A novel route for the preparation of monodisperse silver nanoparticles via a pulsed sonoelectrochemical technique

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Abstract

Monodisperse silver nanoparticles stabilized with PVP have been prepared in a saturated solution of silver citrate (Ag₃C₆H₅O₇) in the presence of poly(vinyl pyrrolidone) (PVP) by a pulsed sonoelectrochemical technique.

Keywords: Sonoelectrochemistry; Silver; Nanoparticles; PVP

Noble metal nanoparticles have been extensively studied in recent years because of their unique catalytic, electric, magnetic, optical and mechanical properties that are different from bulk materials [1–4]. Therefore, various approaches have been employed for the preparation of nanosized metal particles. These approaches include the following: solution phase method [5–8], laser ablation [3], sonochemical method [9,10], electrochemical synthesis [11–14] and so on. Among the noble metal nanoparticles, silver nanoparticles have been widely studied. Silver nanoparticles have various important applications in many aspects such as photographic process [15], surface-enhanced Raman spectroscopy [2] and catalysis process[10]. It is well known that the catalytic reactivity of metal nanoparticles depends on their size and shape greatly. Therefore, it is very essential to develop a simple and effective preparation method of metal nanoparticles for well-controlled size and shape.

Sonochemical method has been used extensively to generate novel materials with unusual properties since 1934. The chemical effects of ultrasonic irradiation are due to the very high temperature and pressure that are transiently formed (sub-μs) in collapsing bubbles [16,17], which enable many chemical reactions to occur. In recent years, sonochemistry combined with electrochemistry have attracted great interest. Reisse et al. [18] and Mason [19] have described a novel method for the production of particulate metals, alloys and semiconductors using a pulsed sonoelectrochemical reduction. With this method, several kinds of metal and semiconductors nanoparticles have been prepared [13,14,18–21].

In the present paper, a novel route was used to prepare monodisperse silver nanoparticles in a saturated solution of silver citrate in the presence of poly(vinyl pyrrolidone) (PVP) by a pulsed sonoelectrochemical technique. The products were characterized by powder X-ray diffraction (XRD), transmission electron microscope (TEM) and UV–Vis spectroscopy. The influence of current density and the concentration of PVP were also discussed in the present paper.

In the experiments, all chemicals were of analytical grade and were used without further purification. The experimental setup employed in this study was similar to those of Reisse et al. and Gedanken et al. [13,20,21]. Ultrasound irradiation was accomplished with a high-intensity ultrasonic probe (Xinzhi Co., China, JY92-2D, 0.6 cm diameter; Ti-horn, 20 kHz). A titanium horn acts both as the cathode and the ultrasound emitter. The electroactive part of the sonoelectrode is the planar circular surface, of area 0.28 cm², at the bottom of the
horn. The immersed cylindrical part is covered by an isolating plastic jacket. The sonoelectrode produces a sonic pulse that is triggered immediately following a current pulse [14]. The home-made potentiostat is operated in the constant current regime (without using a reference electrode). The basis of the sonoelectrochemical technique to form nanoparticles is massive nucleation by using a current pulse, followed by a burst of ultrasonic pulse that removes the deposit from the electrode before the next current pulse. The typical current pulses were 70 mA/cm². The duration of the current pulse was 3 s and the duration of ultrasonic pulse was also 3 s. A platinum sheet (5 × 5 mm²) was used as the counter electrode in our electrochemical cell. The volume of electrolysis cell was 50 ml.

The XRD pattern was recorded using a Philp X’pert X-ray diffractometer. The TEM images were recorded on a JEOL JEM-200CX transmission electron microscope, using an accelerating voltage of 200 kV. The UV–Vis absorption spectrum was obtained using a SHIMADZU UV–3100 spectrophotometer, the prepared silver nanoparticles were dispersed in distilled water under ultrasound, and the concentration of silver nanoparticles was 1.2 × 10⁻² mol/l.

Silver citrate was prepared as follows: 0.05 mol sodium citrate (Na₃C₆H₅O₇·2H₂O) and 0.15 mol silver nitrate (AgNO₃) were dissolved in water, respectively, then Na₃C₆H₅O₇ solution was added dropwise into the AgNO₃ solution, and white silver citrate (Ag₃C₆H₅O₇) began to precipitate. The prepared Ag₃C₆H₅O₇ was centrifuged, washed by distilled water, absolute alcohol in sequence and dried in air. A pH = 4.6 NaAc–HAc buffer solution was prepared according to the literature [22]. In a typical synthesis, 0.15 g Ag₃C₆H₅O₇ was dissolved in a pH = 4.6 NaAc–HAc buffer solution, and the concentration of poly( vinyl pyrrolidone) (PVP-K30, Mw 40,000) is 0.2 g/l. The electrolyte volume was 40 ml. The pulsed sonication was continued for an hour. After that, aqua ammonia was added into the solution in order to remove remnant reaction materials. Then the precipitate was centrifuged, washed repeatedly with water, alcohol and dried in air. The products were characterized by XRD, TEM and UV–Vis spectroscopy.

Fig. 1 is the typical powder XRD pattern of the prepared silver nanoparticles. The diffraction peaks correspond to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes, which can be indexed to a face-centered cubic structure (JCPDS no. 4-0787).

As is shown in Fig. 2, the prepared silver nanoparticles were spherical and monodisperse and the prepared silver nanoparticles have an average size of 20–25 nm. Fig. 3 indicates that the particle size distribution is very narrow and is in accord with Gaussian distribution. Fig. 4 is the UV–Vis absorption spectrum of the prepared silver nanoparticles. The absorption peak centered at 410 nm is the characteristic peak for silver nanoparticles [11,13,23].

Current density affects the size and shape of the prepared silver nanoparticles. According to [24], current density can affect crystal size in at least two opposing
directions. A smaller size would be expected, on the basis of the small amount of material deposited at a lower current. On the other hand, lower current density allow more time for atomic diffusion processes to occur which can lead to larger crystal size. Fig. 5 shows the TEM images of silver nanoparticles under different current density. When current density was set as 70 mA/cm², monodisperse silver nanoparticles could be obtained (Fig. 5(a)). When the current was set as 140 mA/cm², the products had a larger size and some of them even agglomerated (Fig. 5(b)). This indicates that the former effect is dominant in this case, that is, small amount of material deposited at a lower current.

The presence of PVP is a key factor for the formation of monodisperse silver nanoparticles. When PVP was not used, silver dendrites became the main products (Fig. 6(a)); when the concentration of PVP was used as 0.1 g/l, agglomerated silver nanoparticles were the main products (Fig. 6(b)); when the concentration of PVP increased to 0.2 g/l, spherical monodisperse silver nanoparticles formed. It can be interpreted as follows: the electrodeposition is carried out in a saturated solution of \( \text{Ag}_3\text{C}_6\text{H}_5\text{O}_7 \), in which there is dissociation equilibrium as follows:

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\text{Ag}_3\text{C}_6\text{H}_5\text{O}_7 \rightleftharpoons 3\text{Ag}^+ + \text{C}_6\text{H}_5\text{O}_3^-\]

Therefore, the concentration of \( \text{Ag}^+ \) could be controlled through this equilibrium in a certain buffer solution of a certain pH value. **PVP could serve as one kind of stabilizer which prevents the prepared silver nanoparticles from being agglomerated [5,9,11]**. PVP molecules have a structure of a polyvinyl skeleton with polar groups and they strongly adsorb on the surface of silver particles through the coordination bond between the silver atom and oxygen atom of the carbonyl group. When PVP was not

Fig. 4. UV–Vis absorption spectrum of the prepared silver nanoparticles.

Fig. 5. Silver nanoparticles prepared under different current density: (a) 70 mA/cm²; (b) 140 mA/cm².

Fig. 6. Silver nanoparticles prepared under different concentration of PVP (a) without PVP (b) 0.1 g/l PVP.
used, the prepared silver nanoparticles agglomerated to be dendritic crystals through “diffusion-limited aggregate” [13,25]; when 0.1 g/l PVP was used, silver nanoparticles were less agglomerated; when the concentration of PVP became 0.2 g/l, monodisperse silver nanoparticles stabilized with PVP were the main products.

In summary, the spherical monodisperse silver nanoparticles stabilized with PVP were prepared by a pulsed sonolectrochemical technique. Saturated solution of Ag3C6H5O7 precipitate was used as the starting material in our experiments. The residual Ag3C6H5O7 could be removed through the addition of aqua ammonia so that the products could be purified easily. The shape of prepared silver nanoparticles could be controlled by varying the current intensity of the electrodeposition and the concentration of PVP. Thus, a novel method could be applied to prepare monodisperse silver nanoparticles. This convenient and simple method could be also applied to other precipitate of metal ions with other organic acid.

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