One-Dimensional PbS/Polymer Nanocomposite of Core/Sheath Structure Fabricated by Hydrothermal Polymerization and Simultaneous Sulfidation

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A novel hydrothermal method has been developed for the synthesis of rod-shaped PbS/poly(vinyl acetate) composites. These one-dimensional (1-D) PbS/polymer composites were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared (FT-IR), and Raman spectroscopy. The results show that the products are of rod-shaped core/sheath structure with good crystallinity.

Semiconductor nanoparticles have been the subject of numerous investigations in the past few years.[1–7] In the recent years, semiconductor/polymer nanocomposites, especially those of one-dimensional, have been synthesized by some novel techniques.[7,8] Lead sulfide, because of its small effective mass, shows a large blue shift in its absorption edge with a small change in cluster size. Bulk lead sulfide has an infrared bandgap (0.41 eV),[7] which shifts to the visible region for the nanoclusters. As a result, lead sulfide nanoclusters may find use in electroluminescent devices such as light-emitting diodes. In addition, lead sulfide nanoclusters are expected to have exceptional third-order nonlinear optical properties compared with their bulk counterparts.[9]

There have been many routes to produce lead sulfide nanoparticle and lead sulfide/polymer composites. They have been synthesized solvothermally,[10] or by γ irradiation,[11] in the inorganic and polymer matrix.[12,13] However, the preparation of 1-D PbS nanorods, especially 1-D PbS/polymer nanocomposites, is rarely reported.[14]

In this paper, we report a novel in situ hydrothermal polymerization and simultaneous sulfidation (HPSS) process to prepare PbS/poly(vinyl acetate) (PVAc) 1-D nanocomposite of core/sheath structure. This process is based on the hydrothermal polymerization of VAc rods and the simultaneous sulfidation of Pb^{2+} coordinated with carboxyl groups on VAc.

All chemicals are analytical reagents, purchased locally and used without further purification. Thiourea (tu; 0.3 g) was added to the 40 mL 3×10^{-2} mol $Pb(NO_3)_2$ aqueous solution. Then 1 mL vinyl acetate (VAc) was added to the above solution. AIBN (0.075 g) was used as the initiator. The solution was then moved into an autoclave. The autoclave was put into a furnace and heated at 180 °C for 12 h. The black product was filtered, washed with distilled water, and then with absolute ethanol several times, and dried in a vacuum at 60 °C for 30 min.

The X-ray powder diffraction (XRD) pattern was collected on a Rigaku Dmax γA diffractometer equipped with a monochromized Cu Kα radiation (λ = 1.5418 Å). Fourier transform infrared (FT-IR) spectrum was measured on a Bruker Vector-22 FT-IR spectrometer from 4000 to 400 cm^{-1} at room temperature. Transmission electron micrograph (TEM) image was taken on a HITACHI H-800 microscope, applying an accelerating voltage of 200 kV. Raman spectrum was collected on a SPEX-1403 Laser Raman Spectrometer in the range of 50–450 cm^{-1} at room temperature by means of back scattering technique, using 514.5-nm wavelength laser as the excitation source.

The XRD pattern is shown in Figure 1. All the diffraction peaks can be indexed to well crystallized PbS (gelena) with rock-salt structure. The cell constant is a = 5.93 Å, which is in good agreement with the value in the literature (JCPDS card No. 5 – 592). Although there is no apparent broad diffraction peak corresponding to the polymer matrix, the existence of PVAc was certified by FT-IR spectrum. The PVAc sheathes capping PbS nanorods were also directly observed in the TEM microimage.

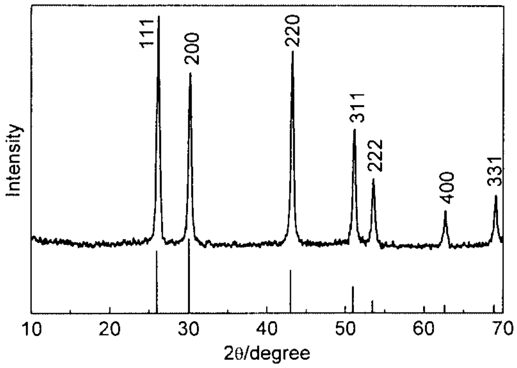

Figure 1. Top: XRD pattern of PbS/PVAc nanorod composite. Bottom: Standard XRD pattern of PbS.

The IR spectrum is similar to the standard IR spectrum of PVAc and apparently different from that of the vinyl acetate monomer. The strongest peak at 1738.5 cm^{-1} ($\nu_{C=O}$) and the characteristic peaks at 1239.0 cm^{-1}, 1021.1 cm^{-1} ((ν_{C-O}), and 1375.4 cm^{-1} (δ_{CH_3}) of PVAc suggest the existence of PVAc in the final product.

The core/sheath structure of PbS/PVAc is observed in the TEM microimage. Figure 2 shows 1-D PbS nanorods of ca. 10 nm in width and 250 nm in length coated in the 5-nm PVAc sheath. Since polymers show low contrasts in the TEM images comparing with the inorganic crystallites, the low-density shades around the nanorods indicate the existence of the PVAc sheath.

A typical Raman spectrum shows some characteristic peaks at 65, 135, 275 and 430 cm^{-1}. Minceva-Sukarova, et al. pointed out that the strongest Raman shift of PbS film originated by the lattice mode vibration is at 141 cm^{-1}.[15] Other results suggest that the strongest peak should appear at ca. 210 cm^{-1},

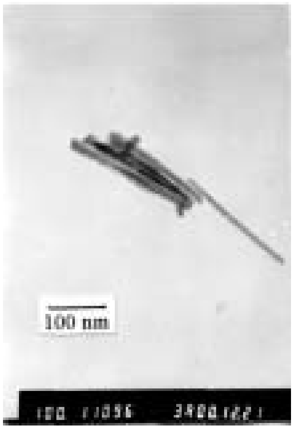

Figure 2. TEM micrograph of PbS/PVAc nanorod composite.

which is originated from first order longitudinal optical phonon mode when excited with a 514.5 nm wavelength laser.[16] When the nanoparticle is embedded in a medium the Raman peak should shift to lower frequency if the dielectric constant of the medium increases. Polymers have dielectric constants much larger than that of the air. The strongest Raman peak at 135 cm^{-1} of the present product is believed to be shifted to the lower frequency due to the capping of PVAc sheathes on the PbS nanorods. When the PVAc sheath of the PbS/PVAc composite is dissolved in CCl_4, the Raman peak is shifted to 138 cm^{-1}, which again suggests the capping of the PVAc sheath on the surface of PbS cores. The other peaks at 65, 275 and 430 cm^{-1} are generated by acoustic mode, two-phonon process, and the excitation light overtone peak, respectively.[15] An apparent shoulder peak at 130 cm^{-1} can also be detected. This shoulder has been identified as the surface phonon mode .[15]

The mechanism of the formation of the PbS/PVAc composite can be explained by the self-assembly of VAc micelle rods, maintenance of the superstructure during the afterward polymerization and simultaneous sulfidation of Pb^{2+} coordinated with the carboxyl groups of VAc. Stoll and his co-worker have simulated the bridging flocculation process of inorganic/polymer hybrids. They pointed out that at certain inorganic ion/polymer concentration ratio, the inorganic/ polymer hybrids could develop into 1-D morphology automatically.[17] Leontidis et al. proved the kinetic simulation by the synthesis of PbS aggregation in the PEO-SDS system.[18] However, their simulation and experiment suggested that a surfactant is very important in the 1-D formation process. The mechanism of the present process is similar to theirs except that VAc itself serves as the surfactant as well as the monomer. VAc micelle rods were formed in the early stage of the process, and the superstructure is maintained during the afterward polymerization from VAc to PVAc. When the temperature is over ca. 45 °C, AIBN is decomposed to release $(CH_3)_2C(CN)\bullet$, which initiates the radical chain polymerization.[19] At the same time, the cations originally coordinated with carboxyl groups on VAc react with the released S^{2-} from tu to form PbS clusters. The clusters attract several PVAc micelle rods to form the sheath, while PbS itself develop into PbS nanorod. The increasing viscosity of the PVAc sheath prevents PbS nanorods from growing large.

In conclusion, 1-D PbS/PVAc with core/sheath structure nanocomposite was fabricated by the present HPSS process. The PbS nanorods of 10 nm in width and 250 nm in length were capped with 5-nm PVAc sheath forming nanocomposites. The experiments indicated that the VAc micelle rods play the key role in the synthesis of PbS/PVAc composite. The polymerization of VAc keeps the superstructure of the micelles, affects the growth behavior of PbS, and prevents the PbS nanorods from growing large. The present HPSS technique may provide a new route to prepare other 1-D metal sulfide semiconductor/polymer hybrid nanocomposites.

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References and Notes

1 P. E. Lippens and M. Lannoo, *Phys. Rev. B,* **41**, 6079 (1990).
2 N. A. Hill and K. B. Whaley, *J. Chem. Phys.*, **99**, 3707 (1990).
3 A. Eychmuller, L. Kaisikas, and H. Weller, *Langmuir*, **6**, 1605 (1990).
4 D. Schooss, A. Mews, A. Eychmuller, and H. Weller, *Phys. Rev. B*, **49**, 17072 (1994).
5 C. B. Murray, D. J. Norris, and M. C. Bawendi, *J. Am. Chem. Soc.*, **115**, 8706 (1993).
6 R. S. Kane, R. E. Cohen, and R. Silbey, *J. Phys. Chem.*, **100**, 7928 (1996).
7 Y. Wang, A. Suna, W. Mabler, and R. Kasowski, *J. Chem. Phys.*, **87**, 7315 (1987).
8 Y. Xie, Z. P. Qiao, M. Chen, X. M. Liu, and Y. T. Qian, *Adv. Mater.*, **11**, 1512 (1999).
9 Y. Wang, *Acc. Chem. Res.*, **24**, 133 (1991).
10 J. J. Zhu, S. W. Liu, O. Palchik, Y. Koltypin, and A. Gedanken, *J. Solid State Chem.*, **153**, 342 (2000).
11 Z. P. Qiao, Y. Xie, Y. J. Zhu, and Y. T. Qian, *Mater. Sci. and Engin. B – Solid State Mater. for Adv. Tech.*, **77**, 144 (2000).
12 L. Z. Yao, C. H. Ye, C. M. Mo, W. L. Cai, and L. D. Zhang, *J. Cryst. Growth*, **216**, 147 (2000).
13 S. H. Yang, S. H. Wang, and K. K. Fung, *Pure Appl. Chem.*, **72**, 119 (2000).
14 W. D. Hergeth, W. Lebek, R. Kakuschke, and K. Schmutzler, *Makromol. Chem.*, **192**(10), 2265 (1991).
15 B. Minceva-Sukarova, M. Najdoski, I. Grozdanov, and C. J. Chunnilal, *J. Mol. Struct.*, **410**, 267 (1997).
16 T. D. Krauss and F. W. Wise, *Phys. Rev. B*, **55**, 9860 (1997).
17 S. Stoll and J. Buffle, *J. Colloid Interface Sci.*, **180**, 548 (1996).
18 E. Leontidis, T. Kyprianidou-Leodidou, W. Caseri, and K. C. Kyriacou, *Langmuir*, **15**, 3381 (1999).
19 G. Odian, “Principles of Polymerization,” McGraw-Hill Book Company, New York (1970).