PVP Protective Mechanism of Ultrafine Silver Powder Synthesized by Chemical Reduction Processes

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Polyvinyl pyrrolidone (PVP) as a protective agent plays a decisive part in controlling superfine silver particle size and size distribution by reducing silver nitrate with hydrazine hydrate. The particle size and particle aggregation decrease with the PVP/AgNO₃ mole ratio. Mechanisms of PVP protection were divided into three stages. First, PVP donates loan pair electrons of oxygen and nitrogen atoms to s_p orbitals of silver ions, and thus the coordinative complex of Ag ions and PVP forms in aqueous solution. Second, PVP promotes the nucleation of the metallic silver because the Ag ions–PVP complex is more easily reduced by hydrazine than the pure Ag ions owing to Ag ions receiving more electronic clouds from PVP than from H₂O. Third, PVP prohibits silver particle aggregation and grain growth as a result of its steric effect. All of the hypotheses were supported by ultraviolet spectra, infrared spectra, and heterogeneous nucleation and grain growth by addition of silver nuclei.   © 1996 Academic Press, Inc.

INTRODUCTION

Ultrafine silver powders have been widely used in the electronics industry for the manufacture of conductive thick film circuits and for the internal electrodes of multilayer ceramic capacitors. In recent years, with the small size and precision of electronic components, there are growing demands for a decrease in the thickness of conductive films to several micrometers and a further narrowing of the width of printed circuits and the space between these circuits (for instance, 100-μm). It is thus required that the conductive metal powder composing the paste should have small particle diameter and as close as possible to spherical shape with narrow particle size distribution.

Many methods currently have been applied to prepare silver powder, such as physical processes of atomization or milling, chemical methods of thermal decomposition, and electrochemical processes. Silver powders used in electronic applications are generally manufactured by chemical precipitation processes, in which an aqueous solution of soluble silver salts was reacted with an appropriate reducing agent of both nonorganic and organic materials. However, the conventional processes usually produce powders with large size (sometimes more than 2 μm), and irregular shape and aggregation. This kind of powder was difficult to use in thick-film and multilayer ceramic capacitors (1).

Fortunately, a newly developed chemical method, known as the polymer protected reduction process, has been used to prepare monodispersed silver powder with submicrometer size and quasi-spherical shape (2–4). G. Tosun and H. D. Glichsman (2) have reported a gelatin-protected processing, in which silver nitrate was reduced by alkylacid phosphate in aqueous solution and finely divided silver particles with narrow particle size distribution and with a mean particle size of about 0.1–1.0 μm. They also found that the gelatin played a key role in regulating the silver particle size. F. Fievet *et al.* (3) and Ducamp-Sanguesa *et al.* (4) have employed polyvinyl pyrrolidone (PVP) as a protective agent to synthesize ultrafine silver powder with 300 nm diameter, by reducing silver nitrate with hot polyol solution. We also prepared the superfine silver powders with spherical shape and about 100 nm diameter using a chemical reduction method protected by PVP (5). However, the polymer protective mechanisms have not been systematically studied.

Polymer protective mechanisms originated from colloidal chemistry. H. Hirai *et al.* (6) suggested that a complex of the polymers and the metal ions was formed. According to chemical equilibrium, the effective metal ion concentration decreased, so the polymer had impaired the metal ion reduction, i.e., the nucleation of metal particles, the coordinative bonds between the polymers and the ions being too strong. On the other hand, the polymers usually have the back bone of polyvinyl as hydrophobic and hydrophilic groups. The backbone of the vinyl polymer forms a hydrophobic domain, which surround metal particles, whereas the hydrophilic pendant groups of the polymer interact with water or polar solvent, i.e., the steric effect of the polymer in the surface of metal particles prevents the particles from agglomeration. This hypothesis had, indeed, explained why
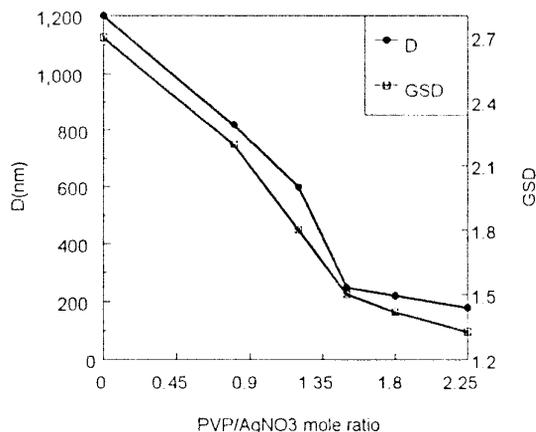
FIG. 1. Silver particle size and the size geometric standard deviation (GSD) as a function of PVP/AgNO$_3$ mole ratio.

the colloidal metal particles in polymer solution were well dispersed. The coordinate bonds between the polymers and metal ions, however, have not been supported by experiments. Recently, Fievet *et al.* (7) reported that a protective polymer agent, D-sorbitol, enhanced the nucleation of the copper phase during the reduction of copper ions by ethylene glycol, which was not inconsistent with the model's induction of polymers hindering the metal particle nucleation. Furthermore, this hypothesis cannot explain the fact that polymers absorbed on the surface of metal particles cannot be washed out by several applications of water and acetone (5, 7), if only physical absorption between the metal surface and hydrophobic groups of the polymers occurred.

In this paper, we focus on the effect of the PVP/AgNO$_3$ mole ratio on the silver particle size and the size distribution. Based on ultraviolet spectra, infrared spectra, and other experimental data, a PVP protective mechanism for synthesizing superfine silver particles by chemical reduction of silver nitrate with hydrazine hydrate in aqueous solution will be proposed.

EXPERIMENTAL PROCEDURES

All chemicals were reagent grade. Both silver nitrate and hydrazine hydrate were purchased from Xin Da Chemical Company, Shanghai, China. PVP (K30, polymerization degree 360) was imported from the United States. The above materials were dissolved in deionized water to form an aqueous solution. The reactant solutions were mixed drop by drop with the aid of a peristaltic pump. The hydrazine was in stoichiometric excess of five times the silver nitrate to achieve complete reduction of the silver salt. The reaction solution was kept under agitation at a rate sufficient to maintain the uniformity of the system and to keep the precipitated particles dispersed until the reduction was completed. Also, the dipping rate was sufficiently low to avoid foaming of the reaction dispersion. At the end of all reactions, the solids were separated from the liquid solution by centrifugation, and subsequently were washed with acetone or alcohol several times until a clear solution was obtained. The particles were then dried at 40°C in air.

Characterization of the metallic particles was achieved by different techniques. The phase composition was determined with X-ray diffractometer using Cu$K\alpha$ radiation.
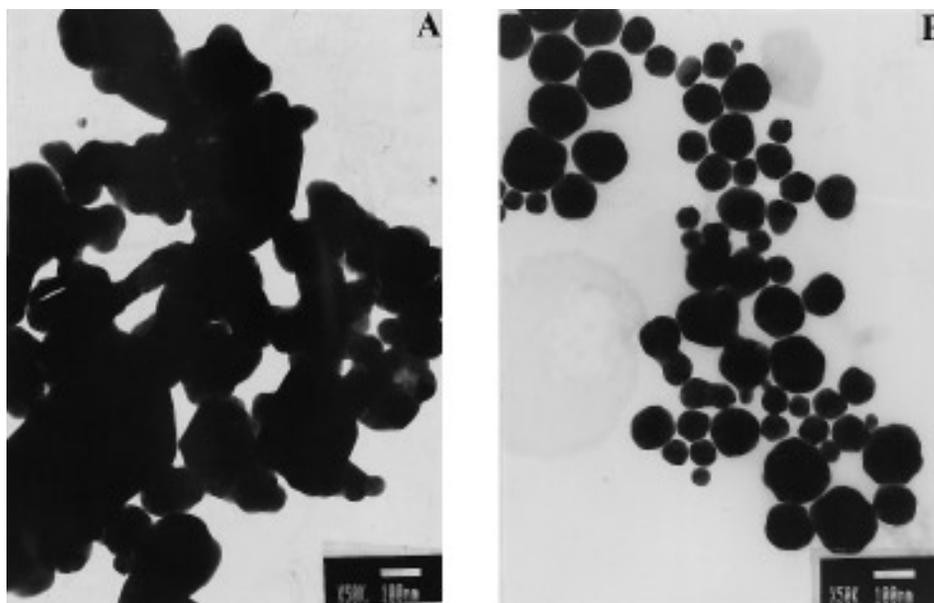
FIG. 2. TEM micrographs of silver powders synthesized at the mole ratios of (A) PVP/AgNO$_3$ = 0 and (B) PVP/AgNO$_3$ = 1.5.

The shape of the final products was observed by transmission electron microscope (TEM, Model H-800, Japan). The particle size and size distribution were measured with a BI-90 laser particle sizer.

RESULTS AND DISCUSSION

1. Influences of PVP/AgNO₃ Mole Ratio on the Silver Particle Size and the Size Distribution

Varying amounts of the protective agent PVP were used for investigating the effect of the surfactant on silver particle size and particle size distribution (GSD, geometric standard deviation) (8). This is shown in Fig. 1, where the silver ion concentration was 0.5886 mol/liter and the reaction was performed at room temperature for 20 min. We show in Fig. 1 that the average particle size of the silver powder was more than 1000 nm and the GSD was 2.7 at PVP/AgNO₃ = 0. With an increase in the PVP/AgNO₃ ratio (one mole of PVP means one unit of PVP, shown in Eq. [1]), both particle size and GSD decreased. When PVP/AgNO₃ ≥ 1.5, the particle size and GSD fell weakly. This means that PVP/AgNO₃ = 1.5 is a critical value. If the ratio was less than 1.5, the PVP protection effect was not complete, whereas if the ratio was more than 1.5, further polymer protection became unnecessary.

Figure 2 shows TEM micrographs of the silver powders. It can be seen that the particle shape and degree of aggregation distinctly depend on different PVP/AgNO₃ mole ratios. When PVP/AgNO₃ = 0, it reveals irregular shape and strong sinter-like particles several micrometers in size (Fig.

2A). In contrast, the well-dispersed quasi-spherical-shaped silver particles and a narrow particle size distribution (Fig. 2B) were obtained in the cease of PVP/AgNO₃ = 1.5. The experimental results demonstrated that the PVP as a protective agent plays a decisive role in controlling the metallic silver size, size distribution, and particle agglomeration. The mechanisms will be discussed in the next section.

2. Mechanisms of PVP Protection

PVP protection in the silver nitrate–hydrazine system was generally proposed on the basis of the following reactions. PVP has a structure of a polyvinyl skeleton with polar groups, shown in the formula

$$[CH_2-CH]_n \qquad [1]$$
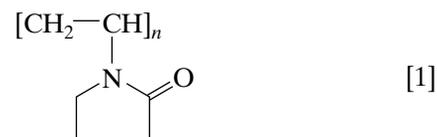
where n is the polymerization number. The donated lone pairs of both nitrogen and oxygen atoms in the polar groups of one PVP unit may occupy two sp orbitals of the silver ion to form a complex compound. Also, because sp orbitals form a linear coordinative bond, 1 mole PVP and 1 mole silver ion may form one mole complex. We suppose that these two kinds of possibilities were equal. The reaction of PVP and silver ions may be as in Eq. (2). Subsequently, hydrazine hydrate may react with the complex of silver ion and PVP as in Eq. (3):

$$[2]$$

$$[3]$$
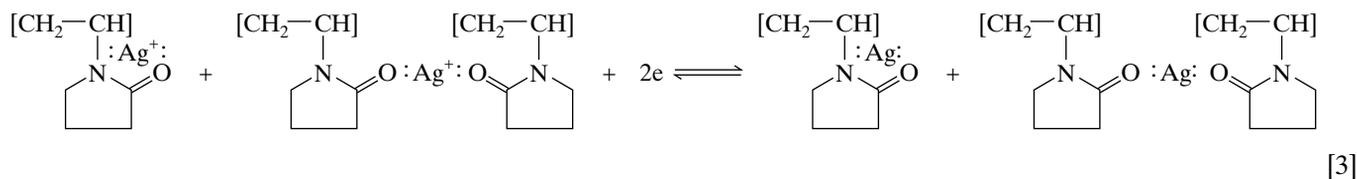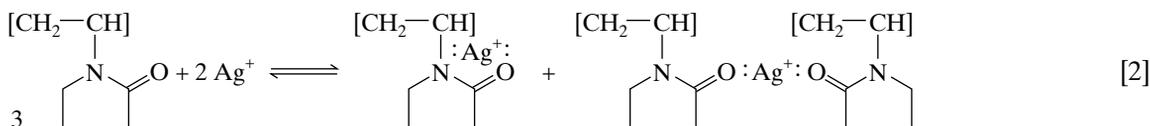
The PVP protective mechanism of the silver reduced by hydrazine hydrate can be explained as three steps.

The first step was the formation of coordinative bonding between PVP and silver ions, which was identified by comparing ultraviolet spectra (Fig. 3) of the AgNO₃ solutions containing and not containing PVP. It is noted that pure PVP has no absorption peak in ultraviolet spectra. All the samples contained silver ions; however, the exhibit peaks at 320 nm resulted from the coordinative bonds of $H_2O:Ag:OH_2$. At the same silver ion concentration, the addition of PVP to the AgNO₃ solution produces more

ultraviolet absorption at lower wave length than solutions not containing PVP. Furthermore, the higher the concentration of the PVP and AgNO₃ solution, the greater was the fraction at the lower wave length absorption. These ultraviolet absorption valley shifts may be attributed to the PVP–Ag⁺ complex substituted for the H_2O–Ag⁺ complex, since the nitrogen and oxygen of the PVP have a stronger coordinative field than H_2O.

The second step involves PVP-promoted silver nucleation, which is supported by the photoreduction experiments. Two silver nitrate solutions containing and not con-
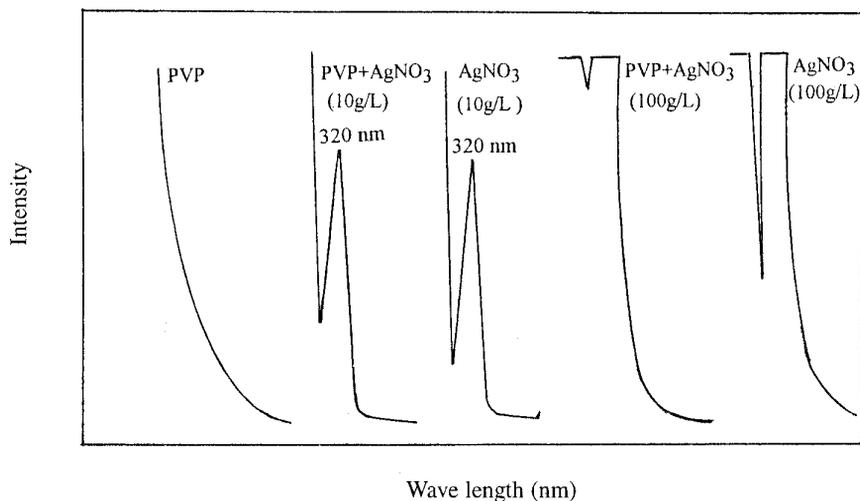
FIG. 3.   Ultraviolet ray absorption spectra.

taining PVP with the same silver nitrate concentration 100 g/liter were subjected to photo radiation by sunlight of the same intensity for 20 min. The ultraviolet (UV) spectra of the samples are illustrated in Fig. 4, where the first peaks at 320 nm are the silver ion UV absorption and the second peaks at about 520 nm are the silver particle UV absorption. It is obvious from the results in Fig. 4 that the area of the silver absorption peak for PVP/AgNO$_3$ = 1.5 is much larger than for PVP/AgNO$_3$ = 0, whereas the area of the silver ion absorption peak shows the reverse trend in comparison with the silver absorption ones. PVP, therefore, increases the silver ion reduction rate. The same result was reported by Fievet *et al.* (7) in copper oxide reduced by polyol using D-sorbitol as protective agent.

Cleary, the above experimental results cannot be explained according to the traditional mechanisms suggested

by Hirai *et al.* (6). Fortunately, these phenomena can be understood in terms of chemical bonding. Since the ligand of C–N and C=O in PVP contributes more electronic density to the *sp* orbital of silver ions than does H$_2$O, the silver ions in the Ag$^+$–PVP complex may obtain electrons from oxidizing agents more easily than those in Ag$^+$–H$_2$O.

The subsequent step is PVP-accelerated formation of a large amount of silver nuclei. It was found that the color of the solutions changes gradually from pink at the initial reaction to violet, black, and gray at the end of the reaction for system containing PVP, whereas a gray color always appears during the silver nitrate and hydrazine hydrate reaction without PVP. TEM observation showed that the scattering of sunlight by nuclei with diameters of 10, 20, 50, and 100 nm is responsible for the pink, violet, black, and gray solutions. It was concluded that a large amount of small silver nuclei at the beginning of the reductive reaction was produced when PVP was used; conversely, a small amount of larger silver nuclei was generated if PVP was not employed.

The effect of the nuclei on the silver particle size was investigated by designing two experiments, as shown in Table 1. The synthesized nuclei, prepared by refluxing alcoholic silver nitrate solution using PVP as a protective agent as reported as literature (9), were subsequently added to the AgNO$_3$–N$_2$H$_4$·H$_2$O–PVP reaction system. After the

FIG. 4.   Ultraviolet spectra of AgNO$_3$ solution after radiation of solar ray for 20 min.

TABLE 1
Influence of Silver Nuclei on Silver Powder Size

Nuclei size (nm)	Nuclei content (wt%)	Silver particle size (nm)
30	5	50
90	5	110
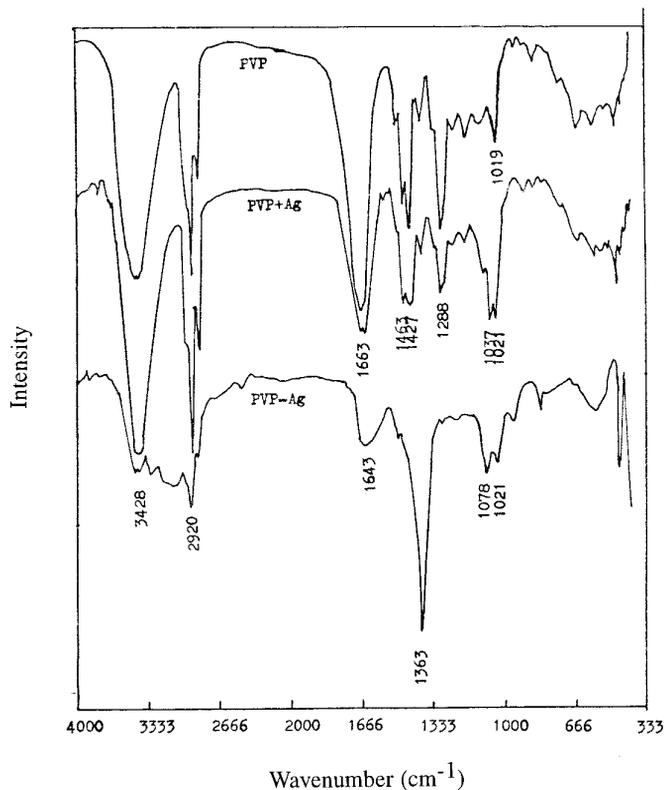
FIG. 5. FTIR spectra of PVP and silver powder.

reaction ended, silver particles 50 and 110 nm in diameter were observed with TEM, using 30 and 90 nm nuclei, respectively. Thus the small generation of nuclei at the initial stage of the reaction by addition of PVP protectant should be an important factor of the average small particle size of the silver powder.

The third step is PVP prohibiting grain growth and particle aggregation. There is no doubt that the PVP was physically bonded with silver, according to previous works (5). The chemical bonding between the PVP and silver powder (reaction [3]) is demonstrated in Fig. 5. The wavenumbers 2920 and 3428 cm^{-1} correspond to C–H and O–H bond vibrations, respectively. The values 1463 and 1427 cm^{-1} were obtained for
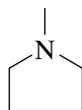
of PVP bond absorption. The wavenumbers 1363 and 1288 cm^{-1} were due to bond vibrations of the NO$_3^{-1}$ group and the N → H–O complex, respectively. Now we concentrate on the wavenumbers of about 1019 and 1663 cm^{-1}, which were, respectively, generated by the C–N and C=O bond vibrational absorption. It is found that most of the IR spectrum (Fig. 5) of PVP mechanically mixed with pure silver powder (PVP + Ag) is nearly identical to that of pure PVP, but the C–N absorption peak at 1019 cm^{-1} is separated into two peaks at 1037 and 1021 cm^{-1}, and the C=O absorption peak at 1663 cm^{-1} was slightly widened. This implies that there is weak coordinative chemical bonding of C–N to Ag at the interface between PVP and the powder. Furthermore, for Ag particles covered by PVP during the reduction, the degree of separation of the C–N vibrations becomes more obvious, the one peak at 1019 cm^{-1} becoming two peaks at 1078 and 1021 cm^{-1}. Also, the absorption peak of the C=O bond at 1663 cm^{-1} for pure PVP is shifted to 1643 cm^{-1} for Ag particles covered by PVP. This decrease in wavenumber for C=O absorption may result from bond weakening via partial donation of oxygen loan pair electrons of PVP to the vacant orbitals of the silver surface. All the IR spectra prove that the chemical bonds of N : Ag : O remain in the PVP–Ag powder, i.e., reaction [3] is correct.

PVP strongly absorbed on the surface of silver particles is an obstacle to silver diffusion and may decrease the silver grain growth in the aqueous suspension. In addition, because of the excellent dispersion of the silver particles owing to the PVP in water, the diffusion distance of the silver particles is larger that of the silver particles without PVP covering, due to poor dispersion of the silver. The diffusion barrier and the large diffusion distance may be another mechanism for PVP protection against silver grain growth.

PVP preventing the silver particles from aggregation is the main role of the surfactant, which occurs both during the growth step and the washing processes. For the former case, the steric effect arising from the long polyvinyl chain of PVP on the surface of silver particles may contribute to the anti-agglomeration. Because the steric effect is largely determined by the covered fraction of PVP on the surface of the silver particles, it was, therefore, necessary that there be enough PVP to absorb on silver particles. For the latter case, chemical bonding between the PVP and silver powders may play an important role in prohibiting aggregation of silver particles, because washing with water and acetone six times did not completely remove the PVP from the surface of the silver particles. These experiments imply that the steric effect also exists during the washing processes.

On the basis of the steric effect, we can explain the relationship between PVP/AgNO$_3$ mole ratio and the agglomeration behavior (shown in Fig. 2). The more strongly aggregated or sinter-like silver particles (Fig. 2A) are due to lack of steric protection by PVP. Although the steric effect has been seen in solutions of PVP/AgNO$_3$ = 0.4–0.8, partial agglomeration also takes place as a result of incomplete covering of the silver particles by PVP. In the case of PVP/AgNO$_3 \geq 1.5$, the entire surface of the silver particles was coated by PVP. Consequently, the steric influence against the agglomeration was fulfilled and the silver particles were separated from each other by PVP.

CONCLUSIONS

1. Well-dispersed silver powder with 50–100 nm size and quasi-spherical shape has been prepared by reducing silver nitrate with hydrazine in the presence of PVP as a protective agent.

2. The mechanism of PVP protection, proved by the ultraviolet spectra, infrared spectra, and experiments with added silver nuclei, were divided into three stages. First, the complex of PVP–silver ions via coordinative bonding was constructed. Second, the complex promotes silver nucleation, which tends to produce small silver particles. Third, the steric effect of PVP covering the silver surface via physical and chemical bonding inhibits particle–particle contact and thus the agglomeration of the powder. The steric effect worked both during the grain growth step and during the washing process.

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