# The preparation of nano-scale plate silver powders by visible light induction method

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Silver can dissolve from the uncovered parts of the nanoparticles under the visible light irradiation and form extremely small spherical silver clusters. The latter can be further converted into nano-scale plate-like silver powders (PSP) in the presence of polyvinylpyrrolidone (PVP). The wavelength and intensity of visible light, the irradiation time and the weight ratio of protecting polymer to reducing agent have a significant effect on the formation and shape of PSP. The conversion process was monitored by ultraviolet-visible spectroscopy (UV-Vis). The product was characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray powder diffractometer (XRD). © *2004 Kluwer Academic Publishers*

## 1. Introduction

Silver (Ag) provides superior conductivity and has reasonable costs associated with it, compared to other precious metals utilized in the electronics industry. PSP are widely used as conductive fillers for isotropic conductive adhesives and the conductivity of PSP is superior to spherical silver powders (SSP) [1, 2]. As a result, the production of PSP has developed into an industry of its own. The particle size, size distribution and the thickness of PSP have a great influence on the ohmic resistance of conductive film of carbon diaphragm potential components and other electronic components, in which PSP was further processed into silver paste and printed on the surface of above components by silk screen method. For the space padding efficiency of conductive layer, thin PSP is better than thick one.

The traditional method of manufacturing PSP is mechanical milling method, by which the SSP are milled strongly to change the particle shape from sphere to plate. The SSP are mainly prepared by reducing method [3–10] in which some suitable silver salts such as silver nitrate, the complex ions of ammonia silver and potassium silver cyanide are reduced by inorganic reducing agent such as ferrous sulfate and zinc powders or organic reducing agent such as methanol, hydrazine hydrate, formaldehyde and ascorbic acid (Vc). The apparent density, tap density, the size and thickness of single PSP, the agglomeration and electrostatic charges of the resulting PSP are related remarkably to the oper-

ation conditions of chemical reduction and mechanical milling. As a result, the qualities of PSP, silver paste and electronic components are seriously unstable.

Except for the milling method, photoinduced method [11–13], sonochemical method [14, 15], template method [16–18] and many others [19–20] have also been used to prepare non-spherical silver nanoparticles. Dendritic, triangular prism, cuboid and plate-like precious metals nanoparticles have been prepared. But those non-spherical particles are only as a byproduct in most cases, and the contingency and uncertainty of these methods make it impossible to apply directly in the manufacture of PSP in industry at present. Jin [12] and coworkers have converted large quantities of silver nanospheres into triangular nanoprisms using photoinduced method. Bis(*p*-sulfonatophenyl) phenylphosphine dihydrate dipotassium salt (BSPP) was used as protect agent and visible light was used as a light resource. Electron energy loss spectroscopy analysis (EELS) and theoretical calculations showed that the particles formed in the photoinduced process are indeed silver nanoprisms, not tetrahedral. But it is difficult to separate the nanoprisms from each other, because they are stack together firmly and appear as the nanorods that can be seen from the TEM images. Exploring the advanced preparation method of PSP that can be used in industry is beneficial not only to PSP itself but also to the subsequent products and is fairly important.

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We have obtained SSP with good stabilization and narrow size distribution using reduction-protection method [21, 22]. The key point is that during the reduction of silver salts, the resulting particles should be protected concomitantly to avoid the aggregation of the particles. In this paper, we use reduction-protection technique to prepare silver colloid clusters first and then use photoinduced method to obtain PSP. Visible light and PVP are used as an irradiation light source and a protect polymer respectively. Changing the experimental parameters such as the wavelength and intensity, the irradiation time and the sorts of protection agents, the thickness and size of the resulting PSP particles can be adjusted.



*Figure 1* Time-dependent UV-Vis spectra showing the formation of PSP: (a) before irradiation and after, (b) 30 h, (c) 50 h and (d) 70 h.

## 2. Experimental section

$AgNO_3$ with high purity supplied by Changzhou Rare and Noble Metal Refining Factory (China). PVP (average molecular weights of 29 000 and 40 000), ascorbic acid (Vc), and other reagents were obtained from Shanghai Chemical Reagent Company with analytical grade. The water used was purified through a Milli-Q system. All glassware used in all preparations was scrupulously cleaned with chromic acid solution and rinsed with deionized water.

50 g Vc and a certain amount of PVP with a given weight ratio to Vc were dissolved in 100 ml water in 50°C, and 0.001 mol/L solution containing 50 g $AgNO_3$ was dropped into the resulting solution of Vc and PVP. A colloid solution of silver was obtained and was removed into quartz glass container with a quartz jacket, in which some colored solution was filled to filter some special light from visible light. The jacketed quartz container was then irradiated in an irradiation box with a mercury lamp of 250 W. The reaction products were isolated by high speed ($4000\,r \cdot min^{-1}$) centrifugal separation and then dried under vacuo to obtain PSP.

The disappearance of $Ag^+$ ions and the formation of PSP were monitored by ultraviolet-visible (UV-Vis) spectra with a Shimadzu UV-2201 recording spectrophotometer. The transmission electron microscopy (TEM) and selected area electron diffraction (ED) images of PSP were taken with a Jeol model JEM-200CX TEM, using an accelerating voltage of 200 KV. Samples for TEM and ED were prepared by dispersing a bit of the resulting PSP into absolute alcohol and placing a drop of the PSP dispersion onto a carbon-coated copper grid, dried at room temperature. The scanning electron microscopy (SEM) images were taken with a Hitachi model X650 SEM. The X-ray powder diffraction (XRD) patterns of PSP were determined at a scanning rate of $0.02° \, s^{-1}$ in $2\theta$ ranging from $30°$ to $85°$, using a D/MAX-RA rotating anode X-ray diffractometer with high-intensity Cu $K_\alpha$ radiation ($\lambda = 0.151478$ nm) and a graphite monochrometer.

## 3. Results and discussion

In a typical experiment, PSP particles were prepared by adding aqueous solution of $AgNO_3$ (0.001 mol/L, 50 ml) drop-wise to 50 ml aqueous mixture of PVP
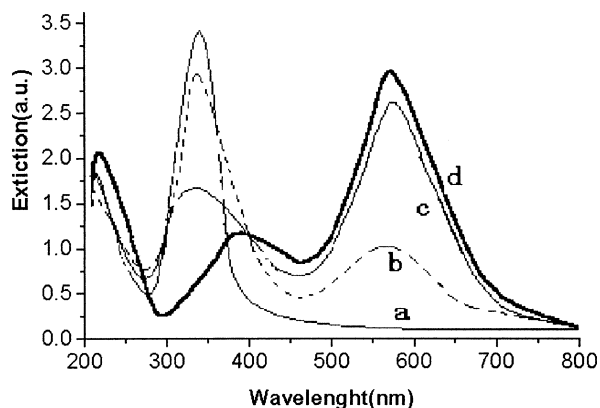
and Vc (the weight ratio of PVP to Vc is 0.02) with constant stirring. The system is then irradiated with a 250 W mercury lamp. A set of color changes not typical for the preparation of spherical particles was observed during the course of irradiation. At the beginning, the solution turned the characteristic yellow of the spherical particles, then green after 20 h and finally dark-blue. A decrease in intensity of the characteristic surface plasmon band in UV-Vis spectra for the spherical particles at $\lambda_{max} = 340$ nm with a concomitant growth of two new bands at $\lambda_{max} = 385$ (weak) and 575 nm (strong), was observed respectively (Fig. 1). After 70 h, the band at 340 nm completely disappeared.

Transmission electron microscopy (TEM) combined with the time-dependent spectroscopic observations shows that the initial spherical silver particles (about 10–20 nm, Fig. 2a) were converted to plates with triangles, hexangles or other polygons. During the initial stages of growth, both spheres and plates can be seen (Fig. 2b and c). The latter exhibit edge lengths or diameters between 10 and 80 nm. Both the size and amount of the plate-like silver particles increase with time a concomitant decrease in the number of spherical particles. After 70 h, nearly all of the initial spheres (>99%) are converted to PSP as shown in Fig. 2d (about 40 to 100 nm). The tilting sample experiments confirm that the thickness (~50 nm) of the plate-like silver is smaller than the edge length (~280 nm) of the polygon, so, it is a really silver plate, not a nanoprism. These data clearly show that the plate-like silver evolves from the initial spherical nanoparticles.

In order to insight into the mechanism of the efficient conversion of silver nanospheres to PSP, we investigated the effect of a variety of experimental parameters, including the silver salt precursor and its concentration, the weight ratio of PVP to Vc, and the wavelength of irradiation light, on the conversion process. The conversion process is initiated by light at wavelengths between 350 to 700 nm. When irradiated with near-infrared light (>700 nm) or in the dark, the conversion does not take place. Therefore, the conversion process can be selectively turned on or off simply by the light wavelength. The conversion rate decreases as increasing weight ratio of PVP to Vc (range 0.01 to 0.5). The conversion of nanoparticles to PSP does not take place when the weight ratio of PVP to Vc is larger than 0.5
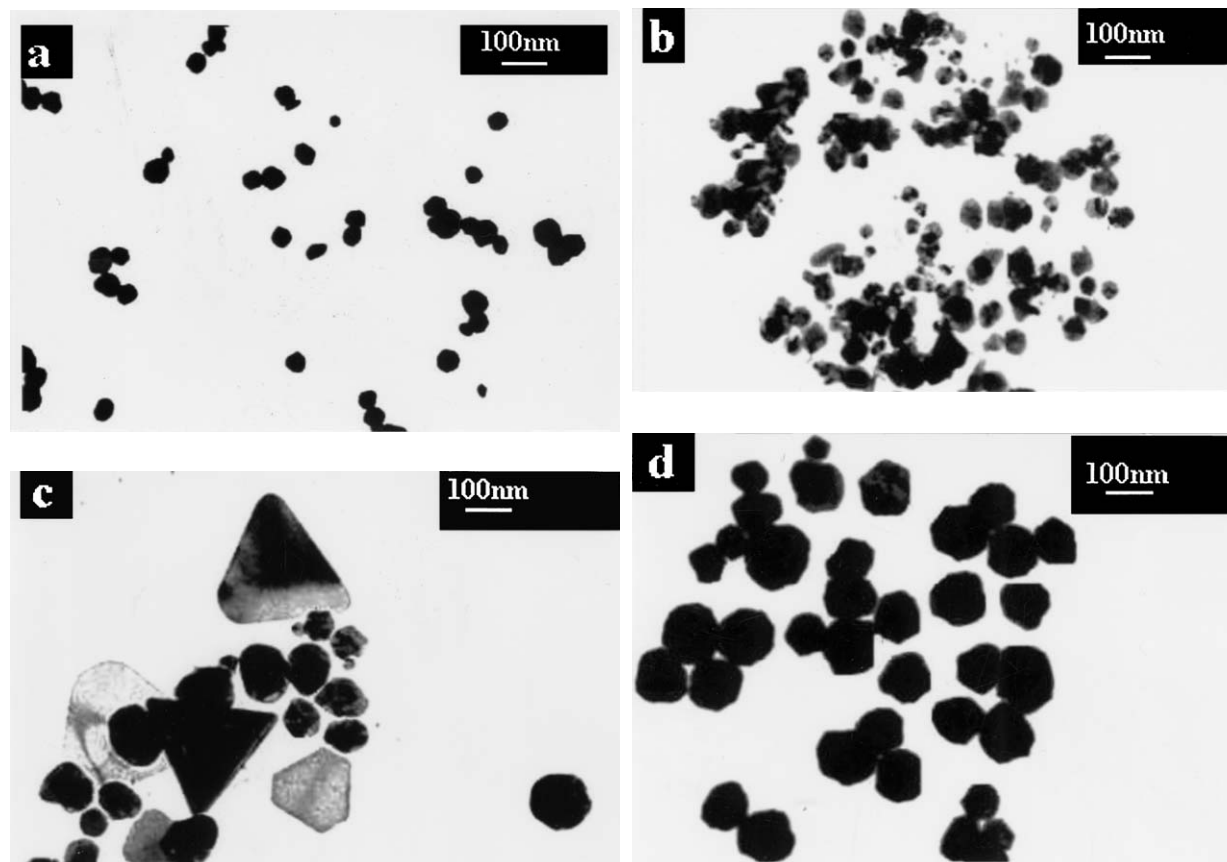
*Figure 2* TEM images mapping the morphology changes: (a) before irradiation and after (b) 30 h, (c) 50 h and (d) 70 h of irradiation.

and the optimum results were obtained with a 0.02:1 ratio. Comparable results are also obtained with spherical particles formed from $Ag (NH_3)_2^+$, except the particle size is smaller than that formed from $AgNO_3$.

Jin and coworkers have suggested the mechanism of transferring nanoscale spherical silver clusters into nanoprisms. Using bis($p$-sulfonatophenyl) phenylphosphine dihydrate dipotassium salt (BSPP) as a protecting agent, nanoprisms were formed within the entire ratio of BSPP to citrate range from 0.01 to 1 [12]. In this work, BSPP and $NaBH_4$ are replaced by PVP and Vc respectively. The latter are cheaper than the former, which is suitable for massive production of PSP. PVP is a polymer with some suitable coordination sites from N and O atoms, which can bind to the facets of the silver nanoparticles. Compared with BSPP, PVP binds preferentially to the facets, which are different from in BSSP case, and also the coordination reaction is weaker than in BSSP case. It makes the photoinduced conversion of the spherical silver nanoparticles into PSP easy. The weight ratio of PVP to Vc is fairly sensitivity for the formation of PSP. The formation process can be divided into three distinctive stages: induction, growth, and termination as showing in Fig. 3. During the induction period the partial protected silver particles by PVP molecules can dissolve from uncovered part of the particles and some small plate-like silver nanoparticles were formed concurrently and act as seeds and grow until the small spherical clusters are digested. Once the small nanoclusters are consumed, the reaction terminates. Both the photoinduced conversion of spherical silver nanoparticles into small clusters and PVP acts as
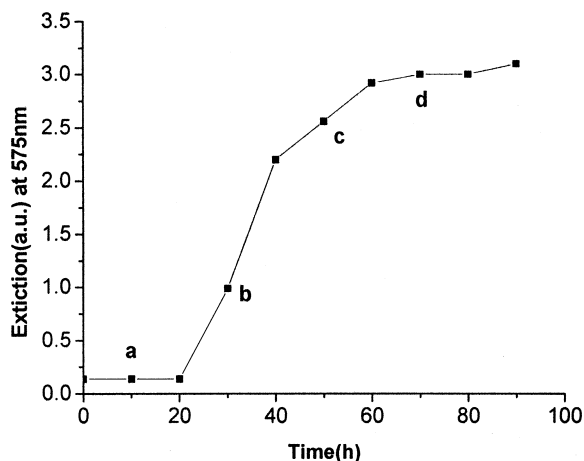


*Figure 3* Extinction profiles of silver colloid at 575 nm as a function of time: (a) before irradiation, (b) 30 h, (c) 50 h and (d) 70 h.

a protective agent provides an efficient way to control the growth of PSP. The mechanism of partial protected Ag particles transferring to PSP by irradiation of visible light can be schemed in Scheme 1.

Fig. 4 shows the typical SEM images of PSP obtained by irradiation of 250 W mercury lamps at different time. Fig. 4a shows a SEM image of Ag nanoparticles before irradiation, which was obtained by high-speed centrifugal separation and then dried under vacuum. It aggregated seriously. Fig. 4b and c show the SEM images of the samples irradiated for 60 and 70 h. We can see the morphologies of the samples look like flowers. The segments of the flowers are composed of the aggregates of

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**uncovered part of the particles**
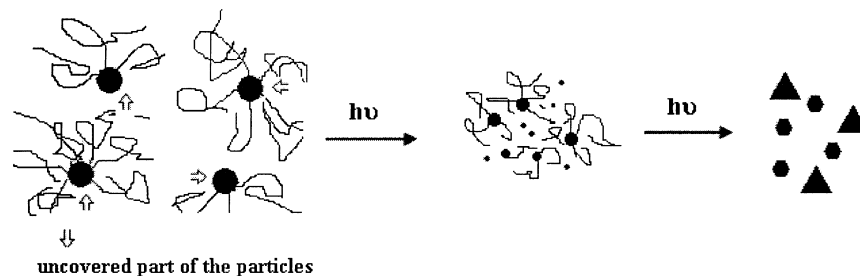
*Scheme 1* The mechanism of partial protected Ag nanoparticles transfer to PSP by irradiation of visible light. The uncovered parts of silver nanoparticles dissolve first under the effect of visible light and form extremely small spherical silver clusters as the seeds and grow to form nanoplates in the presence of PVP.
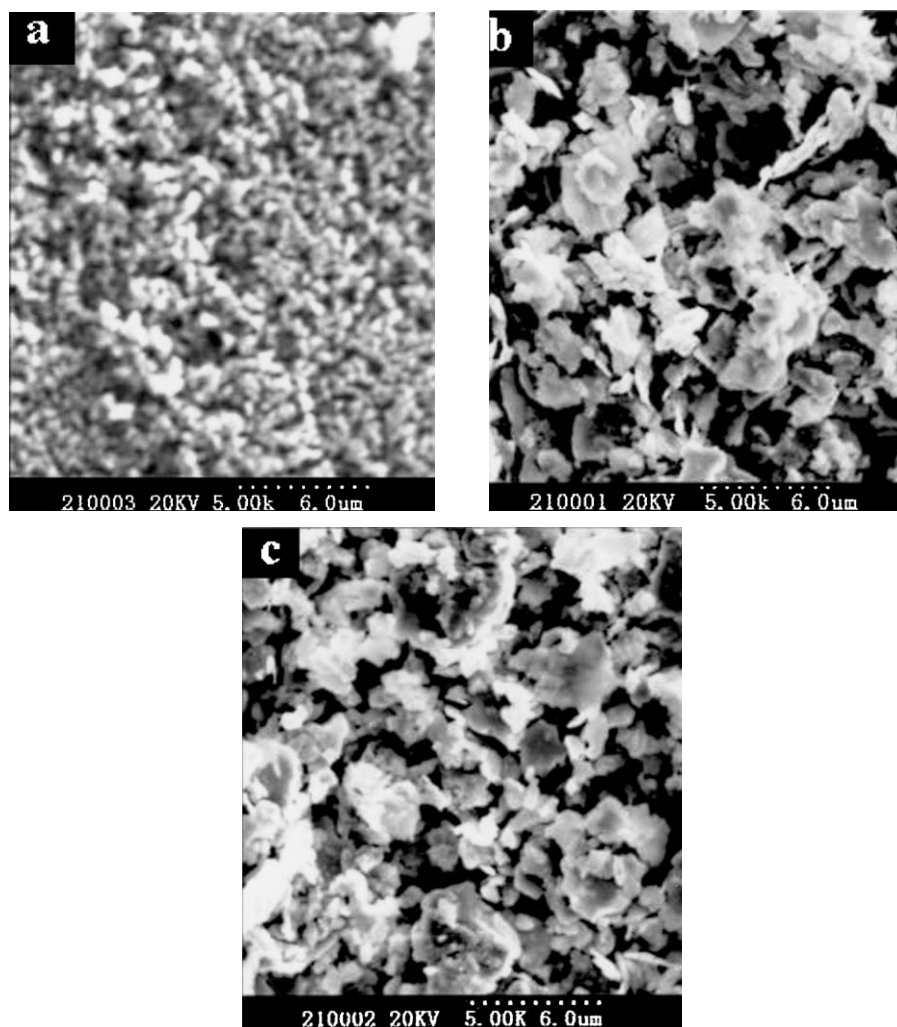


*Figure 4* The SEM images of PSP before irradiation (a) and after 60 h (b) and 70 h (c).
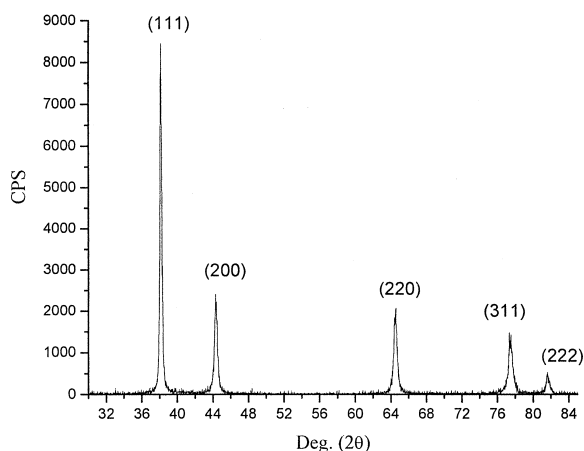


*Figure 5* The XRD pattern of PSP after irradiated 70 h.

PSP. The corresponding ED image shows that the PSP is polycrystalline with high purity (about 99.95%). The XRD pattern (Fig. 5) also proved that the PSP is pure and the peaks can be indexed to cubic system Ag (111), (200), (220), (311) and (222), which have a good match with the standard diffraction spectrum of JCPDS No. 4-0783.

## 4. Conclusion

PSP were obtained by visible light induction conversion method. The wavelength and intensity of visible light, the irradiation time and the weight ratio of protecting polymer to reducing agent have a significant effect on the formation and shape of PSP. The light

induction conversion process can be divided into three stages: induction, growth and termination, according to the extinction characteristics of PSP. The visible light induction conversion might be a candidate method to substitute the traditional ball milling method. But the color of PSP obtained in this method is not silvery white as obtained by ball milling method because the size of the particles is nanoscale. The performance of the silver paste and electric components remains for further study and many other works should be done before industrializing this method.

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