K.S. Suslick, M. Fang, and T.H. Hyeon, *J. Am. Chem. Soc.* 118[47] (1996) 11960-11961.
16. P. Toneguzzo, G. Viau, O. Acher, F. Fiévet-Vincent, and F. Fiévet, *Adv. Mater.* 10[13] (1998) 1032-1035.
17. C. Ducamp-Sanguesa, R. Herrera-Orbina, and M. Figlarz, *J. Solid State Chem.* 100[2] (1992) 272-280.
18. (a) P.Y. Silvert, R. Herrera-Urbina, and K. Tekaia-Elhsissen, *J. Mater. Chem.* 7 (1997) 293-299. (b) P.Y. Silvert, R. Herrera-Urbina, N. duvauchelle, V. Vijaykrishnan, and K. Tekaia-Elhsissen, *J. Mater. Chem.* 6 (1996) 573-577.
19. K.-S. Chou, and Y.-S. Lai, *Materials Chemistry and Physics* 83 (2004) 82-88.
20. H.C. van de Hulst, *Light Scattering by Small Particles*, Dover, New York, p. 1957.
21. A. Henglein, *J. Phys. Chem.* 97[21] (1993) 5457-5471.
22. B. Wiley, Y. Sun, B. Mayers, and Y. Xia, *Chem. Eur. J.* 11 (2005) 454-463.