JOURNAL OF
Materials
CHEMISTRY

Synthesis of PbS/polyacrylonitrile nanocomposites at room temperature by γ-irradiation

Zhengping Qiao,[a,b] **Yi Xie,**[b]* **Yingjie Zhu**[b] **and Yitai Qian**[a,b]

[a]*Structure Research Laboratory, University of Science & Technology of China*
[b]*Department of Chemistry, University of Science & Technology of China, Hefei, Anhui, 230026, P. R. China*

Received 17th November 1998, Accepted 14th January 1999

γ-Irradiation was successfully used to prepare nanocrystalline composites of PbS/polyacrylonitrile with 23 wt.% lead sulfide at room temperature, in which the inorganic component displays homogeneous dispersion in the polymer matrix. X-Ray powder diffraction and infrared spectra were used to characterize the product. Its morphology was determined by transmission electron microscopy.

Introduction

Most research has concentrated on the preparation and characterization of inorganic–organic materials.[1] This class of totally innovative materials synergizes properties of both components, leading to many applications.[2] Among these materials, semiconductor–polymer nanocomposites have recently aroused much interest and attention.[3]

Only a few methods have been used to prepare metal sulfide/polymer nanocomposites. In general, two steps were needed: firstly, metal ions were introduced into polymer, for example, Wang *et al.*[4] use ion-exchange to introduce metal ions and Yang *et al.*[5] complete the first step by co-polymerization of metal salt and monomer. Secondly, H_2S gas was imported for preparation of nanocrystalline sulfides. In these methods, the polymerization of organic monomer and the formation of nanocrystalline metal sulfide particles are performed separately and the use of the toxic gas H_2S could not be avoided. Furthermore, to date most of the products prepared by these methods at room temperature are amorphous phase.[6] Post-treatments under high temperature and pressure are necessary in these methods. So, for extension to applications, these are always likely to be limiting factors. Materials chemists are looking for an ideal method to prepare PbS/polymer nanocomposites in a single step.

Here, we report a new method for the preparation of lead sulfide–polyacrylonitrile by γ-irradiation at room temperature and ambient pressure for the first time. Nanocrystalline PbS with narrow size distribution was well dispersed in the polyacrylonitrile matrix. Polymerization and the formation of lead sulfide were performed in a single step, which is much simpler and easy to control. In this work polyacrylonitrile, being a good heat-insulator and aging-resistive material, was chosen as the polymer. As for the preparation of PbS, the selection of the sulfur source is critical since the usual sulfur source (sodium thiosulfate) as reported in the preparation of CdS[7] can form precipitates with Pb^{2+}, which would limit the formation of PbS. As it is a good sulfur source which may produce sulfur radical under γ-irradiation[8] and avoid the formation of intermediate precipitates, carbon disulfide was initially used as the sulfur source. In addition, for preparing composites in which the inorganic nanocrystalline phase displays a narrow particle size distribution and well dispersed particles, a good solvent is an important factor, which should possess at least two properties as follows. On the one hand, solvated electrons can be produced in it upon γ-irradiation. On the other hand, it must be able to provide a homogeneous system, which will make sure the reactants are mixed at the molecular level in the solution in order to prepare homogeneous composites. In our experiments, absolute ethanol was used due to its good solvating properties for many inorganic and organic materials and for solvated electrons upon γ-irradiation.[9]

Experimental

A typical solution was prepared by dissolving analytically pure carbon disulfide (0.1% v/v), lead acetate ($0.02\ \mathrm{kmol\ m^{-3}}$), acrylonitrile (7% v/v) and isopropanol (23% v/v) in anhydrous ethanol. The solution was irradiated in the field of a 2.59×10^{15} Bq ^{60}Co γ-ray source. The precipitates were collected and washed with dilute acetic acid, absolute ethanol and distilled water in sequence to remove the by-products. The final products were dried in vacuum at room temperature for 4 hours.

The sample was characterized by X-ray powder diffraction (XRD) studies employing a scanning rate of $0.05^\circ\ \mathrm{s^{-1}}$ in the 2θ range from 10 to 70°, using a Japan Rigaku Dmax γ_A X-ray diffractometer equipped with graphite monochromatized Cu-Kα radiation ($\lambda = 1.54178$ Å) at the same time. In order to distinguish the two phases in the product, pure polyacrylonitrile was determined by XRD. The infrared spectra were recorded in the wavenumber range 4000–500 $\mathrm{cm^{-1}}$ 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 content of lead sulfide in the polyacrylonitrile matrix, 0.010 g samples were dissolved in $10^{-4}\ \mathrm{m^3}$ analytically pure nitric acid. The lead ion content was determined using an atomic absorption spectrometer (model WYX-40).

Results and discussion

A typical XRD pattern of product is shown in Fig. 1. It is seen that all of the diffraction peaks can be indexed as cubic PbS (JCPDS Card File No. 5–592) except for the peak at $2\theta = 17.2^\circ$, which is consistent with the XRD pattern of pure polyacrylonitrile. The diameter of lead sulfide, calculated from the half-width of diffraction peaks using the Scherrer formula, is 7.8 nm.[13]

Fig. 2 is the IR spectrum of the product, which is similar to the standard infrared spectrum of polyacrylonitrile and totally different from that of acrylonitrile. The strongest peak (δ_{CH_2}) and the characteristic peak ($\nu_{C\equiv N}$) of polyacrylonitrile at 1453.7 and 2242.9 $\mathrm{cm^{-1}}$, respectively, confirm the polymerization of

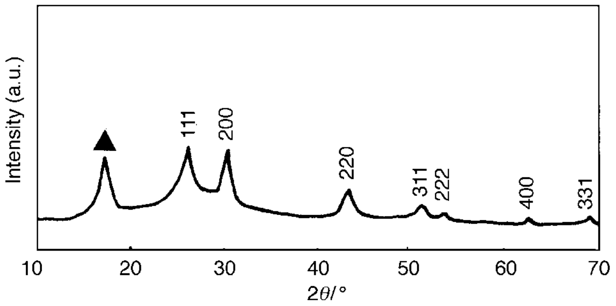

Fig. 1 XRD pattern of the product (▲ = polyacrylonitrile).

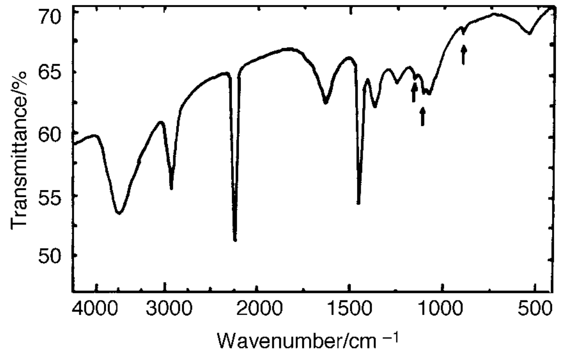

Fig. 2 IR spectrum of the product in Fig. 1.

the acrylonitrile monomer and the formation of polyacrylonitrile in ethanol upon γ-irradiation. More careful observation shows that there are more peaks at 1110, 1160 and 835 cm^{-1} by comparing with the polyacrylonitrile peaks. These peaks, which are rather weak and are only resolved due to the low content of the inorganic component, correspond to Pb–S bonds.[10]

Transmission electron microscopy was used to observe PbS nanoparticles in the polymer matrix. From the TEM image, which is shown in Fig. 3, one can see that the nanocomposites consist of fine quasi-spherical PbS particles homogeneously dispersed and well separated in the polyacrylonitrile matrix. The diameter of the resulting PbS particles is 8 nm, which is consistent with the XRD result.

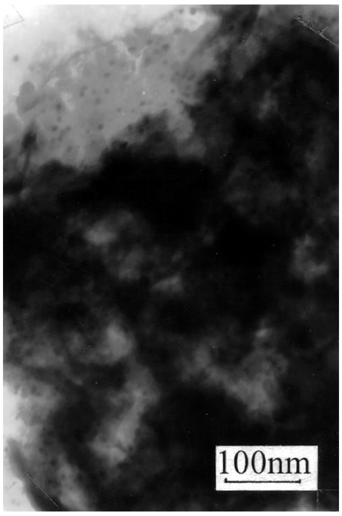

Fig. 3 TEM image of the product in Fig. 1.

In these γ-irradiation processes, the polymerization mechanism of acrylonitrile monomer has been studied extensively,[11] but the formation mechanism of nanocrystalline sulfides is not very clear up to now. However, some probable reactions may be going on under γ-irradiation. It is clear that as a result of reduction of metal ions with solvated electrons produced in solution by γ-irradiation, lower valent metal ions are formed.[9,12]

$$\mathrm{Pb}^{2+} + \mathrm{e}^{-}_{\mathrm{solv}} \rightarrow \mathrm{Pb}^{+}$$

Research on γ-irradiation of carbon disulfide[8] shows the formation of non-ionic intermediates, which possibly exist as S radicals. The free sulfur may be liberated when the S radicals collide in the solution.

$$\mathrm{CS}_2 \rightarrow \mathrm{S}^{\bullet} + \mathrm{CS}^{\bullet}$$

However, we do not find the appearance of sulfur and metal in the products. The precipitation of metal sulfides probably prevents the formation of sulfur from S radicals and metallic lead from Pb^{+} under irradiation.

$$\mathrm{S}^{\bullet} + \mathrm{Pb}^{+} \rightarrow \mathrm{PbS}$$

Conclusions

In summary, γ-irradiation was firstly used to prepare, at room temperature, PbS/polyacrylonitrile nanocrystalline composites, in which the inorganic phase displays homogeneous dispersion. X-Ray powder diffraction and infrared spectra were used to characterize the product. Its morphology was determined by transmission electron microscopy. The content of lead sulfide in the composites was measured by atomic absorption spectroscopy. By appropriate control of the experimental conditions, we predict that the γ-irradiation method may be extended to the preparation of a variety of metal sulfide semiconductor/polymer nanocomposites in non-aqueous systems.

Acknowledgements

Financial support from the Chinese National Foundation of Natural Science Research through No. 29771027 and the Outstanding Youth Science Fund is gratefully acknowledged. This work is also supported by the Climbing Plan from the State Science and Technology Commission of China.

References

1 P. Judeinstein, P. W. Oliveira, H. Krug and H. Schmidt, *Chem. Phys. Lett.*, 1994, **220**, 35.
2 H. Krug and H. Schmidt, *New J. Chem.*, 1994, **18**, 1125.
3 J. Lin, E. Cates and P. A. Bianconi, *J. Am. Chem. Soc.*, 1994, **116**, 4738.
4 Y. Wang, A. Suna and W. Mahler, *J. Phys. Chem.*, 1987, **87**, 7315.
5 M. Y. Gao, Y. Yang and B. Yang, *J. Chem. Soc., Chem. Commun.*, 1994, 2779.
6 P. A. Bianconi, J. Lin and A. R. Strzelecki, *Nature*, 1991, **349**, 315.
7 Y. Yin, X. Xu, X. Ge, C. Xia and Z. Zhang, *Chem. Commun.*, 1998, 1641.
8 F. Johnston, *J. Phys. Chem.*, 1975, **79**, 419.
9 R. Janes, A. D. Stevens and M. C. R. Symons, *J. Chem. Soc., Faraday. Trans. 1*, 1989, **85**, 3973.
10 N. N. Parvathy, G. M. Pajonk and A. V. Rao, *J. Crystal Growth*, 1997, **179**, 249.
11 T. Wada, T. Watanabe and M. Takehisa, *Polymer J.*, 1973, **4**, 136.
12 P. N. Moorthy and J. J. Weiss, *Nature*, 1964, **201**, 1317.
13 C. N. J. Wagner and E. N. Aqua, *Adv. X-Ray Anal.*, 1964, **7**, 46.

Paper 8/08965E