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Electrochemical Synthesis of Silver Nanoparticles in the Presence of Poly(N-vinylpyrrolidone) and the Study of Phase-Transfer

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Poly(N-vinylpyrrolidone)-protected spherical shape silver nanoparticles with diameter about 30-100 nm were prepared by electrochemical method using the rotating glassy carbon as working electrode. The result showed that the electrode rotation rate had a great effect on the silver colloids. UV-Vis absorption spectra, X-ray diffraction and scanning electron microscopy (SEM) were employed to characterize the silver nanoparticles. Moreover, based on the decrease of the solubility of poly(N-vinylpyrrolidone) in water with the temperature increase, the obtained silver nanoparticles were transferred from aqueous phase to organic phase successfully by phase-transfer method, which improved the catalytic activity of silver nanoparticles.

Key Words: Electrochemical method, Poly(N-vinylpyrrolidone) (PVP), Silver nanoparticles, Phase-transfer.

INTRODUCTION

Silver nanoparticles have attracted considerable interest because of their potential applications in areas such as nanoelectronics, electromagnetic interference shielding and surface-enhanced Raman scattering[1]. During the past few decades, many methods including both physical and chemical methods have been reported for the synthesis of silver nanoparticles[2-7]. As a simple and feasible method, electrochemical deposition has been widely used to synthesize the metal nanoparticles[8,9]. For preparation of metal nanoparticles, some water-soluble polymers such as poly-(vinyl alcohol), poly(N-vinylpyrrolidone) (PVP) and poly(methylvinyl ether) have been used to prevented the particles from growth or agglomeration[10-12]. Jiang *et al*.[13] and He *et al.*[14] reported that dendritic silver nanoparticles were prepared by ultraviolet irradiation photoreduction technique or by sonoelectrochemical methods in the presence of poly(N-vinylpyrrolidone). Tai *et al.*[15] also obtained the silver nanoparticles using a spinning disc reactor in a continuous mode using poly(N-vinylpyrrolidone) and hydroxypropylmethyl cellulose as protecting agents, respectively. But on the other hand, the strong adsorption of poly(N-vinylpyrrolidone) on the surface of metal nanoparticles greatly lowers the catalytic activity of particles. It is necessary to remove a portion of poly(N-vinylpyrrolidone) polymers that wrap the metal nanoparticles in order to enhancing the catalytic activity of metal nanoparticles.

Therefore, it is important to transfer the metal nanoparticles from aqueous phase to organic phase and to maintain the monodisperse of the particles during the process of phase-transfer.

Herein, silver nanoparticles have been prepared by reduction of silver nitrate using electrochemical methods in the presence of poly(N-vinylpyrrolidone) and the influence of rotation rate on silver nanoparticles has been studied. At the same time, we developed a novel phase-transfer method of nanoparticles based on the decrease of the solubility of poly(N-vinylpyrrolidone) in water with the temperature increase. The poly(N-vinylpyrrolidone)-protected silver nanoparticles can spontaneously leave the aqueous phase and enter into an organic phase when heating the oil-water mixture containing silver nanoparticles to an appropriate temperature. The silver nanoparticles transferred to the organic phase exhibit a high catalytic activity since most poly(N-vinylpyrrolidone) polymers were removed in the course of phase-transfer.

EXPERIMENTAL

Silver nitrate ($AgNO_3$, analytical reagent) and butanol were purchased from Beijing Chemical Company of China and were used without further purification. Poly(N-vinylpyrrolidone) (PVP) with a weight-average number of 40000 (Scientific Polymer Products) was used as received. Water used in the experiment was double distilled water.

Preparation of silver nanoparticles and phase-transfer: The electrochemical experiments were performed with a CHI650A potentiostatic/galvanostat. The working electrode was rotating glassy carbon (GC) disc electrode (3 mm in diameter) and a platinum sheet was used as counter electrode. The preparation of silver nanoparticles was carried out in 5 mM $AgNO_3$ aqueous solution containing 0.25-1.00 wt % poly(N-vinylpyrrolidone) at a constant current of 10 mA for 20 min with different rotation rate.

About 20 mL of butanol were added into the silver colloids synthesized by electrochemical method under stirring. The mixture was heated to 80 °C, stop stirring and silver nanoparticels could spontaneously transferred from water to butanol at 80 °C.

Measurements: UV-Vis absorption spectra were recorded with a UV-2800 spectrophotometer. Scanning electron microscopy (SEM) image was taken on a FEI Sirion200 system (operated at 1 kV). The produced mesophase structures were characterized using an XD-3A X-ray diffraction system.

RESULTS AND DISCUSSION

Effects of electrode rotation rate: UV-Vis absorption spectra have been proved to be quite sensitive to the formation of silver colloids[16]. An intense absorption peak around 420 nm was generally observed and attributed to the surface plasma excitation of silver particles. Fig. 1 shows the UV-vis spectra of silver colloids for the different electrode rotation rate. It can be seen that the absorption peak intensity at about 420 nm rose and the symmetry of peak become better when the rotation rate increased from 1000-1500 r/min, which indicated the increase of the diameter and better dispersion of silver particles[17]. However, when the rotation increased to 2000 r/min, the absorption peak intensity decreased and the symmetry of peak become poor, which showed the decrease of the diameter and poor dispersion of silver particles. Therefore, rotation rate had a great effect on the silver colloids and too high or too low speed are not beneficial for the electrochemical synthesis of silver nanoparticles. In this experiment, rotation rate of 1500 r/min was chosen for the electrochemical synthesis of silver nanoparticles.

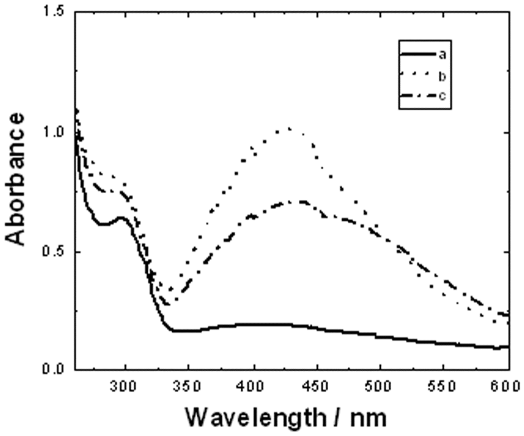

Fig. 1. UV-Vis spectra of silver colloids. Rotation rate: (a) 1000, (b) 1500, (c) 2000 r/min

Characterization of silver nanoparticles by XRD and SEM: Fig. 2 shows the power XRD patterns of silver nanoparticles. The reflection peaks at 2θ of 38.5º, 43.5º, 64.5º and 77.5º corresponds to the 111, 200, 220 and 311 crystal planes, respectively. They are well consistent with JCPDS files (No. 41-1402) and indicate that the gained silver nanonarticles are of face-centered cubic.

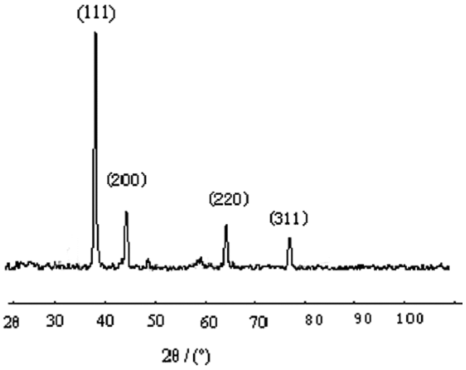

Fig. 2. XRD spectrum of silver nanoparticles

The microscopic morphology of silver nanoparticles was characterized by scanning electron microscopy (SEM). As can be seen from Fig. 3, the particles were spherical and the diameter was about 30-100 nm. Poly(N-vinylpyrrolidone) was used as a protective medium for the colloids in this experiment and it affected the molecular motion of reduced silver and subsequently limited the aggregation of colloids. Therefore, the obtained particles were sphere shaped and had good dispersion.

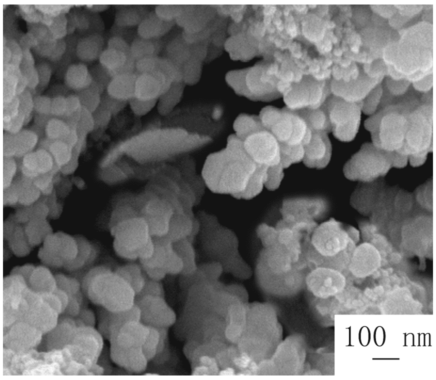

Fig. 3. SEM image of the silver nanoparticles

Phase-transfer of silver nanoparticles: In order to have a better dissolution or dispersion of the nanoparticles in organic phase, phase-transfer accelerant or protective agent such as thioalcohol, amide and surfactant are often needed during the process of conventional phase-transfer. In this experiment, a new method was employed. Based on the property that the solubility of poly(N-vinylpyrrolidone) in water decreases with increasing temperature, the poly(N-vinylpyrrolidone)-protected silver nanoparticles could spontaneously leave the aqueous phase and enter into an organic phase. Fig. 4 shows the UV-vis spectra of aqueous phase before (a) and after (b) phase-transfer. As is shown in Fig. 4, the absorption peak at 420 nm corresponding to the surface plasma excitation of silver particles disappeared when the temperature increased to 80 °C, which indicated that most silver nanoparticles had been transferred from water to butanol. The reason may be that the poly(N-vinylpyrrolidone) transferred from water to butanol when the temperature increased, which induced the transfer of silver nanoparticles.

Conclusion

Well-dispersed spherical shape silver nanoparticles with diameter about 30-100 nm have been prepared by constant current method using poly(N-vinylpyrrolidone) as a protective agent. Rotation rate has a great effect on the silver colloids and rotation rate of 1500 r/min was chosen for the electrochemical synthesis of silver nanoparticles in this experiment. Based on the decrease of the solubility of poly(N-vinylpyrrolidone) in water with the temperature increase, the silver nanoparticles can spontaneously transfer from aqueous phase to organic phase when temperature increase, which can be verified by UV-vis absorption spectra.

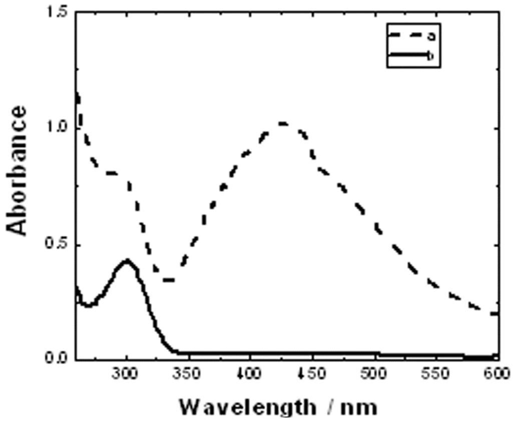

Fig. 4. UV-Vis spectra of aqueous phase before (a) and after phase-transfer (b)

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