

# Dispersion mechanisms of Arabic gum in the preparation of ultrafine silver powder

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**Abstract**—Finely divided silver micro-spheres were prepared with Arabic gum (AG) as dispersant through the chemical reaction of  $\text{AgNO}_3$  and ascorbic acid. AG dispersive mechanisms in the preparation of silver powder are proposed in the paper. The  $-\text{COOH}$  and  $-\text{NH}_2$  groups of AG reacted with  $\text{Ag}^+$  to form  $\text{Ag}^+-\text{AG}$  complexes, followed by the nucleation of silver on AG polymer chains, which yielded silver spheres with an AG protection layer by reducing  $\text{Ag}^+-\text{AG}$  complexes with ascorbic acid. With the steric effect of AG, the prepared silver particles exhibit improved dispersibility. UV-Vis and FTIR spectra confirmed that silver particles were stabilized by AG.

Keywords: Arabic Gum, Silver Powder, Sphere, Dispersive Mechanism, Chemical Reduction

## INTRODUCTION

Ultrafine silver powder has been widely used in microelectronics [1], optical devices [2], and chemical catalysis [3] due to its unique electrical, optical, catalytic, and thermal properties. Recently, silver paste for front side metallization of crystalline silicon solar cell has been in commercial use, which employs silver powder as a major component. The rheology of silver paste and the electrical performance of solar cell are influenced by the parameters of silver particles, such as shape, size distribution and tap density (TD) of the silver particles [4-6]. Thus, it is necessary to explore the synthesis process of silver powder.

To date, a variety of methods have been developed to prepare silver powder, such as wet-chemical reduction [7,8], spray pyrolysis [9], and electro-reduction [10]. From a practical point of view, the wet-chemical reduction process is most preferable for obtaining ultrafine silver powder because of its versatility and simplicity [7,8,11]. To obtain silver powder with good dispersibility, most wet-chemical reduction processes are conducted in the presence of dispersants, such as polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA), and gelatin [12-15]. However, the majority of studies focus on the preparation of silver powder. Only a few reports have emphasized the dispersive mechanisms of dispersant in the synthesis of silver powder. Zhang and Wang et al. reported the PVP protective mechanisms of ultrafine silver powder synthesized by chemical reduction processes. They found that the O and N atoms of PVP reacted with silver ions and accelerated the reduction of silver ions. The silver particles were protected by a PVP steric layer [12,13]. Guo et al. proposed the dispersive mechanisms of PVA in the preparation of silver powder: chemical adsorption mechanism and steric effect mechanism. They believed that PVA adsorbed on the surface of silver particles by coordination bond prevented diffusion and aggregation of silver particles. The long chain structure of PVA may help

to reduce aggregation due to steric effect [14]. Ao et al. proposed the gelatin dispersive mechanisms in the preparation of spherical silver particles. They found that the coordinative complex of silver ions with gelatin could enhance the reduction of silver ions and the nucleation of metallic silver particles, thus enhancing the availability of the monodisperse spherical silver particles [15].

Recently, a natural polymer, Arabic gum (AG), has been widely used as dispersant in the synthesis of well-dispersed silver particles. Liu and co-workers synthesized spherical and mono-disperse micro-silver powder with average particle size of about 1-2  $\mu\text{m}$  in the presence of AG [16]. Balantrapu et al. reported the preparation of highly dispersed silver nanoparticles with AG as both reductant and dispersant as well as its application in flexible printed electronics. The silver nanoparticles could be converted into conductive films at 100 °C, which displayed good electrical conductivity [17]. Ramirez et al. prepared silver nanoparticles with four reducing agents (sodium borohydride, sodium citrate, ascorbic acid and dimethylamine borane) in the presence of AG. The silver particles were found to be monodispersed and highly crystalline with near-spherical appearance [18]. Unfortunately, the dispersive mechanisms of AG in the preparation of silver powder have been seldom reported because of its complex structure. In this paper, the dispersive mechanisms are discussed based on ultraviolet spectra, Fourier transform infrared spectra and other experimental data.

## EXPERIMENTAL

### 1. Preparation of Silver Powder

All chemicals used in this study were of AR grade without further purification. Deionized water was used in all the preparations. Silver powder was prepared with AG as dispersant through chemical reaction between  $\text{AgNO}_3$  and ascorbic acid. In a typical experiment, 250 ml solution containing 5 g  $\text{AgNO}_3$  and 0.1 g AG was quickly added into 250 ml solution containing 4 g ascorbic acid with vigorous agitation for 1 h by a variable high-speed stirrer (1,000 rpm) at constant temperature of 40 °C. The pH value of  $\text{AgNO}_3$  solution was adjusted with 0.01 M  $\text{HNO}_3$  solution. Alternatively,  $\text{AgNO}_3$

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solutions with different AG/AgNO<sub>3</sub> weight ratios and different HNO<sub>3</sub>/AgNO<sub>3</sub> molar ratios were prepared and used for reference experiments. Other reaction conditions (such as silver ion concentration, C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>/Ag<sup>+</sup> molar ratio, and reaction temperature) in reference experiments were the same as that in typical experiment. The as-prepared silver powder was separated from the solution and washed with deionized water and anhydrous ethanol for three times, respectively. Subsequently, it was dried at 60 °C in an oven for 10 h.

## 2. Characterization

The morphology of silver powder was observed by SEM (FEI QUANTA-200) and TEM (FEI Tecnai-G2-20ST). The FTIR spectra of silver powder and Arabic gum were recorded on an FTIR spectrometer (Nicolet 6700). The UV-vis spectra of aqueous solutions were measured by UV-vis spectrophotometer (Rayleigh UV-1801). The zeta potential of silver particle dispersion was measured by zeta potential analyzer (Malvern Nano-zs). The yield stress of silver particle dispersion was measured with a Brookfield DVII+ digital viscometer.

## RESULTS AND DISCUSSION

The AG dispersive mechanism for synthesizing ultrafine silver powder has generally been proposed from the three perspectives: the formation of coordinative complex between AG and Ag<sup>+</sup>; the nucleation of silver particles on the AG polymer chains; and the protection of AG on the silver particles.

### 1. Formation of Coordinative Complex between AG and Ag<sup>+</sup>

Arabic gum is a natural biopolymer derived from exudates of Acacia Senegal and Acacia seyal trees. As shown in Fig. 1, the main chain of AG consists of 1, 3-linked  $\beta$ -D-galactopyranosyl units. The side chains are composed of two to five units of 1, 3-linked  $\beta$ -D-galactopyranosyl and linked to the main chain by 1, 6-linkages. Both the main chain and the side chains contain the units of  $\alpha$ -L-arabinofuranosyl,  $\alpha$ -L-rhamnopyranosyl,  $\beta$ -D-glucuronopyranosyl and 4-O-methyl- $\beta$ -D-glucuronopyranosyl. The latter two units are the end units [19,20].

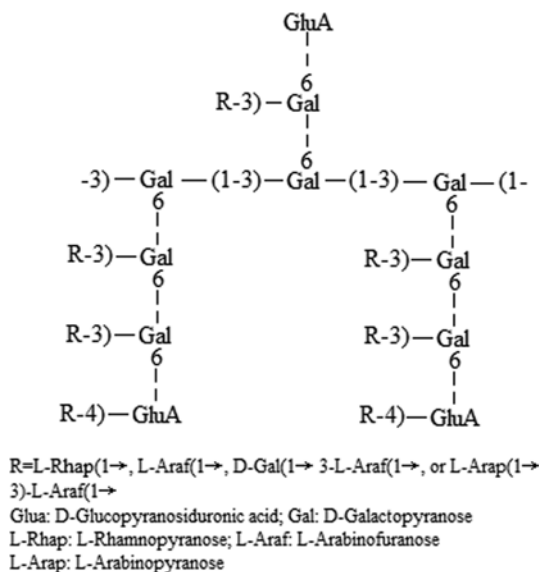


Fig. 1. Structure of Arabic gum.

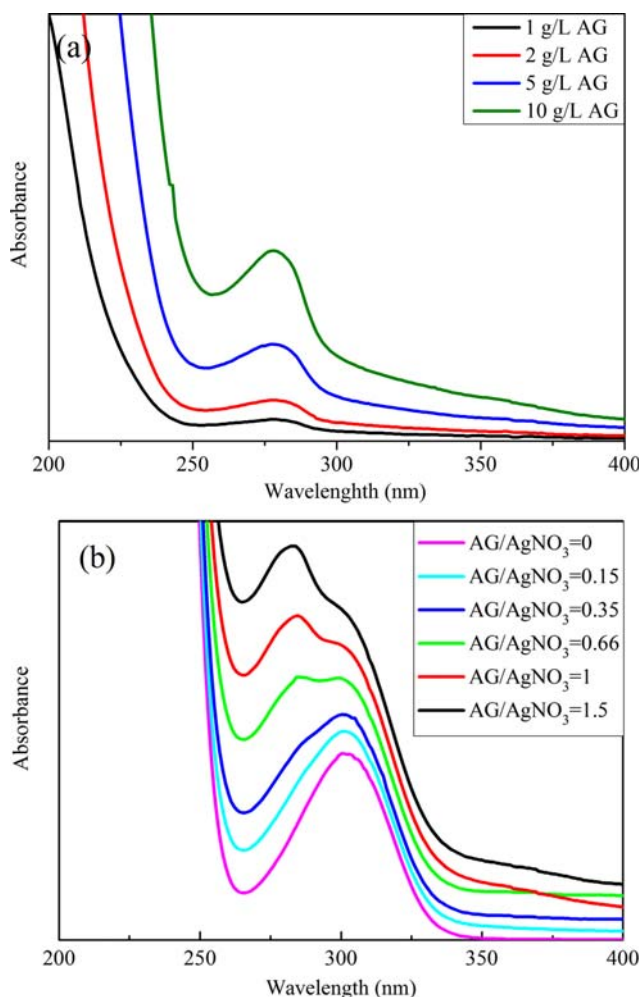


Fig. 2. UV spectra. (a) Pure AG solutions; (b) AgNO<sub>3</sub> solutions (without HNO<sub>3</sub>) with different AG/AgNO<sub>3</sub> weight ratio.

The formation of coordinative complex between AG and Ag<sup>+</sup> can be confirmed by the UV spectra (Fig. 2) of AG and AgNO<sub>3</sub> solutions. Pure AgNO<sub>3</sub> solutions exhibit absorption peaks at 300 nm due to the coordinative bonds of H<sub>2</sub>O : Ag : OH<sub>2</sub> and pure AG solutions have UV absorption peaks at 278 nm owing to the aromatic heterocycle  $\pi$ - $\pi^*$  transitions of amino acids [21]. The AG added into AgNO<sub>3</sub> solution allows more ultraviolet absorption at 300 nm than the solution without AG when the mass ratio of AG to AgNO<sub>3</sub> is smaller than 0.66. However, there are two peaks at 284 nm and 300 nm when the mass ratio of AG to AgNO<sub>3</sub> is 0.66, which is a turning point. With the increasing mass ratio of AG to AgNO<sub>3</sub>, the peak at 300 nm becomes a shoulder with only one peak at 284 nm.

AG is a 150 nm long “twisted hairy rope” with a 5 nm diameter. In the structure, carbohydrate blocks are linked to a common polypeptide chain. It is composed of an arabinogalactan (~90 wt%), an arabinogalactan-protein complex (~10 wt%), and a glycoprotein (~1 wt%). The protein in AG is rich in hydroxypropyl, prolyl and seryl residues covalently linked to carbohydrate moieties while the arabinogalactan is rich in -COOH groups [19,20,22]. For the donated lone pairs of both nitrogen and oxygen atoms tend to occupy the *sp* orbits of silver ions to form complex compounds, the -NH<sub>2</sub> and -COOH groups of AG react with Ag<sup>+</sup>. The nitrogen and oxygen in

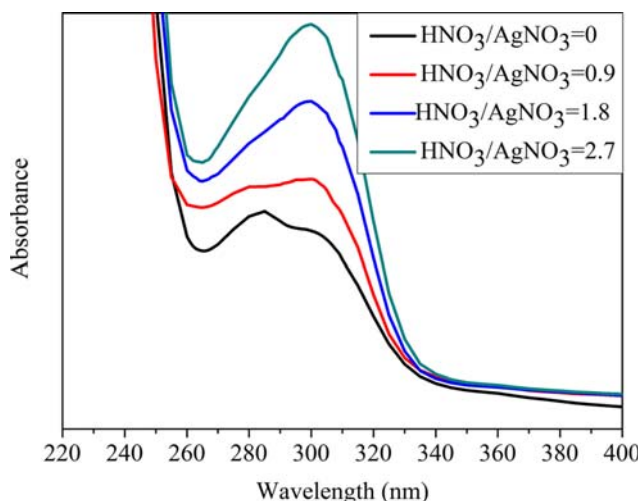


Fig. 3. UV spectra of  $\text{AgNO}_3$ -AG ( $w(\text{AG})/w(\text{AgNO}_3)=1 : 1$ ) solutions with different  $\text{HNO}_3/\text{AgNO}_3$  molar ratio.

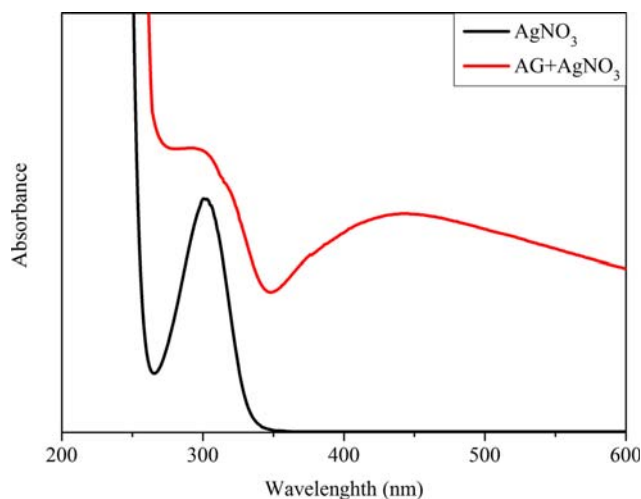
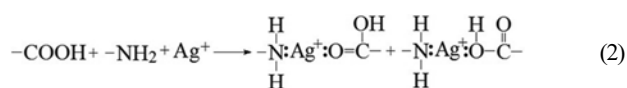


Fig. 4. UV-vis spectra of  $\text{AgNO}_3$  solutions after being heated to  $40^\circ\text{C}$  and kept for 30 min.

dispersants have a stronger coordinative field than  $\text{H}_2\text{O}$  [12,13,15], so the absorption peaks corresponding to  $-\text{NH}_2\text{-Ag}^+\text{-HOOC-}$  (284 nm) and  $-\text{COOH-Ag}^+$  (300 nm) replace that of  $\text{H}_2\text{O} : \text{Ag} : \text{OH}_2$  (300 nm). Similar phenomena were reported in the preparation of silver powder by PVP, PVA and gelatin [12-15]. Moreover, in the ion exchange process between  $-\text{COOH}$  and  $\text{Ag}^+$ ,  $-\text{COOAg}$  and  $\text{H}^+$  were formed [23]. The ion exchange process is conducive to the protonation reaction of the  $-\text{NH}_2$  groups of AG [24,25], which could increase the electrostatic repulsion between  $\text{Ag}^+$  and AG. With the conversion of  $-\text{NH}_2$  groups to  $-\text{NH}_3^+$ , there are few  $-\text{NH}_2$  groups available for  $\text{Ag}^+$  complexation. This mechanism could be enhanced through the addition of  $\text{HNO}_3$  (Fig. 3). Compared to the  $\text{HNO}_3$ -free solutions, the UV spectra of AG- $\text{AgNO}_3$  solutions containing  $\text{HNO}_3$  show the reverse trend. But  $-\text{NH}_3^+$  has little effect on the complexation of  $\text{Ag}^+$  with  $-\text{NH}_2$  in AG- $\text{AgNO}_3$  solution under the natural pH value (5-6) (Fig. 2(b)). And because the amount of protein in AG is much less than that of arabinogalactan [19,20],  $-\text{NH}_2\text{-Ag}^+\text{-HOOC-}$  could be formed by increasing the mass ratio of AG to  $\text{AgNO}_3$ . Therefore, the reaction between  $\text{Ag}^+$  and AG can be provided as the following equations:



## 2. Nucleation of Silver Particles on AG Polymer Chains

Unlike the previous methods [12,13,15], the  $\text{AgNO}_3$  solutions were heated to  $40^\circ\text{C}$  and stored to prevent exposure to sunlight radiation. However, the nucleation of silver particles on AG polymer chains can be also observed through the changes of UV-Vis spectra and the color of reaction mixtures. As shown in Fig. 4, the pure  $\text{AgNO}_3$  solution can be kept for 30 min at  $40^\circ\text{C}$  without any change. At the same silver ion concentration, the addition of AG into the

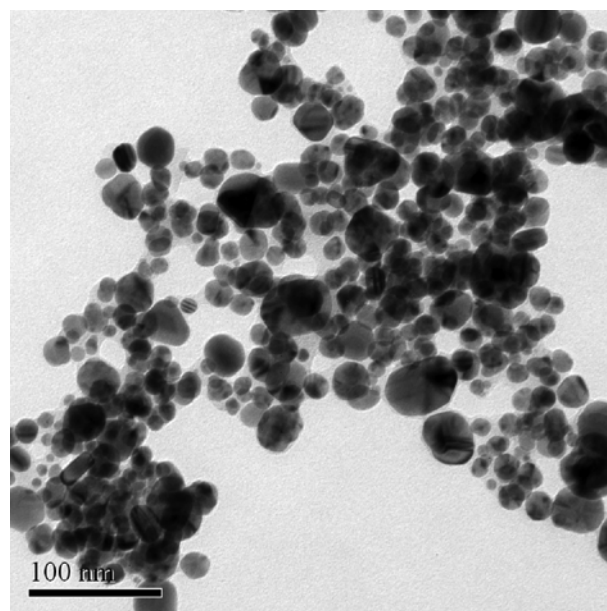


Fig. 5. TEM of silver nanoparticles.

$\text{AgNO}_3$  solution led to obvious changes: in the UV-Vis spectrum of  $\text{AgNO}_3$  solution, an absorption peak at 440 nm corresponding to the silver nanoparticles (Fig. 5) was observed, while the absorption peaks at 284 nm and 300 nm were decreased dramatically. After  $\text{C}_6\text{H}_8\text{O}_6$  solution was introduced in  $\text{AgNO}_3$  solution, the color of pure  $\text{AgNO}_3$  solution turned gray at once, while that of  $\text{AgNO}_3$  solution containing AG turned gradually from brown to black and became gray at the end of the reaction.

Dispersants promoted the nucleation of silver particles because of the complex compounds of dispersants,  $\text{Ag}^+$  and  $\text{H}^+$  [12,13,15]. But the above phenomena cannot be interpreted as the promotion role of the nucleation of silver particles. AG consists of a small fraction of monosaccharides and a large amount of polysaccharide, which are effective reducing agents [17]. The molecular association of AG leads to the formation of networks within the polymer chains. These networks provide nanoscopic domains for the nanoparticle growth



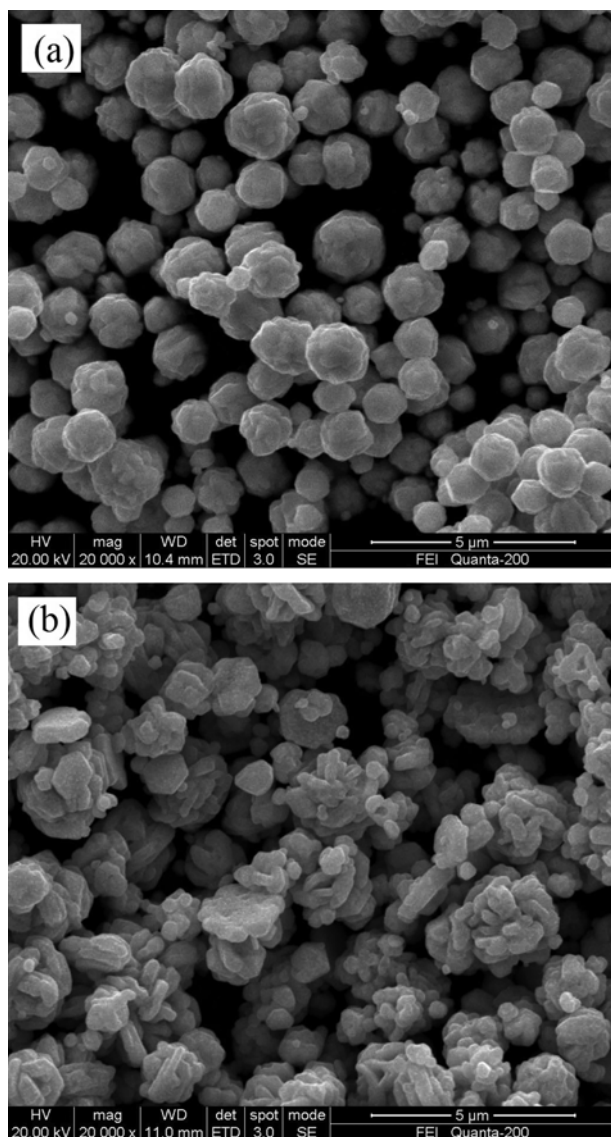


Fig. 6. SEM micrographs of silver powders prepared with (a) or without (b) AG.

like hydrogel network systems [23]. Thus, AG can reduce silver ions to silver nanoparticles through the oxidation mechanism. Since O and N donated lone pairs to the *sp* orbitals of silver ions, the reduction of  $\text{Ag}^+$  on the polymer chains was accelerated. The silver nanoparticles resulting from  $\text{AgNO}_3$  solution containing AG worked as seeds in the growth of primary particles, which then aggregated to form secondary particles. AG polymer chains served as templates during the formation of secondary particles, on which primary particles were guided to form silver spheres (Fig. 6(a)). That is, silver particles can nucleate on the AG polymer chains directly. However, after  $\text{C}_6\text{H}_8\text{O}_6$  solution was introduced in pure  $\text{AgNO}_3$  solution, the reaction mixture was rapidly supersaturated with silver seeds and primary particles. They would aggregate to form secondary particles with irregular shape in the absence of AG as shown in Fig. 6(b).

### 3. Protection of AG on the Silver Particles

Fig. 7 shows the FTIR spectra of silver particles prepared with different AG/ $\text{AgNO}_3$  mass ratios (0.1 and 1). Compared with the

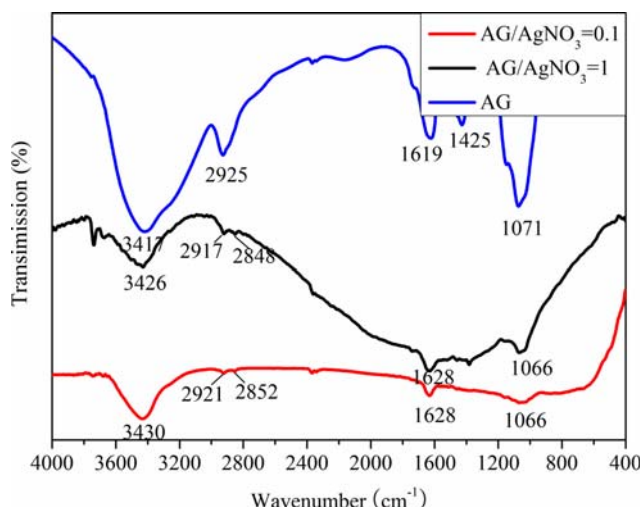


Fig. 7. FTIR spectra of AG and the silver powders prepared with different AG/ $\text{AgNO}_3$  mass ratios.

FTIR spectrum of AG, the C-O absorption peak at  $1,071\text{ cm}^{-1}$  shifts to  $1,066\text{ cm}^{-1}$ . The C=O absorption peak at  $1,425\text{ cm}^{-1}$  is weakened greatly, while the C=O absorption peak at  $1,619\text{ cm}^{-1}$  shifts to  $1,628\text{ cm}^{-1}$ . The C-H absorption peak at  $2,925\text{ cm}^{-1}$  is divided into two peaks at  $2,852\text{ cm}^{-1}$  and  $2,921\text{ cm}^{-1}$  ( $2,848\text{ cm}^{-1}$  and  $2,917\text{ cm}^{-1}$ ). And the -OH absorption peak at  $3,417\text{ cm}^{-1}$  shifts to  $3,430\text{ cm}^{-1}$  ( $3,426\text{ cm}^{-1}$ ). However, the FTIR absorption peaks of  $-\text{NH}_2$  cannot be found in AG and silver powder. The absorption bands due to the N-H stretching (at  $3,310\text{--}3,350\text{ cm}^{-1}$  and  $3,400\text{--}3,500\text{ cm}^{-1}$ ) may be swamped by the broad absorption band due to the O-H stretching (at  $3,000\text{--}3,600\text{ cm}^{-1}$ ) of polysaccharide for AG consists of a high molecular weight glycoprotein and a larger amount of a low molecular weight polysaccharide [25,26].

Usually, a primary factor contributing to the good dispersibility of silver powder is the steric effect of dispersant. When a dispersant is adsorbed on the surface of silver particles, it acts as a steric layer to prevent the agglomeration of silver particles. It is apparent from above results that there is a strong physical adsorption of AG on the surface of silver particles. However, the AG molecule contains charged groups ( $-\text{COOH}$  and  $-\text{NH}_2$ ). When adsorbed on a particle surface, it may give rise to non-DLVO (Derjaguin-Landau-Verwey-Overbeek) surface forces such as steric hindrance or bridging depending on the pH of the particle solution and the type of particle [26, 27]. To evaluate the effects of AG on surface forces of silver particle dispersion, zeta potential and yield stress were measured as a function of pH.

As shown in Fig. 8, the zeta potential of silver particle dispersion decreases with the increase of AG dosage. With the increase of pH, zeta potential reaches a limiting potential at pH of 9. It indicates AG is more anionic in character. Although AG is a macromolecule with charged groups ( $-\text{NH}_2$  and  $-\text{COOH}$ ), the physical presence of the adsorbed AG reduces the surface charge density of silver particles, and the charge compensation from adsorbed AG is not sufficient [27]. The effects of AG on the yield stress-pH behavior of a 60 wt% silver powder are shown in Fig. 9. The increase of AG dosage resulted in a decrease of yield stress. Compared with the yield stress of silver particle dispersion prepared with 10 wt% AG,

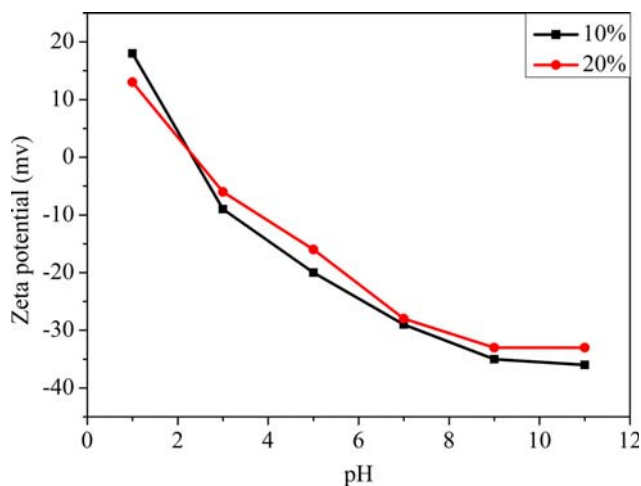


Fig. 8. The effect AG dosage on the zeta potential-pH behavior of a 1.0 vol% silver particle dispersion.

the yield stress of silver particle dispersion prepared with 20 wt% AG was decreased by 30–40%. The decrease of yield stress revealed that AG acted as a steric layer preventing the agglomeration of silver particles.

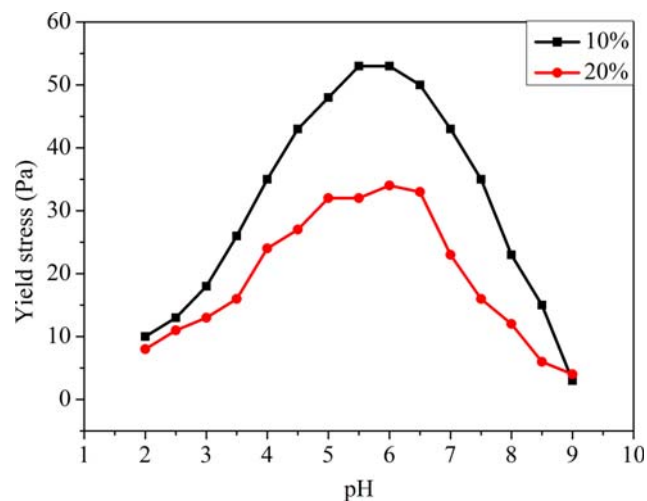


Fig. 9. The effect AG dosage on the yield stress-pH behavior of a 60 wt% dispersion.

The AG molecule is assumed to be a very compact structure with minimal chain-chain interactions with other AG molecules in aqueous solution [28]. Networks can be formed within polymer chains

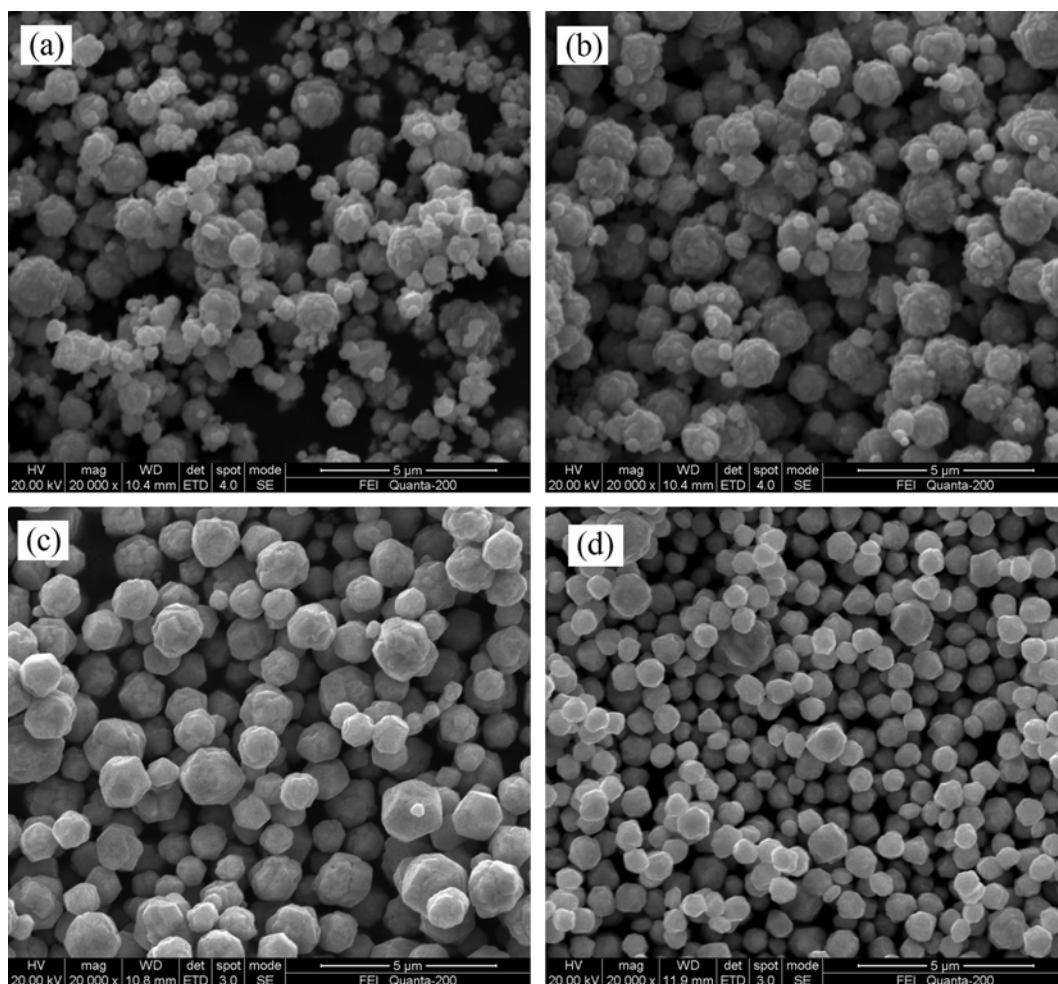


Fig. 10. SEM micrographs of silver powders prepared with different AG/AgNO<sub>3</sub> mass ratios. (a) 0.005, (b) 0.01, (c) 0.02 (d) 0.1.

through the molecular association of AG molecules [22,23]. The strengthening or weakening of networks (yield stress) is attributed to the bridging effect or steric effect. The glycoprotein in AG is capable of strong binding interactions. A bridge is formed when glycoprotein is adsorbed onto the surface of two or more particles, which will lead to the strengthening of network. Thus, the yield stress is increased. This behavior has been observed in  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  dispersion [27]. Unlike these oxides, the silver particles prepared with 20 wt% AG exhibited the smaller yield stress than the silver particles prepared with 10 wt% AG. This suggests that the steric effect overwhelms the bridging effect. In addition, the chemical reaction of  $\text{AgNO}_3$  and  $\text{C}_6\text{H}_8\text{O}_6$  resulted in the formation of  $\text{HNO}_3$ . It led to the free carboxylate group becoming neutral and the amino group becoming positive. The physical adsorption of  $-\text{COOH}$  on particle surfaces and the electrostatic repulsion between silver particle and  $-\text{NH}_3^+$  decrease the probability of particle bridging. Once the silver particle was formed, the adsorbed AG could display stiff-chain behavior and the particle collision was compressed greatly due to the steric stabilization provided by the large proteinic backbone of AG [17]. The steric effect of AG contributed to excellent dispersibility of silver particles. As shown in Fig. 10, the dispersibility of silver particles was improved with the increase of AG dosage. And the particle size decreased with increasing AG dosage. Because large silver particles were formed through the aggregation of primary particles, increasing AG dosage could improve the coverage effect of AG on the surface of primary particles and enlarge the diffusion distance of primary particles. It allows anti-agglomeration [12,13,16].

## CONCLUSIONS

1. Well-dispersed ultrafine silver powder was prepared by reducing silver nitrate with ascorbic acid in the presence of AG as a dispersive agent.

2. The UV-Vis spectra and FTIR spectra proved that the dispersive mechanisms of AG for preparing good dispersive ultrafine silver powders could be divided into three stages. First, the  $-\text{COOH}$  and  $-\text{NH}_2$  groups of AG reacted with  $\text{Ag}^+$  to form complex compounds. Second, silver nuclei formed on AG polymer chains, which work as seeds in the growth of primary particles. And AG polymer chains serve as templates during the formation of silver spheres. Finally, the stiff-chain of AG contributes to excellent dispersibility of silver particles via steric stabilization.

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