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SHORT COMMUNICATION

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Preparation of polyacrylamide/CdS nanocomposites by a combination of reverse microemulsion and CO_2 antisolvent techniques

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Abstract Polyacrylamide(PAM)/cadmium sulfide(CdS) nanocomposites have been successfully prepared by combination of reverse microemulsion and carbon dioxide antisolvent techniques. TEM, XRD, and FTIR were used to characterize the nanocomposites obtained. TEM photographs of the nanocomposites show that their diameter is approximately 30–60 nm. This method has potential advantages, for example the procedure is simple and the solutions can be easily reused.

Keywords Polyacrylamide · CdS nanocomposites · Carbon dioxide · Microemulsion

Introduction

Nanostructured inorganic/polymer composites, mixed at the molecular level or near molecular level, are much different from conventional composites with incorporation of a variety of additives in the polymer matrices [1]. In inorganic/polymer nanocomposites strong chemical bonds or intermolecular interactions exist between the organic and inorganic components. This usually leads to novel nanocomposites with improved properties, which may have large potential applications in the fields of optics [2], electrical devices [3], mechanics [4], photoconductors [5], and so on. In the past few years nanocomposites have attracted considerable attention in both fundamental research and applications [6, 7]. Extensive effort has been focused on the development of new methods to prepare novel hybrids with the desired properties and functions [8, 9, 10]. Conventionally, polymerization of monomers and formation of inorganic nanoparticles were performed separately, and then the polymer and the inorganic nanoparticles were mechanically mixed to form composites [11]. However, it is sometimes difficult to disperse nanoparticles homogeneously into the polymer matrix due to the easy agglomeration of nanoparticles and the high viscosity of polymers. In recent years, more attention has been paid to the in-situ synthesis of inorganic nanoparticles in polymer matrices. Another novel means of synthesizing the inorganic/polymer nanocomposites is the simultaneous polymerization reduction approach in which polymerization of the organic monomers is conducted simultaneously with the sol–gel reaction of metallic precursors to synthesize the inorganic/polymer composites [12].

The microemulsion technique is one of the most popular methods of preparing inorganic/polymer hybrids [13]. Sodium bis(2-ethylhexyl)sulfosuccinate (AOT) is a popular surfactant in applications with reverse microemulsions. The size of the micelle cores is characterized by the molar ratio of water to surfactant, w. Some research has been conducted on the synthesis of organic and inorganic nanoparticles within the water cores of the AOT reverse micelles in liquid organic solvents [14]. Because the reaction is restricted to the water cores, the diameter of the product particles obtained can be controlled by the size of the water cores. Recovery of the product nanoparticles from reverse micelles is a key step in affecting particle size and dispersion. The traditional recovery method is by flocculation [15], evaporation to dryness [16], or adding a chemical reagent to cause phase separation [17], which precipitates the surfactant simultaneously. The post-process is troublesome because the products contain a large amount of surfactant.

Compressed CO_2 is quite soluble in a number of organic solvents and expands them substantially. Many solutes are soluble in organic solvents, but are not soluble in CO_2. Thus the CO_2 in organic solvents can act as a gas antisolvent (GAS). Many GAS processes have been explored, such as extraction and fractionation [18], recrystallization of chemicals [19], and micronization [20]. Recently, a new method of recovery of nanoparticles synthesized in reverse micelles using compressed CO_2 as antisolvent was developed in our group [21], and ZnS nanoparticles synthesized in AOT reverse micelles were recovered. It was found that, by controlling the pressure of CO_2, the ZnS nanoparticles synthesized in the reverse micelles could be directly precipitated, while the surfactant AOT remains in the solution.

In this paper we describe an approach used to prepare PAM/CdS composite materials which in principle can be used to prepare a range of inorganic/polymer composite materials. By controlling the pressure of CO_2, the composite material particles in the reverse micelles can be precipitated while the surfactants remain in the solvent continuous phase.

Experimental

Materials

CO_2 (>99.995% purity) was provided by Beijing Analytical Instrument Factory. Polyacrylamide (PAM) aqueous solution (50% *w*/*w*), average molecular weight ca. 10,000, was from Aldrich. The surfactant AOT (purity 99%) was purchased from Sigma. The isooctane, $Na_2S.9H_2O$, and $Cd(NO_3)_2.4H_2O$ supplied by Beijing Chemical Plant were all A.R. grade. In all experiments double-distilled water was used.

Phase behavior of the CO_2-expanded microemulsion

The apparatus used to study the expansion curves and the cloud-point pressure of the solution was the same as that described previously [22]. The volume expansion coefficients were calculated on the basis of the liquid volumes before and after dissolution of CO_2.

Preparation of microemulsion containing PAM and CdS

The procedures used to synthesize CdS nanoparticles in the reverse micelles were as follows. The solution of AOT in isooctane and aqueous solutions of $Cd(NO_3)_2$ (77 mmol L^{-1}) + PAM(5.6 g L^{-1}) and Na_2S (77 mmol L^{-1}) + PAM(5.6 g L^{-1}) were first prepared. The reverse micellar solutions containing $Cd(NO_3)_2$ + PAM and Na_2S + PAM were then obtained by adding corresponding aqueous solution to the surfactant solution until the desired *w* (water-to-surfactant molar ratio) was reached. When the two micellar solutions were mixed at ambient temperature, CdS nanoparticles were formed in the reverse micelles because the water pools can exchange their contents by a collision process.

Recovery of the CdS and PAM nanocomposites

For recovery of CdS and PAM nanocomposites from the microemulsion, a known amount of micellar solution with the synthesized CdS nanoparticles and PAM was loaded into the cylinder-shaped autoclave, volume 50.0 mL, and then CO_2 was charged by a high-pressure pump until the desired pressure was reached. The solution was stirred (120 r.p.m.) for 1 h. After stirring was stopped, the CdS and PAM nanoparticles were precipitated from the solution and deposited at the bottom of the autoclave. After releasing the solution the precipitates were collected and dried under vacuum at 313.2 K for 6 h. The CdS and PAM nanocomposites were obtained.

High-pressure UV–visible spectral study

To detect whether CdS and PAM can co-precipitate from the reverse micelles at different CO_2 pressures, a TU-1201 Model spectrophotometer equipped with a high-pressure UV cell was used. The temperature-controlled high-pressure sample cell and experimental procedures were the same as described previously [23].

Characterization of the composites

Powder X-ray diffraction analysis of the samples was carried out using an X-ray diffractometer (XRD, Model D/MAX2500, Rigaka) with CuK_α radiation. A Hitachi H-600A transmission electron microscopy (TEM) was used to measure the morphologies and electron diffraction of the obtained particles. The maximum resolution of the microscope was 0.5 nm. The products were dispersed in ethanol and then directly deposited on the copper grid for TEM. 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}.

Results and discussion

Phase behavior of the reverse micellar solution expanded with CO_2

It is known from our previous work that *w* (molar ratio of water to AOT) has no significant effect on the expansion curves of the reverse micelles in CO_2 [24]. We ignored the difference between the expansion curves of reverse micellar solutions with different *w* values. The expansion curve of the reverse micelles with $w = 15$ and AOT concentration of 50 mmol L^{-1} are shown in Fig. 1. As pressure reaches a high enough value the surfactant can be precipitated from the solution, and making the solution cloudy. This pressure is usually denoted as cloud-point pressure P_c. The cloud-point pressure determined was 6.1 MPa, shown in Fig. 1. All the experiments for CdS/PAM nanocomposites recovery were conducted at pressures lower than the cloud-point pressure, so precipitation of the surfactant did not occur.

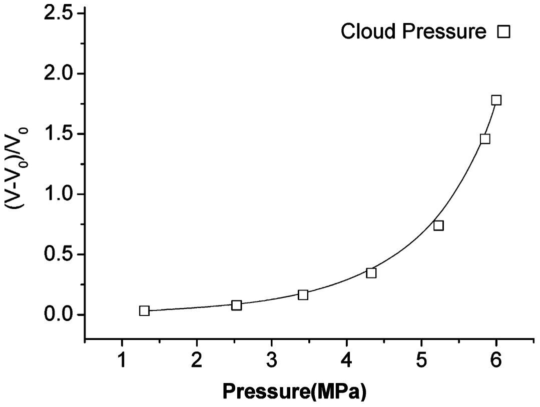


Fig. 1 Cloud pressure and volume expansion coefficient of the reverse micellar solution ([AOT] = 50 mmol L^{-1}, $w = 15$) at 308.2 K and different pressures (V and V_0) are the volume of the solution before and after dissolution of CO_2

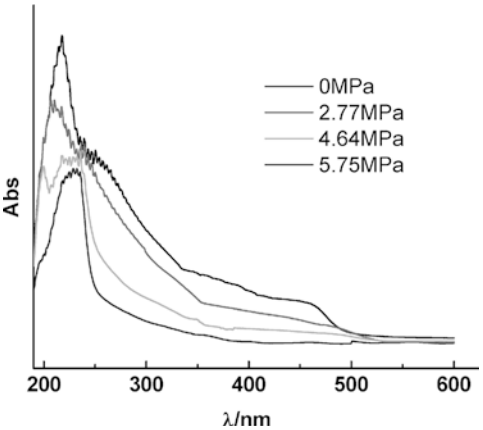


Fig. 2 UV spectra of the CO_2-expanded reverse micellar solution containing CdS and PAM ([AOT] = 50 mmol L^{-1}, $w = 15$, $[Cd^{2+}] = 0.025$ mg mL^{-1}, [PAM] = 0.05 mg mL^{-1}) at 308.2 K and different CO_2 pressures

UV–visible study of coprecipitation of the CdS and PAM from the solutions

CdS and PAM nanoparticles have absorption bands in the UV–visible range. Therefore, the CdS and PAM nanoparticles stabilized in the reverse micelles can be analyzed in situ by UV–visible spectroscopy. The characteristic absorption spectrum for AOT, CdS, and PAM nanoparticles are about 230, 392, and 194 nm, respectively. The UV spectra of the reverse micellar solution ($w = 15$) containing the CdS nanoparticles and PAM at different pressures were determined and some results are shown in Fig. 2. For all the experiments, the concentrations of CdS and PAM in the reverse micellar solutions after expansion should be respectively 0.025 mg mL^{-1} and 0.050 mg mL^{-1} if they were not precipitated.

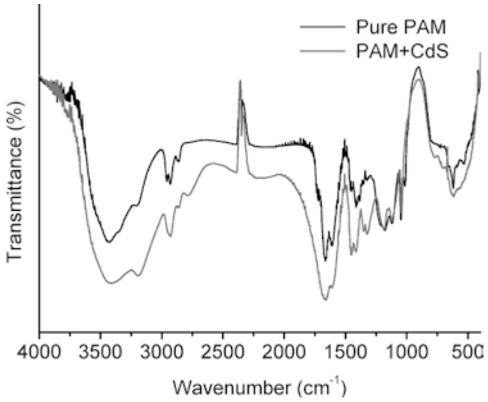


Fig. 3 The FTIR spectra of the pure PAM and the CdS/PAM nanocomposite

The intensity of the peak at about 392 nm (CdS) decreases gradually with increasing pressure, and the absorption of disappears at 5.75 MPa, indicating precipitation of CdS. The peaks of AOT and PAM overlapped and show a peak around 200 nm. Obviously, the intensity of the peak also decreases with increasing pressure. As shown in Fig. 1, the cloud pressure of the AOT micellar solution is 6.1 MPa, while the highest pressure in Fig. 2 is 5.75 MPa. It can be deduced that the reduction of intensity is due to the precipitation of PAM. Thus it can be concluded that by easy control of pressure, coprecipitation of CdS and PAM from the micellar solutions can be realized.

Characterization of the CdS/PAM nanocomposites

From the above analysis, we can select suitable experimental conditions to prepare the CdS/PAM nanocomposites. In order to obtain the largest recovery of the CdS and PAM from the solutions and, at the same time, avoid precipitation of surfactant AOT, we recovered the nanocomposites from the reverse micelles of $w = 10$ and 15 with CO_2 pressure of 5.75 MPa at 308.2 K.

To verify that the resultant composites contain PAM, we determined the FTIR spectra of the pure PAM and the CdS/PAM composite, respectively, and the results are shown in Fig. 3. The strongest peak at 1665.2 cm^{-1} is attributed to $\nu_{C=O}$, and the characteristic peak at 2922.3 cm^{-1} can be assigned to ν_{CH2}. The peaks at 1454.6 and 1403.9 cm^{-1} belong to δ_{CH2}. Obviously, the spectra of the pure PAM and CdS/PAM composites are similar, and are consistent with the standard infrared spectrum of polyacrylamide [25]. This implies that the resulting products indeed contain PAM.

The phase structures of the obtained products were characterized by XRD. Figure 4 shows the XRD patterns of the CdS/PAM composites obtained from the

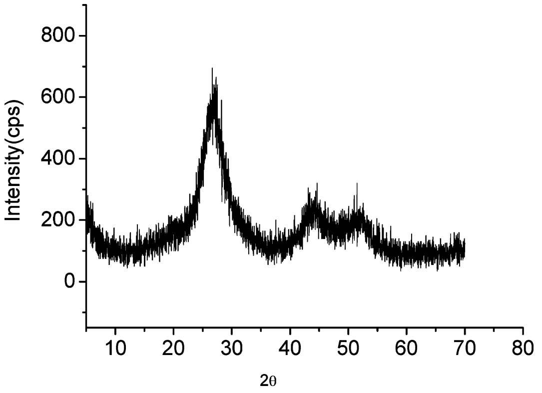


Fig. 4 XRD pattern of the PAM/CdS nanocomposite prepared by AOT reverse micelles ([AOT] = 50 mmol L^{-1}, $w = 15$, recovery pressure = 5.75 MPa)

micellar solutions ($w = 10$) at 5.75 MPa and 308.2 K. The three peaks correspond to the 111, 220, and 311 planes of cubic CdS [26]. This also confirms the existence of CdS in the composite. The XRD peaks of CdS are relatively broad, which suggests the small size of CdS in composite. The electron diffraction of the CdS/PAM composite (Fig. 5) confirms that the morphology of the product was polycrystalline structure.

Figures 5a and 5b are the TEM photographs of CdS/PAM composites recovered from the reverse micelles with $w = 10$ and 15, respectively. It is estimated from TEM photographs that the particle size obtained at $w = 10$ is in the range 30 to 45 nm, and is 40 to 60 nm at $w = 15$, which indicates the CdS/PAM composites obtained are nanocomposites. The particle size is larger at the larger w. This can be partially attributed to the fact that the water cores in the reverse micelles are smaller at smaller w.

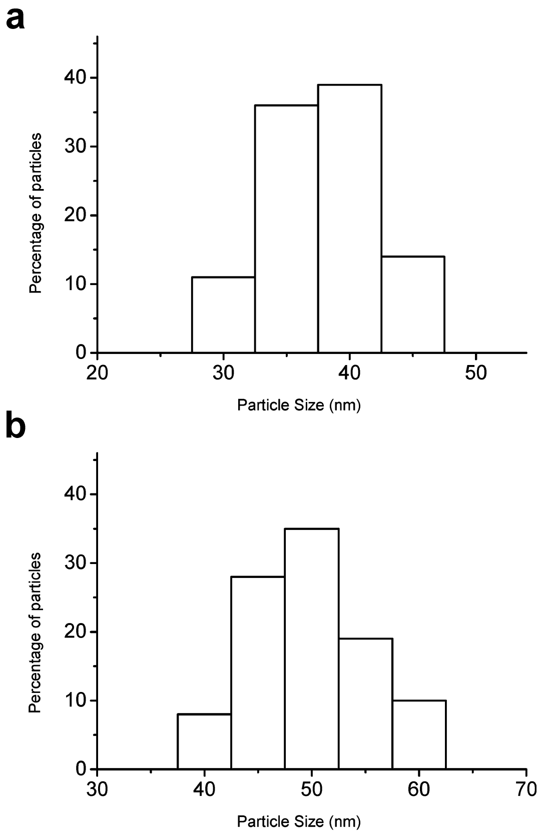
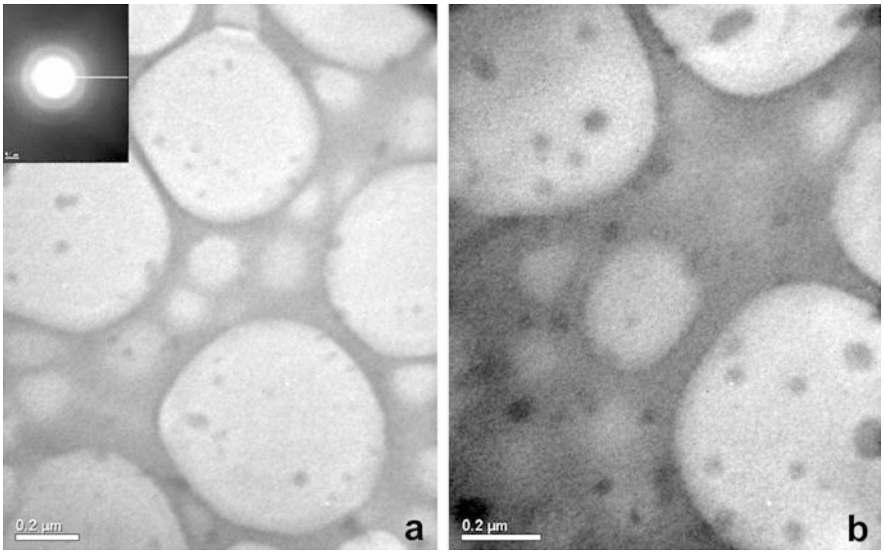


Fig. 6 Histogram of as-prepared particle sizes in the same sample as that in Figs. 5a and 5b

The histogram of as-prepared nanoparticles (Figs. 6a and 6b) shows size distributions ranging from 30 to 45 nm and from 40 to 60 nm respectively. It also indicates that the distribution of the as-prepared nanoparticles is homogeneous.

Fig. 5 TEM photographs of CdS/PAM composites recovered from the reverse micelles at different conditions. [AOT] = 50 mmol L^{-1}: (**a**) $w = 10$, $P = 5.75$ MPa (electron diffraction in the upper left confirms the polycrystalline structure of CdS/PAM); (**b**) $w = 15$, $P = 5.75$ MPa



Conclusion

In summary, we describe a new method of synthesis of the CdS/PAM nanocomposites by the coprecipitation method using compressed CO_2 as antisolvent. This method is simple, and the size of the composites can be controlled by adjustment of the experimental conditions. Moreover, the micellar solution can be easily recycled. We believe this route can be used to prepare other inorganic/polymer nanocomposites.

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