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Preparation of spherical silver particles for solar cell electronic paste with gelatin protection

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Abstract

Spherical silver particles used in electronic paste for solar cell were prepared using the chemical reduction method with ammonia as a complex agent, hydrazine hydrate as a reducing agent, and gelatin as a protective agent. The gelatin protective mechanism in the preparing process of spherical silver particles was studied. Observations of SEM and results of laser particle size analysis and ultraviolet absorption spectra demonstrate the formation of the coordinative complex of silver ions with gelatin in aqueous solution which accelerated the reduction of silver ions. Moreover, gelatin can promote the nucleation of the metallic silver particles, thus beneficiating availability of the monodisperse spherical silver particles.

Keywords: Electronic materials; Metals; Chemical synthesis; Microstructure

1. Introduction

The application of electronic paste in preparation of the front grid for crystalline silicon solar cell is beneficial to the increase of efficiency of the solar cell and the reduction of cost [1]. As a major component in the paste, the silver particles play an important role for the properties of the paste. Especially, the parameters of the silver particles, such as shape, size and surface area of the particles, have shown to affect the rheology of its electronic paste and, in turn, the microstructure of front grid of solar cell [2,3]. Therefore, it is essential to investigate preparing process of silver particles for solar cell electronic paste.

There are many physical and chemical methods which universally have been applied to prepare silver particles, such as milling, atomization, thermal decomposition, electrochemical process, and chemical reduction process. Silver particles used in electronic paste are conventionally manufactured by chemical reduction process from an aqueous or organic solution of the corresponding silver salts [4,5]. Although this method has the advantage of a low preparation cost, it usually produces particles with larger size, irregular shape and aggregation and not suitable to be used in electronic paste for solar cell. The polymer protecting reduction process was effective to prepare monodispersed silver particle with submicrometer size and quasi-spherical shape [6–8]. For example, a gelatin protection processing was developed in which silver nitrate was reduced by alkylacid phosphate in aqueous solution while the gelatin played a key role in regulating the silver particle size, and as a consequence, finely divided silver particles with a mean particle size of about 0.1–1.0 μm and narrow particle size distribution were obtained [6].

In this paper, spherical silver particles for electronic paste of solar cell were prepared by chemical reduction processes with silver nitrate as a raw material, ammonia as a complex agent, hydrazine hydrate as a reductant and gelatin as a protective agent. Based on ultraviolet spectra, SEM and laser particle size analysis, a growth process of spherical silver particles are discussed. In particular, the gelatin protective mechanism in the preparation of spherical silver particles for electronic paste is proposed for the first time.

2. Experimental

All chemicals were reagent grade. Silver nitrate was dissolved in deionized water to form an aqueous solution, then 4 wt.% ammonia solution was added into this solution until a clear solution (solution A) was obtained; solution B was pre-prepared by dissolving gelatin and hydrazine hydrate in deionized water at room temperature. Then solution A was added into solution B drop by drop with the aid of a peristaltic pump, and the dipping rate was sufficiently low to

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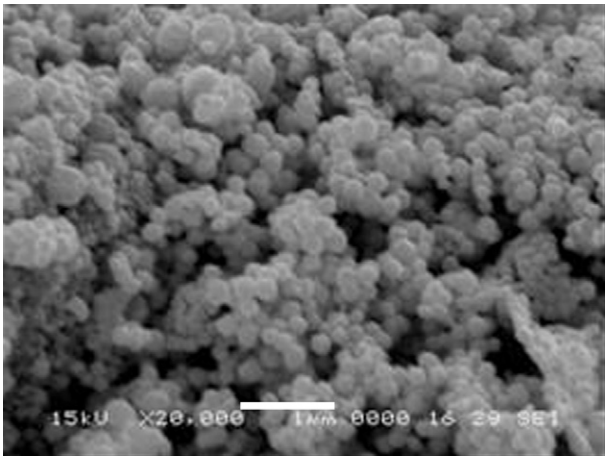


Fig. 1. SEM micrograph of silver particle.

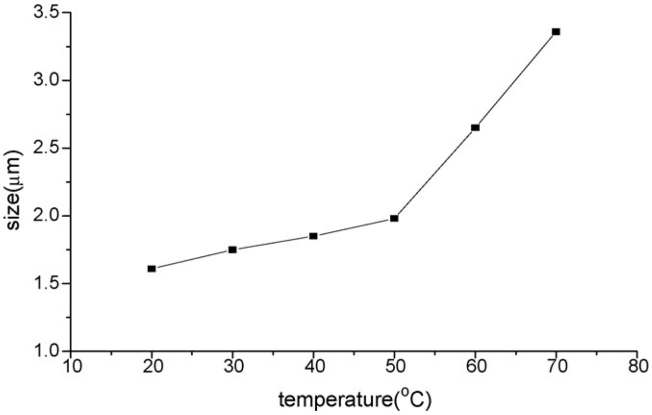


Fig. 2. Effect of reaction temperature on the average particle size of silver powders (concentration of Ag^+: 0.5 mol l^{-1}, concentration of hydrazine hydrate: 1.5 mol l^{-1}, gelatin/silver nitrate mass ratio = 1:100).

control the reaction rate. The mol rate of hydrazine hydrate/silver nitrate was 3:1 to achieve complete reduction of the silver salt. The reaction mixture was stirred with a Teflon coated paddle type stirrer at an adequate rate to maintain the uniformity of the system. At the end of all reactions, the depositions were separated from reaction solutions by Buchner funnel, and were subsequently washed with deionized water and alcohol several times. The silver particles were then dried at 50 °C in vacuum oven for 5 h.

Characterization of silver particles was achieved by different techniques. The ultraviolet absorption spectra of aqueous solutions were measured by ultraviolet spectrophotometer (Spectrumlab-54). The shape of the final products was observed by scanning electron microscopy (SEM, JSM-6360LV). The particle size was measured with BT-9300H laser particle sizer.

3. Results and discussion

3.1. Preparation of spherical silver particles

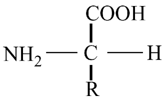
Fig. 1 is the SEM micrograph of silver particles prepared with 0.5 mol l^{-1} Ag^+, 1.5 mol l^{-1} hydrazine hydrate, gelatin/silver nitrate mass ratio = 1.5:100, and reaction temperature at 20 °C. As shown in Fig. 1, spherical silver particles with a particle size between 0.2 and 0.3 μm are well dispersed, but with unshaped surfaces. On the other hand, the average particle size of silver particles evidently increases with an increase in reaction temperature, as shown in Fig. 2, which is not consistent with the previously reported result of the prepared nanosized silver particles [8]. This discrepancy was most likely due to the required micro-size of silver particles in the present experiments which was different from the preparing process of nanosized silver particles.

The well-known LaMer model [9], as illustrated in Fig. 3, can be used to describe properly the preparing process of the present work. It is seen from Fig. 3 that LaMer diagram divides the forming process of the monodispersed particles into three stages: pre-nucleation, nucleation and crystal growth. Unlike nanosized particles, the formation of submicrosized silver particles could be supposed to experience the LaMer process for two times [10]. The first time consisted of the formation of nanosized primary particles which occurred immediately on mixing reducing agent solution with silver ions solution. Although the primary particles increase in number in the first stage, they did not grow appreciably and coagulate with each other owning to the protection of gelatin. However, with an accumulation of the primary particles and the increased consumption of the gelatin, they started coagulation to form clusters which acted as the nuclei of the secondary particles, thus initiating the second LaMer process. The secondary particles with submicrometer size were finally formed by gathering the secondary nuclei with the neighboring primary particles which is similar to the case of forming submicrosized Fe_2O_3 particles in Ref. [11]. Because the increase of reaction temperature would accelerate the coagulation of primary particles, the average particle size of silver particles evidently increase with an increase in temperature (Fig. 2).

3.2. Gelatin protective mechanism

3.2.1. The effect of gelatin on the primary particles

Protection role that the gelatin played in the formation process of primary silver particles was supposed to be related to its structure. As shown in Formula (1), gelatin contains many –COOH and $–NH_2$ polar groups while R denotes the large organic group.



$$NH_2-\overset{\overset{\large COOH}{|}}{\underset{\underset{\large R}{|}}{C}}-H \tag{1}$$

The donated lone pairs by both nitrogen and oxygen atoms in the polar groups may occupy two sp orbits of the silver ion to form a complex compound, which was supported by ultraviolet spectra as well as the results of photo-reduction experiment. The

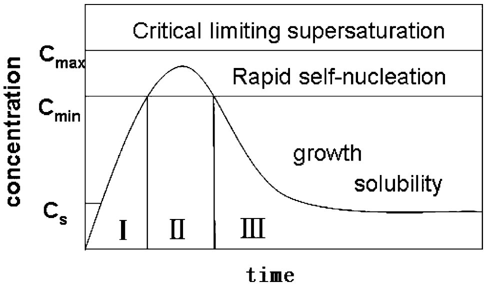


Fig. 3. LaMer model for monodispered particle formation.

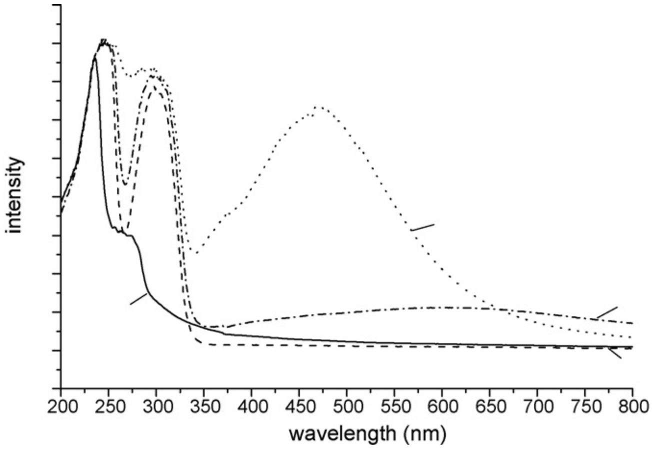


Fig. 4. Ultraviolet absorption spectra. (a: pure gelatin solution; b: 5 wt.% silver nitrate solution; c: 5 wt.% silver nitrate solution plus ammonia; d: 5 wt.% silver nitrate solution plus ammonia and gelatin.)

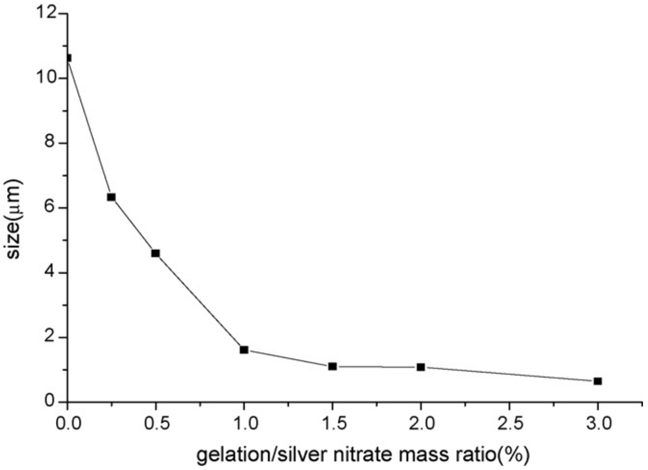


Fig. 5. effect of dosage of gelatin on the average particle size of silver powders.

latter was carried out on three silver nitrate solutions (b: pure silver nitrate solution, c: silver nitrate solution plus ammonia, and d: silver nitrate solution plus ammonia and gelatin) with the same silver nitrate concentration (100 g l^{-1}) by subjecting them to sunlight radiation under the same conditions for 30 min. The ultraviolet (UV) spectra of the samples are illustrated in Fig. 4. Although all the samples containing same concentration silver ions show an almost same peak value at 320 nm resulting from the coordinative bonds of H_2O–Ag complex, the addition of ammonia produces lower absorption valley at 270 nm than the addition of gelatin. These ultraviolet absorption valley changes imply the changes of the absorption peak at 320 nm, most likely due to the substitution of H_2O–Ag complex by ammonia–Ag complex. As shown in Fig. 4a, the pure gelatin solution has an absorption shoulder at 270 nm corresponding to the UV-absorption of large molecule of gelatin, while the higher ultraviolet absorption valley of gelatin containing solution may be attributed to the substitution of complexes (the ammonia–Ag complex and H_2O–Ag complex) by gelatin–Ag complex, because the nitrogen and oxygen of the gelatin have a stronger coordinative field than H_2O and ammonia.

Fig. 4 also shows that the absorption area of the silver absorption peak of the gelatin containing solution centering at 470 nm is obviously larger than that of gelatin free solution. This might be attributed to the fact that the ligands of C–N and C=O in gelatin contributed more electronic density to the sp orbital of silver ions than H_2O or ammonia did. Thus, the silver ions in the gelatin–Ag complex may more easily obtain electrons from hydrazine hydrate than those in H_2O–Ag or ammonia–Ag complex, indicating the easier reduction of the former. In other words, gelatin might play the positive role of promoting the nucleation of the metallic silver particles.

3.2.2. *The effect of gelatin on the secondary particles*

As shown in Fig. 5, in the gelatin free case with the silver nitrate concentration as 0.5 mol l^{-1}, hydrazine hydrate concentration as 1.5 mol l^{-1}, and reaction temperature at 20 °C, average particle size of the silver particles was larger than 10 μm which decreased with an addition of gelatin until mass ratio of gelatin to silver nitrate up to 1:100. This implies that the addition of gelatin influence average particle size of the secondary particles, most likely due to the improved dispersion of secondary particles together with the enhanced nucleation of the primary silver particles. As a protection agent, gelatin played a role of preventing the secondary particles from aggregation owing to the electrostatic effect and the steric effect arising from the gelatin on the surface of secondary particles, and these two effects are largely determined by the covering fraction of gelatin on the surface of the secondary particles. This means that the influence of these effects increases with the increase in the dosage of

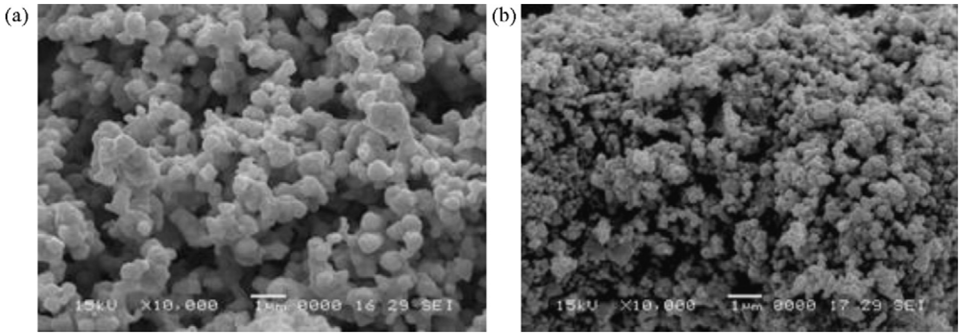


Fig. 6. SEM micrographs of silver particle. (concentration of Ag^+: 0.5 mol l^{-1}, concentration of hydrazine hydrate:1.5 mol l^{-1}, reaction temperature: 20 °C, a: gelatin/silver nitrate mass ratio = 0, b: gelatin/silver nitrate mass ratio = 1:100.)

gelatin until mass ratio of gelatin to silver nitrate up to a critical value where all the surfaces of silver particles are covered by gelatin large molecule. In the present work, however, the critical value of protection agent for all coverage of the particles seems very small (about 1:100) by comparison with previously reported work [5]. This is perhaps because secondary particles are the coagulations of many primary particles so that the total effect surface reduced by large. On the other hand, even after the critical value, the slight decrease in average size of particles with increased gelatin content was still observed. This might be related to the role of gelatin of promoting the nucleation of the metallic silver particles as we discussed above on its effect on the size of primary particles. This effect is apparently independent on the coverage fraction of gelatin on surface of particles as well as less than the electrostatic and steric effects. As a result, the average particle size of secondary particles showed slight reduction even after the critical value.

Moreover, the addition of gelatin also influenced the shape of secondary particles. Fig. 6 shows SEM micrographs of the silver particles. When gelatin/silver nitrate = 0, irregular shape and heavily sintering like particles with a large average particles size was observed (Fig. 6a). This was most likely due to the over-quick growth rate and the coagulation of secondary particles without the protection of gelatin. In contrast, the well-dispersed spherical-shaped silver particles and a narrow particle size distribution (Fig. 6b) were obtained with gelatin/silver nitrate mass ratio at 1:100.

4. Conclusions

The prepared silver particles are secondary particles which are the coagulations of many nanosized primary particles. The average particle size of these secondary particles with unshaped surfaces increases with an increase of reaction temperature. The coordinative complex of silver ions and gelatin which was proved by the ultraviolet spectra and photo-reduction experiments can promote the nucleation of the metallic silver particles. The average particle size of secondary particles decreases with an increase in the gelatin to silver nitrate mass ratio until the mass ratio up to 1:100, after which the average particle size showed slight reduction. Moreover, the addition of gelatin is also propitious to the formation of monodisperse spherical silver particles.

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