Silver nanoparticles prepared by using poly(2-acrylamido-2-methylpropane sulphonic acid) as a surfactant

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Silver nanoparticles were synthesised successfully using poly(2-acrylamido-2-methylpropane sulphonic acid) (PAMPS) as a surfactant. Silver nanoparticles prepared through this approach possess high purity and narrow size distribution. The size distribution result shows that the diameters ranging from 78.82 to 105.709 nm can account for 76.41% of nanoparticles. UV–vis spectra were used to record the formation of silver nanoparticles in detail. It is found that PAMPS can play an important role in the formation and the colloidal stabilisation of silver nanoparticles because of the high affinity of sulphonic and amide with silver ions. The formation is summarised in detail. In addition, a potential application in nanocomposites of this method is explored. The Ag/polyaniline (PANI) nanocomposite prepared using this method shows higher electrical conductivity than that prepared using other methods. This method is novel, convenient, efficient and environmental-friendly, especially suiting those wastewaters treatment facilities containing silver ions. At the same time, it is also promising to prepare Ag/PANI or other metals/polymer composites via *in-situ* polymerisation.

1. Introduction: As an important metallic material, silver nanomaterial has attracted the attention of many researchers because of its easy preparation, high electrical conductivity and excellent antibacterial property and so on [1, 2]. Up to now, nanosilver with various shapes, such as nanoparticles [3], nanowires [4], nanoplates [5], nanocubes [6] and nanobelts [7] have been prepared. Among them, silver nanoparticles are most commonly prepared and are widely used as biosensors, antibacterial materials, electrodes, for energy storage devices and so on [8–13]. When preparing silver nanoparticles, the surfactants play an important role in the morphology, dispersion and stability of silver nanoparticles. Poor dispersion and adsorption of surfactants to silver ions can easily result in agglomeration and in the wide size distribution of silver nanoparticles. Therefore, to develop an efficient, credible surfactant is also attractive for many researchers.

Poly(2-acrylamido-2-methylpropane sulphonic acid) (PAMPS) is a kind of polymer acid polymerised via 2-acrylamido-2-methylpropane sulphonic acid (AMPS) monomers. PAMPS has excellent water-solubility, dispersion, chemical stability and a high affinity for heavy metallic ions because of the presence of many sulphonic acid groups and amide groups in side chains. It is widely used in wastewater treatment, emulsion polymerisation, dispersant, metallic ions remover and so on [14–17]. In this Letter, we aim to use PAMPS as a surfactant to adsorb silver ions and stabilise silver nanoparticles. To the best of our knowledge, it is the first time that silver nanoparticles are synthetised in a PAMPS containing aqueous solution. This method not only removes silver ions from, for example, wastewater but also efficiently transforms them to silver nanoparticles. Compared with others, it is simple and effective in the preparation of silver nanoparticles with high purity and narrow size distribution by using PAMPS with narrow size distribution.

2. Experiment

2.1. Synthesis: AMPS (purity, 99.23%) was supplied by the Shouguang Yuyuan Green Technology Co. Ltd, China. Other reagents (silver nitrate, sodium hypophosphite, ammonium persulphate and acetone) were of analytical grade and commercially available from local chemical shops.

A PAMPS solution was prepared in the following way. AMPS (5.0 g) was dissolved in 20.0 g of deionised water in a 100 ml beaker containing a magnetic stirrer bar. The solution was allowed to stir for 15 min. Ammonium persulphate (0.005 g) was added to this solution. The reaction mixture was kept at 65°C for 4 h and then used as the PAMPS solution. The PAMPS was also characterised for the number-average molecular weight (2006 kg mol^{-1}) and the weight-average molecular weight (2015 kg mol^{-1}) as measured by PL GPC120 gel permeation chromatography. The polydispersity index (PDI) was 1.0045.

PAMPS aqueous solution (5.0 g) was taken in a 250 ml beaker containing 95.0 g of deionised water. A 10 ml solution containing 0.44 g of sodium hypophosphite was added to this beaker. Then, the solution was stirred for 15 min at 40°C. A 15 ml solution containing 1.42 g of silver nitrate was added drop by drop to the PAMPS solution containing sodium hypophosphite. The reduction reaction was sustained for 90 min at 40°C. On completion, the mixture was treated with acetone, then centrifuged and washed several times using deionised water. The products were dried in an oven at 60°C for 24 h.

2.2. Characterisation: The X-ray diffraction (XRD) spectrum of the sample was recorded with Cu Kα radiation ($\lambda = 1.54$ Å) in a diffractometer (Model D/Max 2550). Ultraviolet–vis spectra were recorded on a SHIMADZU spectrophotometer (UV-2450) in the range of 190–900 nm. The morphologies of silver nanoparticles were determined by scanning electron microscopy (SEM, Model Helios Nanolab 600i). The diameters of silver nanoparticles were measured by a particle sizer (Malvern Instruments, Mastersizer 2000). The electrical conductivity of the Ag/PANI nanocomposite was tested by the four-probe method.

3. Results and discussion: Silver ions were reduced to silver nanoparticles efficiently. The yield was calculated according to silver element conservation and was as high as 93%. Fig. 1 is the

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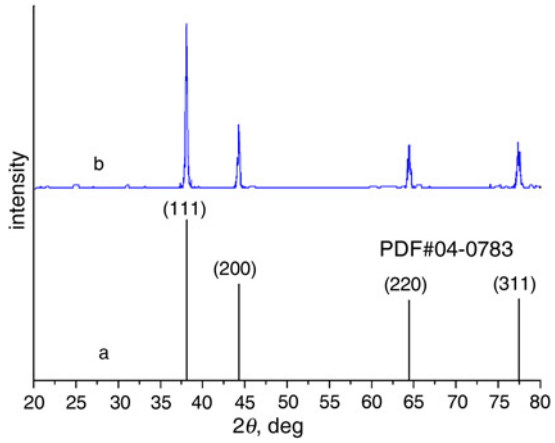

Figure 1 *XRD spectrum of silver nanoparticles*

XRD spectrum of the products. The diffraction peaks at $2\theta = 38.1°$, 44.3°, 64.4° and 77.4° are in good agreement with the (111), (200), (220) and (311) planes (JCPDS No. 4-0783) for crystalline silver. It indicates that the silver particles were synthesised successfully from PAMPS emulsion. According to the Scherrer equation (1) [18], the size of the crystal face of the silver particles is 39.8, 30.5, 31.8 and 35.8 nm, respectively. In addition, the peaks in the XRD spectrum also suggest that silver nanoparticles prepared by this method are of high purity

$$d = K\lambda/(B\cos\theta) \tag{1}$$

where λ is the wavelength ($\lambda = 1.54056$ Å for Cu Kα), θ is the diffraction angle, B is the width at half-height of the peak around θ and K is the correction factor ($K = 0.89$).

To observe the formation process of silver nanoparticles, UV–vis absorption spectroscopy was employed. The reaction solution (0.5 ml) at different stages were extracted and were diluted by distilled water to the one with 50 ppm. Fig. 2 shows the spectra of silver nanoparticles at different synthesis stages. The addition of silver nitrate solution under stirring at 40°C produced a yellow colour (Fig. 2*a*), immediately confirming the reduction of silver ions into silver nanoparticles [19]. The UV–vis absorption peak at 406 nm corresponds to this colour, indicating that a small amount of silver seeds were formed in the initial stage [20]. With the time progressing, the colour of the emulsion changed from yellow to grey (Figs. 2*d* and *e*) and to deep khaki (Fig. 2*f*) at the end. At the same time, the UV–vis absorption peak shifts from

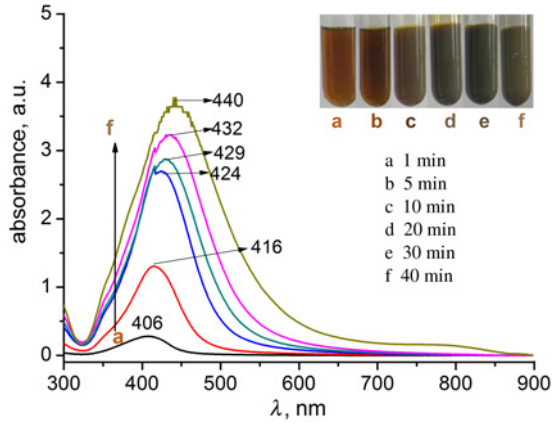

Figure 2 *UV–vis spectra of silver nanoparticles at different stages of the synthesis process*

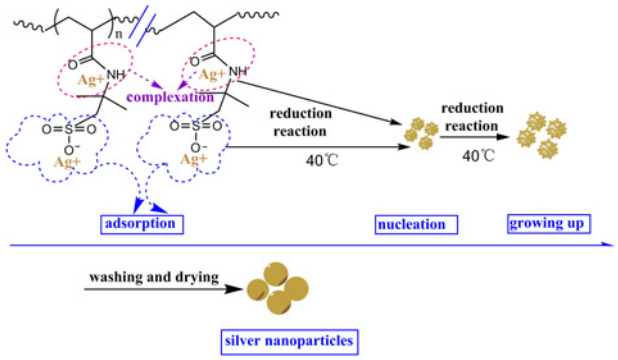

Figure 3 *Schematic of the synthesis process of silver nanoparticles in PAMPS aqueous solution*

406 to 440 nm and its peak intensity increased gradually. All these recorded phenomena reveal that the quantity of silver nanoparticles was generated as the time increased. The transition from silver seeds to nanoparticles results in a concomitant wavelength shift towards a longer wavelength of the band in the UV–vis spectra. The whole formation process is summarised as in Fig. 3.

As shown in Fig. 3, PAMPS is used to prevent silver nanoparticles from aggregation with other particles. In the side chains of PAMPS, the N and O from amide and sulphonic groups probably have a strong affinity for silver ions and silver nanoparticles [16, 21]. The reason is probably the low value of K_{sp} (the solubility product) of R-SO_3Ag (where R is hydrocarbonyl) and the generation of the complex such as $[Ag(NH_3)]^+$. Therefore, at the early stage silver ions were easy to form silver sulphonate with sulphonate or to combine with amino group forming complexes. PAMPS can disperse silver seeds well because of the many polar groups in its side chains. As the reaction proceeds, silver seeds were growing up gradually [22]. After washing and drying, silver nanoparticles were finally obtained.

Fig. 4 shows the SEM images of silver nanoparticles and the size distribution result. It is clearly seen that the silver nanomaterial takes on small twinning granules. The morphology of these twinning granules is regular and uniform. It relates to the two kinds of adsorption mentioned above. The size distribution result shows a narrow distribution with diameters ranging from 78.82 to 105.709 nm, which account for 76.41% of nanoparticles. The probable reason for this narrowness is the narrow distribution of PAMPS molecular weight (PDI, 1.0045) according to the research by Yoo *et al.* [23]. PAMPS with small PDI played an important role in forming silver nanoparticles with good dispersion.

Using PAMPS to synthesise silver nanoparticles has many potential applications, such as in the preparation of Ag/polyaniline (PANI) nanocomposite. The Ag/PANI nanocomposite prepared in PAMPS emulsion by *in-situ* polymerisation possesses high electrical conductivity. When the mole ratio of $R_{\text{silver nitrate to aniline}}$ is only 0.3, the conductivity can reach 3.5 S/cm, which is

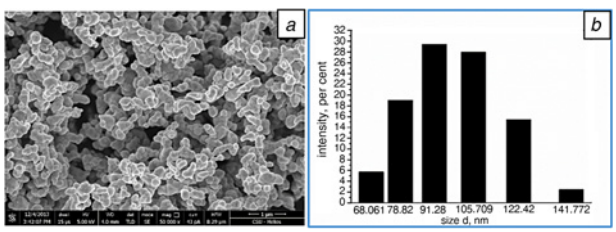

Figure 4 *Morphology of silver nanoparticles and the size distribution of nanoparticles*
a SEM image
b Size distribution

obviously higher than the values (1.7 and 1.4 S/cm) of the Ag/PANI ($R_{\text{silver nitrate to aniline}} = 2.5$) prepared in aqueous camphorsulphonic acid or aqueous toluenesulphonic acid [24]. Analogically, other Ag/polymer nanocomposites also can be prepared using PAMPS as a surfactant. Therefore, it is promising to explore the feasibility of using PAMPS to prepare silver nanocomposites.

4. Conclusion: In summary, we have proposed using PAMPS as a surfactant to prepare silver nanoparticles. The analysis reveals that silver ions were reduced successfully to nanoparticles by means of the process of adsorption with PAMPS and the reduction of sodium hypophosphite. The silver nanoparticles prepared by using PAMPS as a surfactant have a narrow size distribution. The diameters ranging from 78.82 to 105.709 nm can account for 76.41% of nanoparticles. This method is novel, convenient, efficient and environmental-friendly, and especially suitable for the treatment of silver ion containing wastewaters. It is promising to use PAMPS as a surfactant to prepare Ag/PANI or other polymer composites by *in-situ* polymerisation.

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