Preparation of polyvinylpyrrolidone-protected Prussian blue nanocomposites in microemulsion

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Abstract

The polyvinylpyrrolidone (PVP)-protected Prussian blue nanocomposites were synthesized in isooctane/sodium bis(2-ethylhexyl) sulfosuccinate (AOT) microemulsion. Then compressed CO$_2$ was used as antisolvent to recover the PVP-protected Prussian nanocomposites from the solution. The as-prepared nanocomposites were characterized by the transmission electron microscopy (TEM), X-ray diffraction (XRD), and FTIR. By changing the water-to-surfactant molar ratio ($w$), the nanocomposites with different size can be easily obtained.

Keywords: PVP; Prussian blue; Nanocomposites; Microemulsion; Compressed CO$_2$

1. Introduction

In recent years, Prussian blue and related cyanometallate-based coordination polymers have attracted much interest due to their unique versatility [1]. In the field of molecular magnets, the magnetic properties of Prussian blue (PB) analogues have been extensively investigated [2–5]. Controlling the growth of PB analogues under spatial confinement has been a promising subject for fabricating molecular magnets because different shape and size of the molecular magnets can result in different magnetic properties [6–9]. With the development of nanotechnology, synthesis of nano-sized PB will be an important field of the molecular magnets. However, the reports about the nanoparticle synthesis of PB analogue and the investigation of their properties are very limited [1,10,11]. Recently Uemura and Kitagawa [11] synthesized the Prussian blue nanoparticles protected by polyvinylpyrrolidone (PVP) from aqueous solution and investigated the size dependent effect of PB on the magnetic property. The PVP-protected PB broadens the application of PB because it can dissolve in various organic solvents completely.

The use of micellar water droplets as a novel environment for nanoparticle synthesis has attracted much interest for its potential advantages compared with the traditional nanoparticle synthesis method [12–15]. In the surfactants used in synthesizing nanoparticles from microemulsions, sodium bis(2-ethylhexyl)sulphosuccinate (AOT) is usually used because of its ability to solubilize relatively large amount of water in a variety of hydrophobic organic solvents [16–19]. The size of the micelle cores is characterized by the molar ratio of water to surfactant $w$ (=[H$_2$O]/[AOT]). The reaction is restricted in the water cores and the diameter of the obtained product particles can be controlled by the size of the water core. A number of organic and inorganic nanoparticles have been synthesized in the water cores of the AOT reverse micelles in liquid organic solvents [20–23].

In the present work, we synthesized the PVP-protected PB nanocomposites in reverse microemulsion. Then compressed CO$_2$ was used as antisolvent to recover the nanocomposites from the reverse microemulsion. The resultant products were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD) and FTIR spectra.

2. Experimental

2.1. Materials

PVP (K-30; average $M_w$ = 40000), FeCl$_3$·4H$_2$O, K$_3$Fe(CN)$_6$ and isooctane were purchased from Beijing
Chemical Reagent Factory. Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) was obtained from Sigma. CO₂ (99.995%) was supplied by Beijing Analytical Instrument Factory. Double distilled water was used in all the experiments.

2.2. Preparation of PVP-protected PB in reverse microemulsion

The desired amount of AOT was dissolved in isooctane ([AOT] = 0.1 M). Then aqueous solution of FeCl₂ and PVP was added to AOT solution to form the microemulsion. Similarly, the microemulsion containing aqueous solution of K₃Fe(CN)₆ was prepared. Then the equal volume of the above two microemulsions were mixed. After the mixing, the solution turned blue immediately, indicating the formation of PB. The concentration of FeCl₂ and K₃Fe(CN)₆ in the droplet of the final microemulsion were both 6.75 mM. The concentration of PVP in H₂O was 1.5%. The water-to-surfactant molar ratio (w) was 15 in the microemulsion. The microemulsions with w = 10 and w = 20 were also prepared with the same parameters as w = 15. The above solutions with different w values were kept for 3 days to make FeCl₂ and K₃Fe(CN)₆ reacted completely in the presence of PVP at room temperature. The formation of the PVP-protected PB nanocomposites in the microemulsion can be illustrated as Fig. 1. In the droplets of reverse microemulsion, the amide moiety of PVP could weakly coordinate with Fe ion. Therefore, when the two microemulsion were mixed, PVP acted as steric stabilisation substance for the nucleation and growth of PB. After the reaction completed, the PVP-protected PB was formed.

2.3. High-pressure UV–vis spectra

A TU-1201 Model spectrophotometer was used to monitor the precipitation of PVP-protected PB nanocomposites from the microemulsion at different CO₂ pressures. The temperature-controlled high-pressure sample cell and experimental procedures were the same as those used previously [23]. The cell composed mainly of stainless steel body and two quartz windows, which was thermostatted to ±0.1 °C of the desired temperature by an electric heater and temperature controlling system. In the experiment, the suitable amount of the solution with PVP-protected PB nanocomposites was loaded into the sample cell by a syringe. The temperature was controlled at 308.2 K. CO₂ was charged into the sample cell by the high-pressure pump until the desired pressure was reached. The solution was stirred (400 rpm) for half an hour, then the stirrer was stopped and the nanocomposites were precipitated on the bottom of the autoclave. After releasing the solution, the precipitates were collected and dried under vacuum at 303.2 K for 4 h. The PVP-protected PB nanocomposites were obtained.

2.4. Recovery of PVP-protected PB nanocomposites by CO₂

The microemulsion containing PVP-protected PB nanocomposites was transferred into an autoclave. The autoclave was put in a water bath at 308.2 K. Then CO₂ was charged into the autoclave by a high-pressure pump until the desired pressure was reached. The solution was stirred (400 rpm) for half an hour, then the stirrer was stopped and the nanocomposites were precipitated on the bottom of the autoclave. After releasing the solution, the precipitates were collected and dried under vacuum at 303.2 K for 4 h. The PVP-protected PB nanocomposites were obtained.

2.5. Characterization of PVP-protected PB nanocomposites

The morphology of the obtained composites was determined by TEM with a TECNAI 20 PHILIPS electron microscope. X-ray diffraction analysis of the samples was carried out using an X-ray diffractometer (XRD, Model D/MAX2500, Rigaka) with Cu Kα radiation. The FTIR spectrum was recorded using an IR spectrometer (TENSOR 27), and each sample was recorded with 32 scans at an effective resolution of 2 cm⁻¹.

3. Results and discussion

3.1. Precipitation of PVP-protected PB by CO₂

In previous work, we have used compressed CO₂ as anti-solvent to recover some inorganic and organic nanoparticles from the reverse micelles [25–26]. Through the easy control of pressure, the nanoparticles can be precipitated from the micelles, while the surfactant remains in the solution. In this work, we also used compressed CO₂ to precipitate the product particles from the microemulsions. We first studied the precipitation of PVP-protected nanocomposites at different
CO₂ pressures by UV–vis spectra. As examples, Fig. 2 illustrates the UV–vis spectra of the colloidal dispersions of PB at \( w = 15 \) and different CO₂ pressures. The broad band at \( \lambda_{\text{max}} = 690 \) nm is attributed to the intermetal charge-transfer band from Fe²⁺ to Fe³⁺ in PB nanoparticles [18]. As we can see from the figure, with the increasing CO₂ pressure the intensity of the absorbance of PB decreases, indicating the precipitation of PVP-protected PB nanocomposites from the solutions. The absorption of PB nearly disappeared, indicating precipitation of all the PVP-protected nanocomposites in the microemulsion. According to our previous work [27], 4.61 MPa is lower than the pressure where the surfactant AOT begins to precipitate at this condition. Thus, the PVP-protected nanocomposites can be recovered at this pressure, while the surfactant still remains in the solution.

3.2. Characterization of the PVP-protected PB nanocomposites

On the basis of the above UV–vis spectrum study, we can select the suitable experimental conditions to recover the PVP-protected nanocomposites. The TEM photographs of PVP-protected nanocomposites recovered from the microemulsions with \( w = 10, \ w = 15 \) and \( w = 20 \) are shown in Fig. 3a–c, respectively. The particle size was obtained by measuring the diameter of the particles in the micrographs. As the pressure reaches to 4.61 MPa, the absorbance of PB nearly disappeared, indicating precipitation of all the PVP-protected nanocomposites in the microemulsions. The reaction is restricted in the water cores and the higher \( w \) results in larger diameter of the droplet. Thus, larger PB nanocomposites are obtained from the microemulsions with higher \( w \) value. Fig. 3d shows the TEM photograph corresponding to Fig. 3c at higher magnification. From the figure, the structure of the PVP-protected PB nanocomposites can be clearly observed.

X-ray powder diffraction (XRD) was used to characterize the obtained nanocomposites, which is shown in Fig. 4. The very broad XRD peak around \( 2\theta = 24.3^\circ \) is assigned to amorphous PVP. The other peaks at \( 2\theta = 17.5^\circ, 24.7^\circ, 35.4^\circ, 39.7^\circ \) and \( 43.4^\circ \) correspond to 200, 220, 400, 420 and 422 planes of the PB cubic space group \( \text{Fm} \overline{3}m \) [28]. FTIR spectra were also used to characterize the PVP-protected nanocomposites. Fig. 5 shows the IR spectra of the obtained nanocomposites. The peak at 2085 cm⁻¹ is attributed to the
Fig. 4. X-ray diffraction pattern of PVP-protected PB nanocomposites obtained from microemulsion of \( w = 15 \). The vertical lines at the bottom indicate the standard positions and relative intensities of PB.

CN stretching in the Fe\(^{2+}\)-CN-Fe\(^{3+}\) of PB. The band at 1658 cm\(^{-1}\) is assigned to the stretching vibration of the C=O in the PVP amide unit. The other peaks such as band at 1285 and 1425 cm\(^{-1}\) are all the typical adsorption bands of PVP. Both the XRD and FTIR results confirm the formation of PVP-protected PB nanocomposites by the microemulsion method.

4. Conclusion

In this work, the PVP-protected PB nanocomposites were synthesized in reverse microemulsion by reacting FeCl\(_2\) with K\(_2\)Fe(CN)\(_6\) in the presence of PVP, and compressed CO\(_2\) was used as antisolvent to recover the nanocomposites. By controlling the molar ratio of water to surfactant (\( w \)) in the reverse microemulsion, PB nanocomposites with different size can be obtained. The higher \( w \) value of the microemulsion is, the larger PB nanocomposites are obtained. The method using microemulsion to synthesize PVP-protected PB nanocomposites is simple, and the size of resultant products can be easily controlled by \( w \). This method may be extended to prepare some other functional PB nanocomposites, provided that the functional molecules are soluble in the droplets of reverse microemulsions.

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References