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Single-step synthesis of nanocrystalline CdS/polyacrylamide composites by γ-irradiation

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γ-Irradiation has been used to prepare nanocrystalline composites—CdS/polyacrylamide with 18 wt % cadmium sulfide at room temperature, in which the inorganic phase displays uniformity of size and nearly uniform dispersion. The formation of nanocrystalline CdS and the polymerization of acrylamide are in a single step. X-ray Powder Diffraction and Infrared Spectra were used to characterize the product. Its morphology was determined by Transmission Electron Microscopy. © *2000 Kluwer Academic Publishers*

1. Introduction

Recently, a great amount of scientific and technological research has been devoted to hybrid inorganic/polymer nanocomposites, which can frequently provide properties that are combinations of those of the original semiconductor and polymer materials. Furthermore, the synthesized inorganic/polymer composites display controlled inorganic crystallite size, morphology and orientation [1]. Up to now, many methods have been successfully used to prepare nanosized semiconductor particles, such as the solvothermal process [2] and the sol-gel method [3]. However, there are few reports on syntheses of inorganic/polymer nanocomposites due to the limitation of the preparation methods that can produce the nanocrystalline inorganic semiconductor and polymer concurrently. To prepare metal sulfide/polymer nanocomposites, two steps were needed generally. Firstly, metal ions were introduced into the polymer by copolymerization of an organic monomer and metal ions or an ion-exchange process. Secondly, a sulfur source was introduced for the preparation of nanocrystalline sulfide. In these methods, the polymerization of organic monomer and formation of nanocrystalline metal sulfide particles are performed separately. Thus it is very difficult to control the dispersion of metal sulfide in the polymer matrix. Furthermore, the sulfur source used is usually toxic gas H_2S. More important, to date most of the inorganic components prepared in these processes at room temperature are amorphous [1]. Post-treatments under higher temperature or pressure are frequently necessary. Materials chemists have been looking for an ideal method to prepare semiconductor/polymer nanocomposites in a single step.

Many monomers can polymerize upon exposure to γ-irradiation. A γ-irradiation method has been developed to prepare nanocrystalline materials [4]. So it is feasible to devise a single-step synthesis of nanocrystalline/polymer compounds at room temperature. In this work, we report our current progress on the extension of the γ-irradiation method to the preparation of CdS/polyacrylamide nanocomposites in a single step, in which the inorganic phase displays uniformity of size and nearly mono-dispersion. The synthetic factors have been optimized to ensure the uniform dispersion of synthetic composites were (1) good "solvation" of the inorganic components in the polymer matrix, and (2) an ordered, regular polymer environment in which to induce nucleation (matrix preorganization). Being a material with good thermoplastic properties, polyacrylamide was selected to be the polymer matrix. In addition, cross-linked polyacrylamide can provide an homogeneous system in water, which warrant that the nanoparticles are dispersed homogeneously within the polyacrylamide network. For CdS, the optical absorption peak shifts towards higher energies as the crystallite size approaches a value comparable with or below its exciton size, indicating a quantum size effect. Other properties include its nonlinear optical properties, unusual fluorescence behavior, excellent catalytic properties, interesting transport properties and its suitability as a precursor for nanostructured materials processing [5–10]. Recently, Yin *et al*. successfully prepared CdS nanoparticles by γ-irradiation, but the small particles aggregated heavily [11]. In this work, the metal ion source, sulfur source and organic monomer were mixed homogeneously in the solution; the formation of nanocrystalline metal sulfide particles and polymerization of monomer occurred simultaneously, leading to a homogeneous dispersion of nanocrystalline metal sulfide particles in the polymer matrix. This process can be described as follows:

$$\mathrm{CdSO_4} + \mathrm{Na_2S_2O_3} \xrightarrow{\gamma\text{-radiation}} \mathrm{Na_2SO_4} + \mathrm{CdS}$$

$$n\mathrm{CH_2CHCONH_2} \xrightarrow{\gamma\text{-radiation}} (\mathrm{CH_2CHCONH_2})_n$$

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2. Experimental

In the studies reported here a typical solution was prepared by dissolving analytically pure cadmium sulfate (0.05 mol/dm^3), sodium thiosulfate (0.1 mol/dm^3), acrylamide (2 mol/dm^3) and isopropyl alcohol (3 mol/dm^3) in water. The solution was deaerated by bubbling with pure nitrogen for 20 min to remove oxygen, then was irradiated in the field of a 2.59×10^{15} Bq ^{60}Co γ-ray source with absorbed dose of 2.7×10^4 Gy. After γ-irradiation, a yellow, transparent, gelatinous product was obtained. The product was dried in vacuum at room temperature, ground to a powder, and then was washed with distilled water to remove the by-products. The final product was dried in vacuum at room temperature again.

The samples were characterized by X-ray Powder Diffraction (XRD) patterns employing a scanning rate of 0.05° s^{-1} in the 2θ range from 10° to 60°, using a Japan Rigaku Dmax γ_A X-ray diffractometer equipped with a graphite monochromatized Cu K$_\alpha$ radiation ($\lambda = 0.154178$ nm). In order to determine the by-product, the unwashed powder was also determined by XRD. The Infrared (IR) spectra were recorded in the wavenumber range of 4000–500 cm^{-1} with a Nicolet Model 759 Fourier Transform Infrared (FTIR) Spectrometer, using a KBr wafer. The morphology and particle sizes were determined by Transmission Electron Microscopy (TEM). The TEM images were taken with a Hitachi Model H-800 Transmission Electron Microscope with an accelerating voltage of 200 kV. To determine the concentration of the cadmium sulfide in polyacrylamide matrix, 0.010 g samples were dissolved in 10^{-4} m^3 analytical pure nitric acid. The cadmium ion contents were determined using Atomic Absorption Spectrometer (model WYX-40).

3. Results and discussion

Typical XRD patterns of the products, unwashed and washed, are shown in Fig. 1a and b, respectively. From Fig. 1a, one can see that the diffraction peaks labeled $*$ can be indexed in the hexagonal CdS phase, while those labeled • correspond to Na_2SO_4. All the peaks in Fig. 1b can be indexed as the hexagonal CdS phase (JCPDS Card file No. 41-1049) with $a = 0.4141$ nm, $c = 0.672$ nm, which are close to the reported data for CdS with wurtzite hexagonal structure. The diameter of cadmium sulfide, as calculated from the half-width of diffraction peaks using the Scherrer formula, is 15 nm.

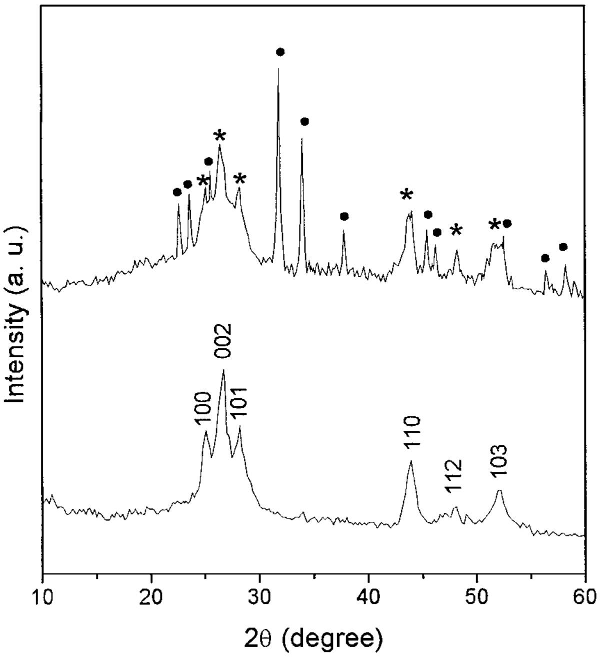

Figure 1 XRD pattern of the product: (a) unwashed product (•—Na_2SO_4, $*$—CdS); (b) final product.

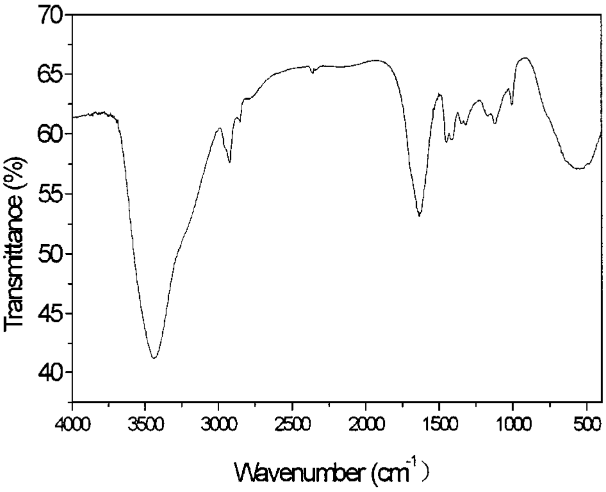

Figure 2 IR spectrum of the product.

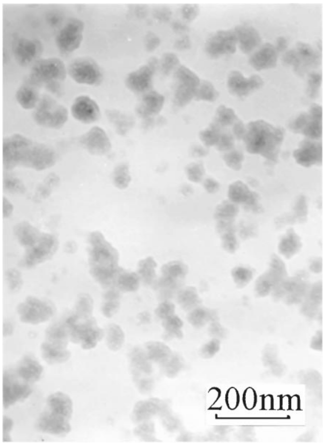

Figure 3 TEM image of the product.

Fig. 2 is the IR Spectra of the final product, which is similar to the standard Infrared Spectrum of polyacrylamide, and totally different from that of monomer acrylamide. It confirmed the polymerization of acrylamide monomer and the formation of polyacrylamide in water upon γ-irradiation. The vibration absorption peak of Cd-S bond, which should be at 405 cm^{-1} [12], can't be observed, since it is covered in the peaks of polyacrylamide.

Transmission Electron Microscopy was used to observe CdS nanoparticles in the polymer matrix in the product materials. From Fig. 3, it can be seen that nanocomposites contained fine quasi-spherical CdS grains nearly mono-dispersed and well separated in the polyacrylamide matrix.

To determine the content of cadmium sulfide in the polyacrylamide matrix, 0.010 g samples were dissolved in 10^{-4} m^3 analytical pure hydrochloric acid. The cadmium sulfide content was 18 wt %.

Polymerization of monomer acrylamide in solution upon γ-irradiation has been extensively studied, and as the absorbed dose is large enough, water-soluble polyacrylamide transformed to water-insoluble cross-linked polyacrylamide [13, 14], which can fill the whole system and provide an ordered, regular network in which the nucleation of CdS can be induced and confined. Research on the formation of CdS nanoparticles under γ-irradiation shows that CdS grains gradually grow larger with increasing absorbed dose [11]. In this work, the earlier-formed polyacrylamide chains lead to increase the viscosity of system, which limit the further growth and aggregation of CdS grains and make them well dispersed in the polymer matrix.

4. Conclusions

We believe that this is the first time that γ-irradiation has been used to prepare nanocrystalline composites—CdS/polyacrylamide with 18 wt % cadmium sulfide at room temperature, in which the inorganic phase displays uniformity of size and nearly uniform dispersion. The formation of nanocrystalline CdS and the polymerization of acrylamide are in a single step. X-ray Powder Diffraction and Infrared Spectra were used to characterize the product. Its morphology was determined by Transmission Electron Microscopy.

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