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Preparation and characterization of polyvinylpyrrolidone films containing silver sulfide nanoparticles

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Polyvinylpyrrolidone (PVP)–Ag_2S nanocomposites were successfully prepared through *in-situ* reaction with CS_2 as the sulfur source in ethanol solution at room temperature. Transmission electron microscopic (TEM) analysis of the nanocomposites revealed a raspberry morphology of the inorganic component with an average particle size of about 8–10 nm and a narrow dispersion. IR and UV-Vis spectroscopies were used to investigate the reaction process and the formation of coordination compounds.

1. Introduction

The study of inorganic–polymer nanocomposites has received considerable interest in recent years because of their novel properties, which are combinations of those of the original inorganic and polymer materials. These nanocomposite materials have found or will find many potential applications in the fields of optics, electrics, mechanics, photo-conductors and so on.[1,2] In the past few years, significant progress has been made on these materials, and many new methods[3–7] have been developed for the preparation of novel nanocomposites with desired properties and functions, such as the sol–gel approach, direct mixing processes, intercalation techniques and ion-exchange reactions.

Due to the unique properties of metal chalcogenide nanomaterials, many studies on metal chalcogenide/polymer nanocomposites have been reported.[7–9] However, to prepare these nanocomposites, the chalcogenide sources used are usually toxic H_2S and H_2Se gases. The reaction may happen only on the surface of the composite thin films.

It is well known that silver sulfide, as well as other silver chalcogenides, is a good prospective material for various semiconductor devices, such as photo-conducting cells, photovoltaic cells and IR detectors. The optical and electronic properties of bulk or film samples of silver sulfide have also been widely studied.[10–13] Recently, polymer–Ag and polymer–Ag_2S nanocomposites have been prepared through different methods.[14,15] For example, Deki *et al.*[14] prepared Ag–nylon 11 nanocomposites through the conventional vacuum evaporation technique, and then sulfated the thin film in a glass cell with mixed H_2S and O_2 gas to obtain the Ag_2S–nylon 11 nanocomposite.

In this study, PVP–Ag_2S nanocomposite was prepared using an *in-situ* reaction with CS_2 as the sulfide source at room temperature and ambient pressure. One prominent feature of this reaction, in contrast to using Na_2S or K_2S as the reaction reagent, is that no by-products such as NaCl or KCl were formed, and this method can avoid the use of gases such as H_2S and H_2Se, which are difficult to use, especially in labs. Another feature is that the formation mechanism of Ag_2S nanoparticles is different from our prior works.[10] Ag_2S was formed by the reaction between CS_2 and the newly formed Ag clusters in the presence of PVP, and the reaction is more rapid and simple. Furthermore, PVP can form a complex with metal ions or metal particles, which can prevent the agglomeration of the cluster—a persistent problem in size-selective cluster synthesis[16]—leading to monodisperse nanoparticles with uniform size. Finally, the reaction process was investigated by IR and UV-Vis spectroscopies.

2. Experimental

It was noted that in absolute ethanol, only a small amount of $AgNO_3$ could be dissolved, while PVP was easily dissolved. In a typical preparation process, 1 g PVP was dissolved in 10 ml ethanol saturated with $AgNO_3$ under vigorous stirring. An excess amount of CS_2 was then introduced and the solution was stirred in dark for sulfuration reaction over 24 hours. The obtained black viscous solution was stable and did not precipitate within 3 months. The resulting solution was spin-cast on a PET (polyethylene terephthalate) plate and dried at room temperature for 12 hours, then at 30 °C in vacuum for 12 hours for the complete removal of ethanol and unreacted CS_2. The film thickness was controlled by the rotation speed of the spin coater. Films with different thicknesses from 5 to 60 μm were peeled off from the plates. The as-prepared films were transparent when they were thinnerthan 10 μm.

The X-ray diffraction patterns (XRD) of powder samples were recorded on a Rigaku D/Max-γA X-ray diffractometer using Cu K_α radiation ($\lambda = 1.54178$ Å). Transmission electron microscopic (TEM) photographs of the nanocomposites were taken on a Hitachi S-530 TEM. Ultraviolet-visible (UV-Vis) spectra of the sample were measured on a Perkin-Elmer Lambda 20 UV-Vis spectrophotometer. The infrared spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR spectrophotometer. The X-ray photoelectron spectra (XPS) were recorded on a VGESCALAB MKII X-ray photoelectron spectrometer.

3. Results and discussion

Fig. 1 shows the XRD patterns of PVP and PVP–Ag_2S nanocomposite thin films. The diffraction peaks at $2\theta = 11.9°$ and 20.9° correspond to the PVP crystalline phase (Fig. 1b). Besides the diffraction peaks of PVP, the other peaks all correspond to the diffraction planes of the β-Ag_2S phase (Fig. 1a), and are close to the reported values in the JCPDS cards (14-72). The crystal size of β-Ag_2S is *ca.* 10 nm calculated from the half-peak width using the Scherrer equation.

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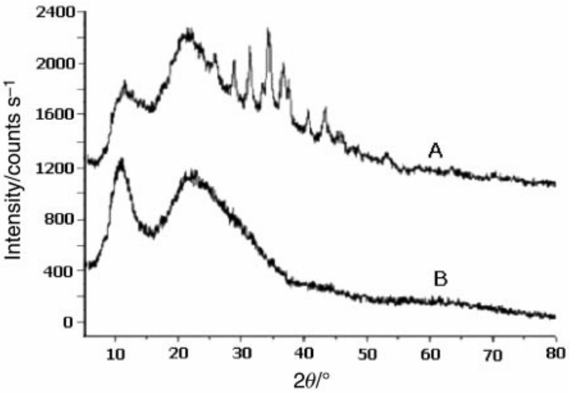

Fig. 1 XRD patterns of PVP and PVP–Ag_2S nanocomposite thin films.

Fig. 2 is the transmission electron microscopic (TEM) photograph of the as-prepared PVP–Ag_2S nanocomposite. The β-Ag_2S particles in the nanocomposite consist of uniform spherical particles, with an average size of about 8–10 nm, which is consistent with the XRD results, indicating that almost no aggregation of Ag_2S particles happens. EDX quantitative analysis revealed that these particles are composed of silver and sulfur, with an atomic ratio of nearly Ag/S = 2, which is in good agreement with the stoichiometric molar ratio of Ag_2S. More interesting is that Ag_2S particles in the PVP–Ag_2S nanocomposites are in raspberry morphology, which was also observed by Ray *et al.* when they studied silica–poly(*N*-vinylcarbazole) nanocomposites.[17] It seems thatthe PVP matrix has great effects on the dispersion of Ag_2S particles, which tend to array according to the polymer matrix. The exact cause is not very clear, but we think that the interactions between PVP and the metal cation may play a major role. The interactions between PVP and the silver cation can also be investigated by IR and UV-Vis spectroscopy.

IR spectroscopy is very useful in the analysis of interactions between two species. Wuepper and Popov[18] reported a shift of the carbonyl band in the IR spectrum of 2-pyrrolidone in the presence of alkali metal ions. They concluded that the band shift was due to the interaction between the carbonyl oxygen of 2-pyrrolidone and the metal ions. Hirai *et al.*[19] also investigated the IR spectra of PVP-stabilized palladium colloids. They observed the carbonyl band shift, and suggested that some of the carbonyl groups of PVP coordinated to palladium atoms on the surface of the palladium particles. The IR spectra of PVP, and PVP–$AgNO_3$ before and after the reaction with CS_2 in the solid state are shown in Fig. 3. The absorption C=O stretching peak of PVP is at 1660 cm^{-1}. After the addition of $AgNO_3$, the absorptionpeak shifted to 1651.9 cm^{-1}, implying the existence of weak coordinative chemical bonding between O and Ag. This band re-shifted to 1660 cm^{-1} after the addition of CS_2. This shift in the C=O absorption band in PVP was due to the interactions between metal ions or metal clusters and the carbonyl groups in PVP. This interaction may be attributed either to the donation of a pair of electrons from the carbonyl oxygen to the metal cations, or to the formation of a complex between nitrogen in the five-membered nitrogen-containing heterocycles and the metal cations, and the electron transfer from nitrogen to the metal cations may affect the polarizability of the neighbouring oxygen atom. We believe the former case is in operation here.[11,18–20] Toshima *et al.*[21] reported that Pt^+ could be reduced by ethanol toform metal clusters in the presence of some water-soluble polymers (such as PVP). So with the presence of PVP, $AgNO_3$ may also be reduced to silver clusters by ethanol. (We also found that water could not reduce Ag^+ if no ethanol was present.) When being introduced into the PVP–$AgNO_3$ ethanol solution, CS_2 may react with the newly formed silver colloids to form Ag_2S nanoparticles, leading to some de-coordination of PVP–silver complex and re-shifting of the C=O stretching band to 1660 cm^{-1}. Toshima *et al.*[21] also indicated that as the metal was reduced, ethanol was oxidized to acetaldehyde, which would be easily removed during the film drying procedure.

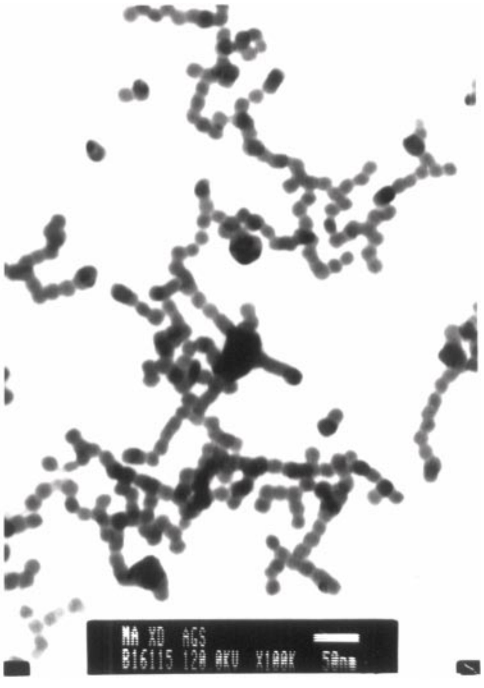

Fig. 2 TEM photograph of the as-prepared PVP–Ag_2S nanocomposite.

The formation of silver clusters is supported by the results of a UV-Vis spectroscopic study. Fig. 4 shows the UV-Vis spectra of PVP and PVP–$AgNO_3$ ethanol solutions before and after reaction with CS_2 for different reaction times. No absorption was observed in $AgNO_3$ ethanol solution. Upon the addition of PVP, a weak absorption peak was observed at 425 nm (Fig. 4(a)), whose intensity increased with time (Fig. 4(b)). This absorption peak may be due to the surface plasmon resonance (SPR) of Ag colloids formed in the PVP ethanol solution of $AgNO_3$. This result is consistent with the literature.[21] Upon the addition of CS_2, the absorption peak shifted to 320 nm as shown in Fig. 4(f).The absorption strength increased, but the peak position did not change with time. The change in the UV-Vis absorption may be caused by the formation of Ag_2S nanocrystallites as a result of the reaction between CS_2 and the newly formed silver colloids.[15] The reaction process can also be monitored by the color of the solution. The original $AgNO_3$ ethanol solution was colorless. Upon the addition of PVP, the solution turned brown. The

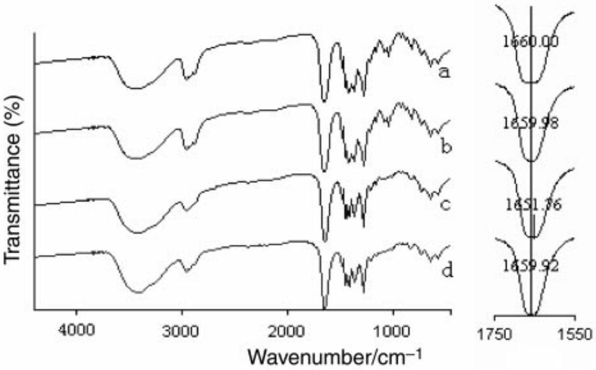

Fig. 3 IR spectra of PVP and PVP–$AgNO_3$ with or without CS_2: (a) PVP thin film; (b) PVP–CS_2 thin film; (c) PVP–$AgNO_3$ thin film; (d) as-prepared PVP–Ag_2S nanocomposite.

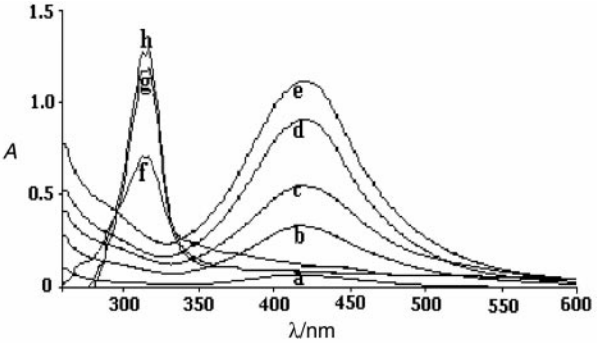

Fig. 4 UV-Vis spectra of PVP and PVP–$AgNO_3$ ethanol solutions with or without CS_2 at different reaction times: (a) the UV-Vis spectrum of PVP immediately upon addition to $AgNO_3$ ethanol solution; (b)–(e) UV-Vis spectra of PVP in the $AgNO_3$ ethanol solution after stirring for 5 minutes, 1, 6 and 12 hours respectively; (f) the UV-Vis spectrum of CS_2 immediately upon addition to the $AgNO_3$ ethanol solution of PVP; (g) and (h) UV-Vis spectra of CS_2 in the $AgNO_3$ ethanol solution of PVP after stirring for 1 and 5 hours, respectively.

solution color was further changed to black when CS_2 was added.

Water was also tried as the solvent in the preparation of the nanocrystalline PVP–Ag_2S nanocomposite. But no Ag_2S was obtained, even when the PVP–$AgNO_3$ aqueous solution was stirred over 96 hours after the addition of CS_2, and the color of the PVP–$AgNO_3$ aqueous solution did not change when CS_2 was added. The UV-Vis spectra of the $AgNO_3$ ethanol solution of PVP and the $AgNO_3$ aqueous solution of PVP are shown in Fig. 5. No absorption peak was observed in the PVP–$AgNO_3$ aqueous solution, indicating that silver colloids and Ag_2S nanocrystalline particles could not form in the PVP aqueous solution. This clearly implies that ethanol served not only as the solvent, but also as the reducing reagent to reduce Ag^+ to the silver colloids. This further confirmed that the Ag_2S nanoparticles wereformed from reaction between CS_2 and the newly formed silver colloids.

The possible formation mechanism of Ag_2S nanoparticles is

$$AgNO_3 \xrightarrow{\text{PVP alcohol solution}} Ag(\text{colloids})$$

$$2Ag + CS_2 \rightarrow Ag_2S + CS$$

$$Ag_2S \rightarrow (Ag_2S)_n$$

$$nCS \rightarrow (CS)_n$$

It is known that PVP plays an important role as a reactive polymer in protecting and stabilizing the colloidal dispersions of noble metals.[19] In this study, PVP can also prevent the silver clusters or silver sulfide particles from aggregating. The main effect may be due to the steric effect and chemical bonding of PVP.[11] In contrast, much larger Ag_2S particles were obtained in the ethanol solution without PVP, though the reaction mechanism was different.[10]

4. Conclusion

Polyvinylpyrrolidone (PVP)–Ag_2S nanocomposites were successfully prepared through *in-situ* reaction with CS_2 as the sulfur source in ethanol solution at room temperature. X-Ray diffraction results showed that a pure β-Ag_2S phase was obtained in the as-prepared nanocomposites. Transmission electron microscopic (TEM) analysis revealed a raspberry morphology for the PVP–Ag_2S nanocomposite with an average particle size of about 8–10 nm. EDX quantitative analysis showed that the atomic ratio of silver and sulfur was about 2. The IR and UV-Vis spectroscopic analysis showed that Ag^+ was reduced to Ag clusters by ethanol in the presence of PVP, which was further reacted with CS_2 to form nanocrystalline Ag_2S.

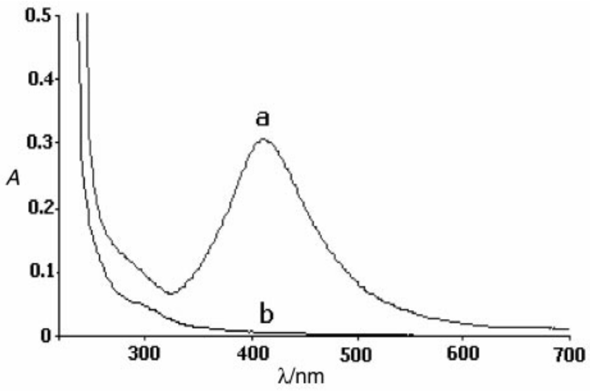

Fig. 5 UV-Vis spectra of the $AgNO_3$ ethanol solution of PVP (a) and the $AgNO_3$ aqueous solution of PVP (b).

Acknowledgements

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