

Polymer–Inorganic Nanocomposites Prepared by Hydrothermal Method: Preparation and Characterization of PVA–Transition-Metal Sulfides

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ABSTRACT: Nanocomposites of poly(vinyl alcohol) (PVA) with iron, cobalt, or nickel sulfides were successfully prepared using a hydrothermal process by an *in situ* reaction with CS₂ at 140°C for 8 h. XRD results showed that pure phases of FeS₂, CoS₂, and NiS were obtained in the as-prepared nanocomposites. They also showed that the crystallinity of PVA was largely decreased after incorporation of the nano-sized sulfides. This was also confirmed by IR spectroscopy. SEM photographs showed that the sulfide particles were homogeneously dispersed in the PVA matrix. UV-visible spectroscopy was also used to characterize the as-prepared nanocomposites. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2744–2749, 2001

Key words: nanocomposites; water-soluble polymers; inorganic materials; metal–polymer composites

INTRODUCTION

Nanostructured organic–inorganic composites, mixed at the molecular level or near molecular level, are much different from the conventional composites with incorporation of a variety of additives in the polymer matrices.¹ In inorganic–organic nanocomposites, strong chemical bonds (covalent or ionic) or interactions such as van der Waals forces, hydrogen bonding, or electrostatic forces, often exist between the organic and inorganic components. This usually leads to some novel nanocomposites with improved performance properties, which may have large potential applications in the fields of optics,² electrical de-

vices,³ mechanics,⁴ photoconductors,⁵ and so on. In the past few years, nanocomposites have attracted considerable attention from both fundamental research and application points of view.^{6,7} Significant effort has been focused on the development of new methods to prepare novel hybrids with the desired properties and functions,^{8–10} such as the sol–gel method^{4,11} and intercalation techniques.^{5,12–16} However, some hydrolysis precursors or special pretreatments must be used, which largely confines the application range of the above methods.

Metal sulfide semiconductor/polymer nanocomposites are considered to be highly functional materials with many applications in photoluminescent, photoelectric, nonlinear optical materials, and so on.^{8,17} Furthermore, the flexibility and processability of polymer matrices based on water-soluble polymers such as PVA with excellent optical properties (good transparency) and good compatibility with additives can provide good me-

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chanical properties. By choosing polymer matrices, various semiconductive chalcogenide/polymer nanocomposites with desired functions have been prepared via an *in situ* reaction, such as II–VI sulfide/polymer nanocomposites.^{8,17} These nanocomposites are usually obtained by treatment with S^{2-} or H_2S . The reaction may, however, occur only on the surface of the composite films. Furthermore, this technology may only be applied to prepare compounds which are easily formed or crystallized under normal conditions, such as ZnS and CdS. To prepare less common sulfides which are not easily formed or crystallized such as transition-metal sulfides or phosphides, one may encounter difficulties using this approach.

The VIII transition-metal disulfides have received considerable attention because of their conductivity, ranging from semiconductive to metallic behavior and a wide range of magnetic properties.¹⁸ Conventionally, these compounds are prepared through their constituent elements at high temperature (500–1000°C) and are not easily prepared through ion-exchange processes at room temperature.¹⁸ In this article, nanocomposites of poly(vinyl alcohol) (PVA) with iron, cobalt, or nickel sulfides have first been successfully prepared using the hydrothermal process, which has been widely used to prepare nanomaterials ranging from oxides, sulfides, phosphates, and zeolites to diamonds,^{19–21} and much progress has been made using it.²²

EXPERIMENTAL

In a typical preparation, an appropriate amount of $FeCl_2 \cdot 7H_2O$ (about 10% based on PVA weight) was dissolved into a 10% (by weight) homogeneous PVA aqueous solution. This solution and CS_2 (50% excess based on $FeCl_2 \cdot 7H_2O$) was put into a Teflon-lined autoclave of 80-mL capacity. The autoclave was maintained at 140°C for 8 h and then cooled to room temperature. The obtained black viscous solution was stable and did not precipitate within 6 months. The resulting viscous solution was cast onto the PET plates and dried at room temperature for 12 h and then dried at 60°C for a further 12 h for the complete removal of water. Films with thicknesses from 5 to 60 μm were peeled off from the plates. The as-prepared films were transparent when they were less than 10 μm thick. Similar processes were

used to prepare the PVA/cobalt sulfide and PVA/nickel sulfide nanocomposites.

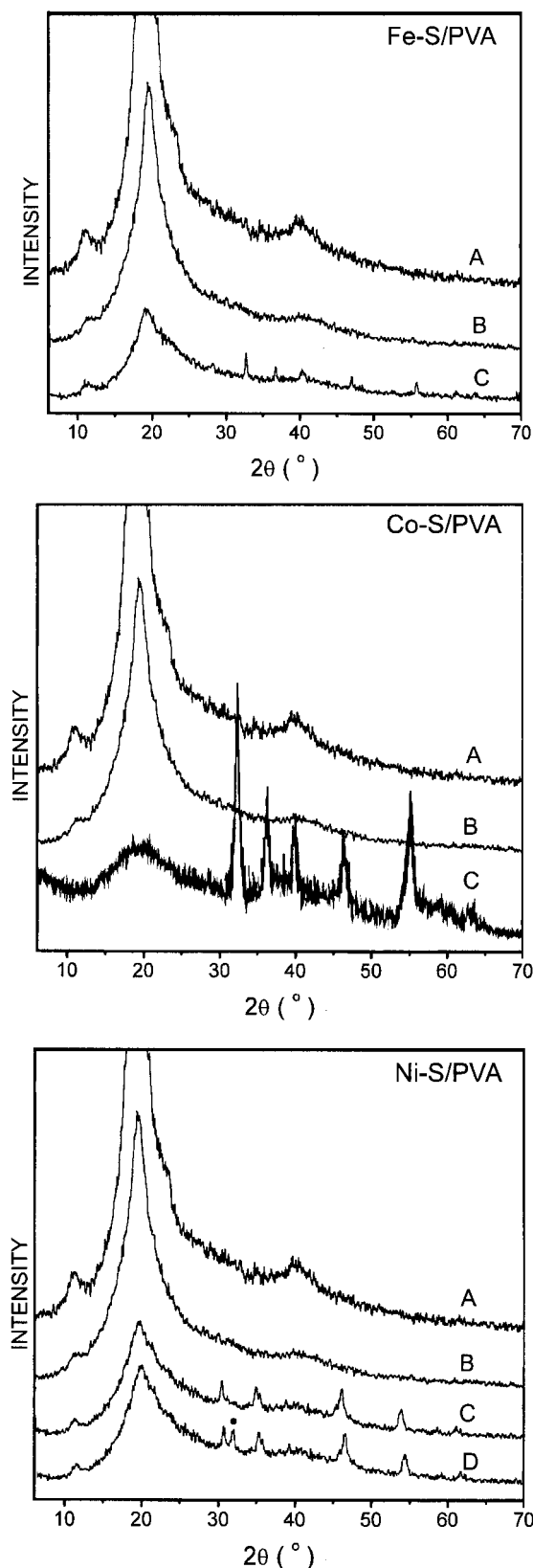
The X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/Max- γA X-ray diffractometer using $CuK\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). Photographs were taken on a Hitachi S-530 scanning electron microscope (SEM). The infrared spectra were recorded on a Perkin–Elmer Paragon 1000 FTIR spectrophotometer. Ultraviolet-visible (UV-vis) spectra were measured on a Perkin–Elmer Lambda 20 UV-vis spectrophotometer.

RESULTS AND DISCUSSION

Figure 1 depicts XRD patterns of the untreated PVA thin film cast from the PVA aqueous solution, the treated PVA thin film by the hydrothermal process, and the PVA/sulfide nanocomposite thin films. PVA is well known to be a partially crystalline polymer, and the diffraction peaks at $2\theta = 11.4^\circ$, 19.4° , and 40.4° correspond to the PVA crystalline phase²³ [Fig. 1(A)]. After hydrothermal treatment at 140°C for 8 h, the intensities of the PVA crystalline diffraction peaks decreased [Fig. 1(B)]. The PVA crystallinity results from the strong intermolecular interaction between the PVA chains due to intermolecular hydrogen bonding. The intensity of the diffraction and also the size of the crystals in PVA are determined by the number of PVA chains packed together.²³ After being complexed with sulfides, the intensities of the PVA diffraction peaks are further decreased. This is because the interaction of PVA with iron, cobalt, and nickel sulfides leads to a decrease of the intermolecular interaction between the PVA chains and, thus, the degree of crystallinity.

Besides the diffraction peaks of PVA, peaks at $2\theta = 28.2^\circ$, 32.7° , 36.7° , 40.4° , 47.1° , and 55.9° correspond to the 111, 200, 210, 211, 220, and 311 planes of the pyrite FeS_2 , respectively [Fig. 1(C)]. After refinement, the cell constant $a = 5.4 \text{ \AA}$ is close to that reported in the JCPDS cards (24-76A). The crystalline size of FeS_2 is about 45 nm, calculated from the half-peak width using the Scherrer equation.

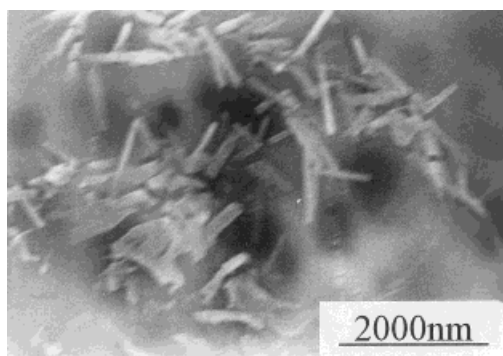
The PVA/ CoS_2 , PVA/ NiS nanocomposites were also successfully prepared using the hydrothermal method. The XRD patterns [Fig. 1(C)] showed that CoS_2 in the as-prepared nanocomposite thin film is in the pure cubic CoS_2 phase with cell constants $a = 5.5 \text{ \AA}$ (JCPDS Card file No. 19-362). The crystalline size of CoS_2 is about 12 nm. Fig-



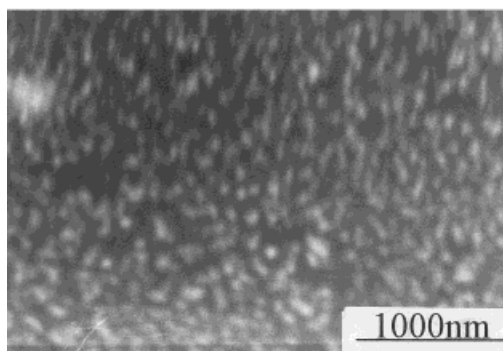
ure 1(D) is the XRD pattern of the as-prepared PVA/nickel sulfide nanocomposite thin film hydrothermally treated at 140°C for 8 h. The peaks at $2\theta = 30.1^\circ$, 34.8° , 46.0° , 53.7° , and 61.1° correspond to the diffraction of the hexagonal NiS phase (JCPDS cards 2-1280). The crystalline size of NiS is about 18 nm. Besides the diffraction peaks of PVA and NiS, a peak (marked with a black dot) at $2\theta = 31.5^\circ$ is also observed, which may be attributed to the diffraction of a NiS₂ phase. The formation of NiS₂ may be due to the high activity of the freshly obtained nanocrystalline NiS and the hydrogen sulfide-rich atmosphere, which leads to the reaction between NiS and H₂S. No NiS₂ diffraction peaks were observed in the XRD pattern [Fig. 1(C)] when the reaction time was shorter than 4 h or the reaction temperature lower than 120°C, which supports this hypothesis. In contrast to the formation of NiS and NiS₂, the reaction temperature and time have not such obvious effects on the formation of FeS₂ and CoS₂.

Figure 2 shows SEM photographs of the as-prepared PVA/sulfide nanocomposite thin films. It is interesting to find that the FeS₂ domain in the PVA/FeS₂ nanocomposite comprised rods with diameters of 100–300 nm and lengths 1500–2000 nm [Fig. 2(a)]. The formation of the FeS₂ nanorods may be caused by “special interactions” such as PVA and FeS₂, but the exact cause of the formation of the rodlike FeS₂ is not clear. Figure 2(b) shows an SEM photograph of the as-prepared PVA/CoS₂ nanocomposite thin film. The CoS₂ phase comprised uniform spherical particles with an average size of 80–150 nm. The as-prepared NiS in the PVA/NiS nanocomposite thin film also comprised uniform spherical particles with an average size of 50–100 nm. The difference between the particle size calculated from the XRD patterns and that observed in SEM may be due to the

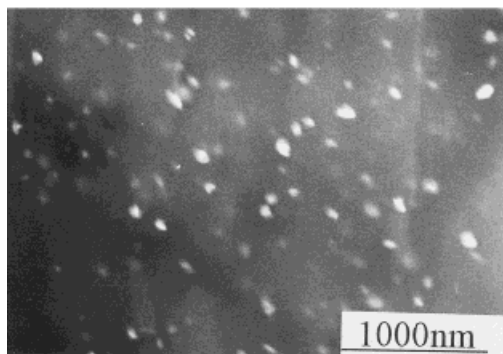
Figure 1 XRD patterns of (A) the untreated PVA thin film cast from the PVA aqueous solution, (B) the treated PVA thin film by the hydrothermal process at 140°C for 8 h, (C) the PVA/iron sulfide, PVA/cobalt sulfide nanocomposite thin film prepared by the hydrothermal process at 140°C for 8 h and the PVA/nickel sulfide nanocomposite thin film prepared by the hydrothermal process at 120°C for 4 h, and (D) the PVA/nickel sulfide nanocomposite thin film prepared by the hydrothermal process at 140°C for 8 h. The peak marked with a black dot corresponds to the phase of NiS₂.



A



B



C

Figure 2 SEM photographs of PVA/sulfide nanocomposites: (a) PVA/FeS₂; (b) PVA/CoS₂; (c) PVA/NiS.

aggregation of the metal sulfide nanocrystals. The data calculated from the XRD results reflect the size of a “single” crystal, while the SEM photographs show the aggregates of the sulfides, which are formed because of the high surface energy of the nanometer-sized crystals.

The formation of the PVA/sulfide nanocomposites can also be identified from both the color

change of the solutions and the ultraviolet-visible (UV-vis) spectra of the films. The films were cast from solution onto quartz substrates. Most commercial PVA absorbs strongly in the 200–400-nm region, as shown in Figure 3.²⁴ When NiCl₂ · 6H₂O was added to the PVA solution and constantly stirred for several hours, a light bluish solution was obtained, and the visible absorption band of the PVA–NiCl₂ solution appeared at 400 nm. After the PVA–NiCl₂ solution was treated with CS₂ using the hydrothermal method, a black solution was obtained, and its visible absorption band shifted to 460 nm. From the above results, it can be inferred that a PVA/NiS nanocomposite was obtained using the hydrothermal process. Similarly, the UV-vis absorption bands of PVA/CoS₂ and PVA/FeS₂ also shifted to longer wavelengths.

To further confirm the formation and investigate the structure of the PVA/sulfide nanocomposites, IR spectra were measured for films prepared from the (A) untreated PVA, (B) hydrothermally treated PVA, and (C) PVA/sulfide nanocomposites (Fig. 4). Although no remarkable changes were observed in these IR spectra, the change in the intensity of the sharp band at 1144 cm⁻¹ is visible *in situ*. The intensity of this band is a measure of the degree of crystallinity of PVA, presumably a $\nu(\text{CO})$ mode in the crystalline region.²⁵ The intensity of the untreated PVA at 1144 cm⁻¹ is greater than that of the hydrothermally treated PVA and much greater than that of the PVA/sulfide nanocomposites. This result is consistent with the XRD results and indicates that the introduction of the sulfides using the hydrothermal process decreases the degree of the crystallinity of PVA.

In the hydrothermal process, several factors such as the reaction temperature, time, and sulfur source were considered. The optimum condition for the preparation of PVA/sulfide nanocomposites was 140°C for 8 h. If the reaction temperature was lower than 100°C or the reaction time shorter than 4 h, the as-prepared sulfides were of low quality and the reaction was not complete.²⁶ CS₂ was chosen as the reaction reagent since it reacted with H₂O at high temperature and yielded H₂S *in situ*, which then reacted with MCl₂ (M = Fe, Co, Ni) to form the desired metal sulfides. One prominent feature of the reaction, in contrast to the use of Na₂S or K₂S as the reaction reagent, is that no by-products such as NaCl or KCl are formed in the as-prepared nanocomposites, which is an important advantage.

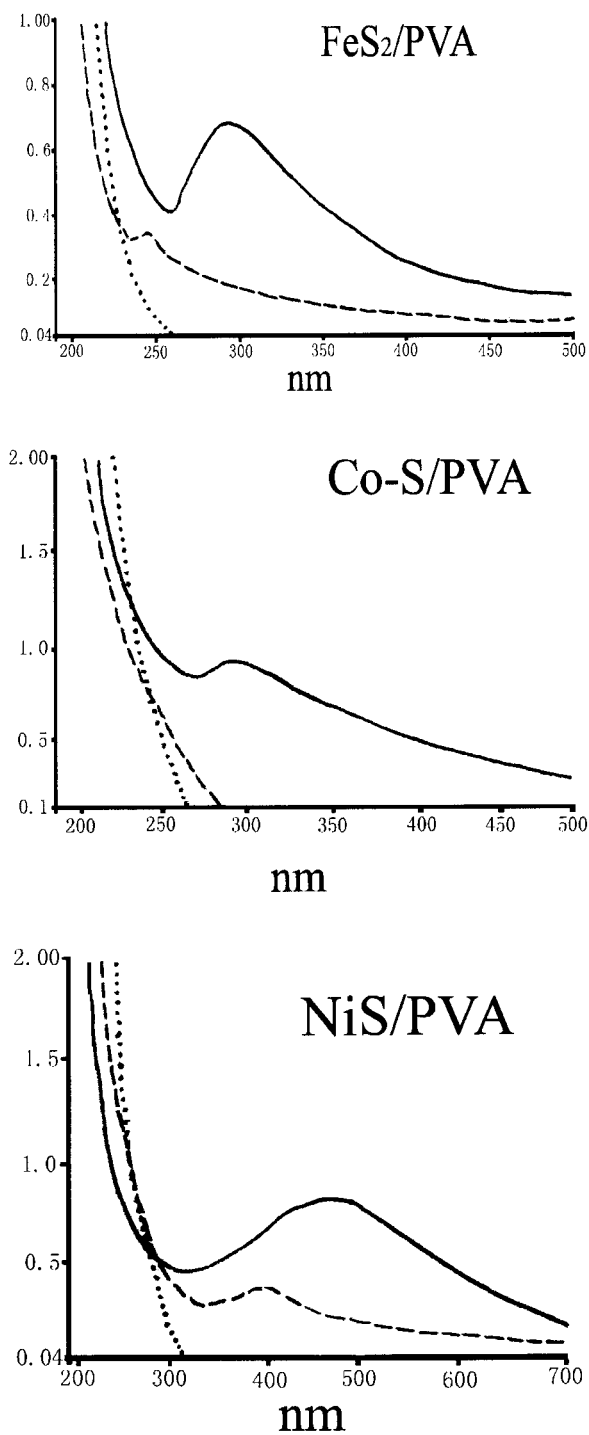


Figure 3 UV-vis spectra of (a) PVA thin film, (b) PVA/iron, cobalt, nickel chloride aqueous thin film, and (c) PVA/iron, cobalt, nickel sulfide nanocomposite thin films.

In general, the proposed hydrothermal process may be extended to other systems, such as poly(ethylene oxide) (PEO), polyacrylamide (PAAm),

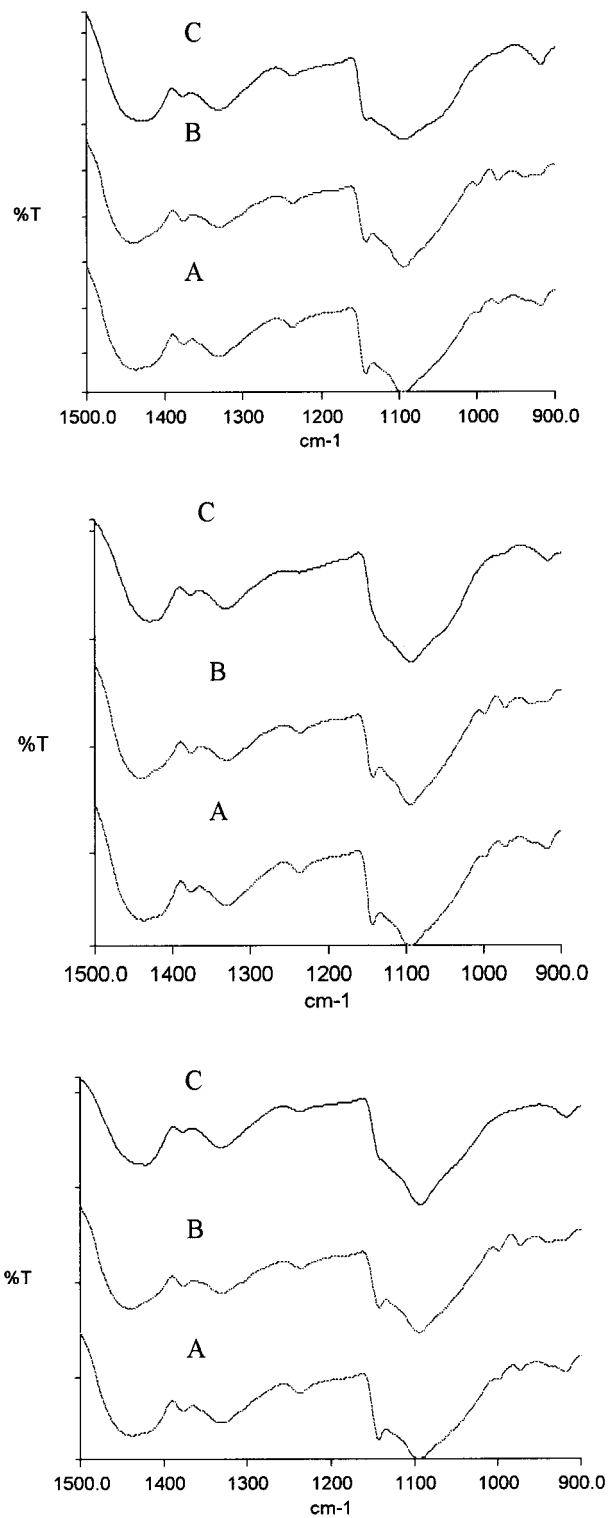


Figure 4 IR spectra of (A) the untreated PVA film, (B) the treated PVA film, (C) PVA/FeS₂ nanocomposite film, (D) the PVA/CoS₂ nanocomposite films, and (E) the PVA/NiS nanocomposite film.

and other water-soluble polymers. It is especially suitable for the preparation of polymer/oxide nanocomposites. Furthermore, by suitable choice of inorganic or organic precursors and solvents, some nanocomposites based on selenides and phosphides may also be prepared by the so-called solvothermal process.

CONCLUSIONS

Nanocomposites of poly(vinyl alcohol) (PVA) with iron, cobalt, or nickel sulfides were successfully prepared using the hydrothermal process by the *in situ* reaction with CS₂ at 140°C for 8 h. The use of CS₂ as the sulfur source can avoid the introduction of by-products such as NaCl or KCl which are obtained when Na₂S or K₂S is used. The XRD results showed that pure phases of FeS₂, CoS₂, and NiS were obtained in the as-prepared nanocomposites. In comparison with those of PVA, the XRD patterns and the IR spectra showed that the crystallinity of PVA was largely decreased after incorporation of the nano-sized sulfides. SEM photographs showed that the sulfide particles were homogeneously dispersed in the PVA matrix. UV-vis spectroscopy was also used to characterize the as-prepared nanocomposites.

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