CHEMISTRY OF MATERIALS

VOLUME 11, NUMBER 12 DECEMBER 1999

© Copyright 1999 by the American Chemical Society

Communications

A Novel in Situ Simultaneous Copolymerization−Decomposition Technique for Fabrication of Poly(acrylamide-*co*-styrene)-Semiconductor CdE (E = S, Se) Nanorod Nanocomposites

Yong Zhou, Ling-Yun Hao, Shu-Hong Yu,
Min You, Yu-Rui Zhu, and Zu-Yao Chen*

Structure Analysis Lab and Department of Chemistry,
University of Science and Technology of China,
Hefei, Anhui 230026, P. R. China

Received July 1, 1999
Revised Manuscript Received September 10, 1999

Synthesis and characterization of inorganic−organic polymer nanocomposites have received much intensive research,[1] owing to their optical, electrical, catalytic, and mechanical properties,[2,3] and potential applications in microelectronics.[4] The hybridization of organic and inorganic semiconductors is expected not only to permit wide-range selection of emitter and carrier transport materials, but to provide a new approach to construct high-performance electroluminescence (EL) devices, taking advantage of organic and inorganic semiconductor, such as high photoluminescent efficiency of organic materials and high carrier density and low resistivity of inorganic semiconductors. In addition, polymers are also expected to provide good mechanical properties, conferring high kinetic stability on nanometer-sized semiconductor particles. To organize the semiconductor nanoparticles in an orderly fashion in a polymer matrix may afford a potential application of their special properties.

Many methods have been exploited to prepare the semiconductor−polymer nanocomposites. Meissner et al.[5] reported the first system involving dispersed semiconductor−polymer arrangements by physically embedding monograins of CdS particles on the order of 40 μm diameter in a thin, unconducting polyurethane membrane, and various photoprocesses were examined. Later, a new method of incorporating a dispersed semiconductor CdS throughout an ionically conductive Nafion polymer membrane was developed.[6] Recently, CdS/polystyrene,[7] CdS/PS−P2VP[polystyrenes-*block*-poly(vinylpyridine)s] composite,[8] PbS/S-MA(styrene-methylacrylic copolymer),[9] PbS/E-MAA(ethylene-15% methacrylic acid copolymer),[10] and the monolayer of PbI_2/MD (molecular deposition)-LB film[11] have been synthesized in different polymer matrixes using a variety of methods. The multisemiconductor nanocomposite Cu_2S/CdS/ZnS was also successfully prepared in a polystyrene system by ion exchange.[12] Y. Wang and N. Herron reported for the first time the synthesis of CdS/PVK (*N*-poly(vinylcarbazole)) polymer composite by using $Cd_{10}S_4(C_6H_5)$ as precursor.[13] Currently, the use of amphiphilic block copolymer (ABC) micelles opens a doorway to utilize these materials as “nanoreactors” for the forma-

---

(1) Antonietti, M.; Göltner, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 910.
(2) Bigg, D. M. *Polym. Compos.* **1996**, *7*, 125.
(3) Chang, L. T.; Yen, C. C. *J. Appl. Polym. Sci.* **1995**, *55*, 371.
(4) Schmid, G. *Chem. Rev.* **1992**, *92*, 1709.
(5) Meissner, D.; Memming, R.; Kastening, B. *Chem. Phys. Lett.* **1983**, *96*, 34.
(6) Krishnan, M.; White, J. R.; Fox, M. A.; Bard, A. *J. Am. Chem. Soc.* **1983**, *105*, 7002.
(7) Huang, J. M.; Yang, Y.; Yang, B.; Liu, S. Y.; Shen, J. C. *Polym. Bull.* **1996**, *36*, 337.
(8) Möller, M. *Synth. Met.* **1991**, *41*, 1159.
(9) Gao, M. Y.; Yi, Y.; Yang, B.; Beng, F. L.and Shen, J. C. *J. Chem. Soc., Chem. Commun.* **1994**, 2777.
(10) Wang, Y.; Suna, A.; Mahler, W. *J. Chem. Phys.* **1987**, *87*, 7315. Mahler, W. *Inorg. Chem.* **1988**, *27*, 435.
(11) Gao, M. Y.; Xi, Z.; Yang, B.; Shen, J. C. *J. Chem. Soc., Chem. Commun.* **1994**, 2229.
(12) Huang, J. M.; Yang, Y.; Yang, B.; Liu, S. Y.; Shen, J. C. *Polym. Bull.* **1996**, *37*, 679.
(13) Wang, Y.; Herron, N. *Chem. Phys. Lett***. 1992**, *200*, 71.

10.1021/cm9904133 CCC: $18.00 © 1999 American Chemical Society
Published on Web 12/03/1999

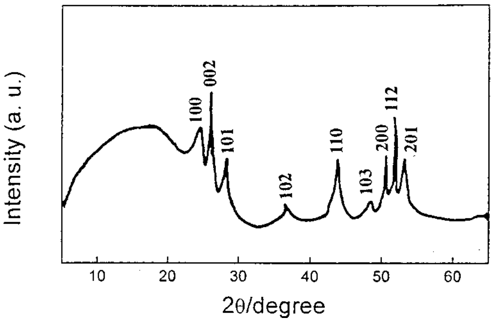

Figure 1. The XRD pattern of the P(AM-*co*-St)-CdSNR nanocomposite obtained by the present SCPD technique, 160 °C for 12 h.

tion of the inorganic nanocrystals.[1,14] Other block copolymer systems/metal sulfide nanoparticles have been prepared by the addition of H_2S.[15]

Since one-dimensional (1D) semiconductor nanometer materials (e.g., nanowires, nanorods, and nanofibers) are of special optical and electrical properties compared with the semiconductor quantum dots, studies and preparation of the 1D semiconductor nanometer materials have received extensive attention recently. However, there are to our knowledge few reports on studies and fabrication of nanocomposites of 1D nanometer semiconductor−polymers. Herein, we report a novel in situ simultaneous copolymerization−decomposition (SCPD) technique for fabrication of poly(acrylamide-*co*-styrene)-semiconductor CdE (E = S, Se) nanorod nanocomposites. The so-called SCPD technique is based on the mechanism of the simultaneous occurrence of the copolymerization proceeding that of organic monomers and the formation of semiconductor CdE nanorods. It was found that the produced CdE (CdS, CdSe) nanorods were well dispersed homogeneously in the poly(acrylamide-*co*-styrene) matrix. The present SCPD technique may be extended to prepare other 1D nanometer metal chalcogenide−polymer hybrid nanocomposites.

In a typical preparation procedure of the poly(acrylamide-*co*-styrene)-CdS nanorod [P(AM-*co*-St)-CdSNR] nanocomposite, 0.001 mol analytical grade $CdSO_4\cdot{}^{8}/{}_{3}H_2O$ and 0.002 mol thiourea (Tu) were dissolved in 100 mL of ethylenediamine (En). The resulting solution was added to a mixture of 0.5 mol acrylamide (AM) monomer, 0.1 mol styrene (St) monomer, and 0.01 g of 2,2′-azobisisobutyronitrile (AIBN) as a radical thermal initiator. The mixture solution was put into a stainless steel tank with a Teflon interior and heated in an oven at 160 °C for 12 h. The product obtained was washed with distilled water and absolute ethanol, dried at room temperature, and ground into powder for characterization.

The X-ray powder diffraction (XRD) pattern for the obtained product was determined at a scanning rate of $0.02°\ s^{-1}$ in 2θ ranging from 10°−70°, using a Japanese Rigakn Dmax X-ray diffractometer with high-intensity Cu Kα irradiation ($\lambda = 0.151478$ nm) and a graphite monochromator was set at the diffracted irradiation. Figure 1 shows the XRD pattern of the P(AM-*co*-St)-CdSNR nanocomposite obtained by the present SCPD technique at 160 °C for 12 h. The broadening peak at about 17° is corresponding with the P(AM-*co*-St) phase. All other peaks in the XRD pattern can be indexed as the hexagonal CdS phase with a cell parameter $a = 0.4172$ nm, $c = 0.6762$ nm, which is in good agreement with the reported data (JCPDS File 4-0783; $a = 0.4141$ nm, $c = 0.6724$ nm).

Figure 2. The TEM image of the P(AM-*co*-St)-CdSNR nanocomposite obtained by the present SCPD technique, 160 °C for 12 h.

The TEM image of the P(AM-*co*-St)-CdSNR nanocomposite obtained was taken with a Hitachi model H-800 transmission electron microscope, using an accelerating voltage of 200 kV. Figure 2 presents the TEM image of the P(AM-*co*-St)-CdSNR nanocomposite obtained by the present SCPD technique at 160 °C for 12 h. The image shows that the formed CdS nanorods with widths of 20−30 nm and lengths up to 500 nm were well dispersed homogeneously in the P(AM-*co*-St) matrix. The average length and aspect ratios of the resulting CdS nanorods were 400 nm and 16, respectively. The corresponding electron diffraction (ED) pattern can also be indexed as the hexagonal CdS phase, corresponding well with the analytical result of XRD pattern.

The UV−vis absorption spectrum of the P(AM-*co*-St)-CdSNR nanocomposite dispersed in ethanol was recorded with a Shimadzu UV-200 spectrophotometer, which was carried out by using pure P(AM-*co*-St) dispersed in ethanol as reference. The result shows that the absorption peak of the CdS nanorods in the present P(AM-*co*-St)-CdSNR nanocomposite was observed at about 492 nm, which shifts toward blue zone compared with the band edge of the bulk material (515 nm).[16] The particle size of the CdS nanorods calculated with the spectrum shift data is consistent with that observed by the TEM image.[17]

The formation mechanism of the CdS nanorods in the P(AM-*co*-St)-CdSNR nanocomposite in the present system using ethylenediamine (En) as reaction medium has been studied by S. Yu et al.[18] It can be formulated as follows:

---

[14] Roescher, A.; Möller, M. *Adv. Mater.* **1995**, *7*, 151.

[15] Moffitt, M.; Eisenberg, A. *Chem. Mater.* **1995**, *7*, 1178.

[16] Yang, J. P.; Meldrum, F. C.; Fendler, J. H. *J. Phys. Chem.* **1995**, *99*, 5500.

[17] Brus, L. E *J. Chem. Phys.* **1984**, *80* (9), 4403.

[18] Yu, S.; Yang, J.; Han, Z.; Yang, R.; Xie, Y.; Qian, Y.; Zhang, Y. *J. Colloid Interface. Sci.*, in press.

$$(NH_2)_2CS + 2OH^- \Leftrightarrow CH_2N_2 + H_2O + S^{2-} \quad (1)$$

$$[Cd(En)_2]^{2+} + S^{2-} \xrightarrow{\text{solvant}} \text{CdS nanorod} + 2\text{En} \quad (2)$$

Since the coordination with Cd^{2+} of ethylenediamine (En) is much stronger than that of thiourea (Tu) [$(NH_2)_2CS$], which was confirmed by the IR spectrum analysis, Tu has no chance to coordinate with Cd^{2+}. Therefore, Tu coordinates with H_2O from $CdSO_4 \cdot {}^8/_3H_2O$ in the reaction medium and decomposes to release S^{2-} anions. The released S^{2-} anions bond with the $[Cd(En)_2]^{2+}$ in the solution and lose the volatile En molecules at higher temperature, resulting in the formation of the CdS, which En medium facililated growing into nanorod shapes.[18-20]

It is well-known that the radical thermal initiator AIBN (2,2′-azobisisobutyronitrile) decomposes about 45−65 °C, of which the decomposition reaction is described as

$$(CH_3)_2(CN)C{-}N{=}N{-}C(CN)(CH_3)_2 \rightarrow 2(CH_3)_2(CN)C^{\bullet} + N_2 \quad (3)$$

In the present system, the produced radicals will initiate the copolymerization of the acrylamide (AM) monomer and the styrene (St) monomer. The copolymerization that proceeds simultaneously accompanys the formation of CdS nanorods. Therefore, the produced CdS nanorods can be well dispersed homogeneously in the P(AM-*co*-St) matrix.

We have also prepared the poly(acrylamide-*co*-styrene)-CdSe nanorod [P(AM-*co*-St)-CdSeNR] nanocomposite via a route similar to the present SCPD technique. Few reports on the preparation of nanocrystalline selenides could be found generally because a selenium source was not like a sulfur source, which could exist in various stable phases, almost all of which were easily obtainable. The present CdSe nanorod was synthesized by employing the method noted in a previous report[19] via a reaction of CdC_2O_4 with Se element using the ethylenediamine (En) as solvent. The possible reaction mechanism can be formulated as

$$CdC_2O_4 + Se \rightarrow CdSe + 2CO_2\uparrow \quad (4)$$

In a typical preparation procedure of P(AM-*co*-St)-CdSeNR nanocomposite, 0.001 mol analytical grade CdC_2O_4, 0.001 mol Se, 0.5 mol AM monomer, 0.1 mol St monomer, and 0.01 g AIBN were added to 100 mL of En. The resulting mixture solution was put into a stainless steel tank with a Teflon interior and heated in an oven at 160 °C for 12 h. The obtained product was dealt with for characterization in the same manner as the above P(AM-*co*-St)-CdSNR nanocomposite.

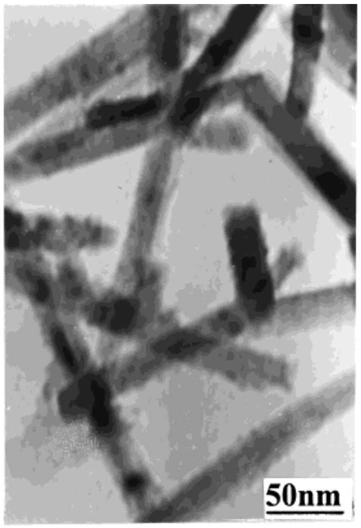

Figure 3. The TEM image of the P(AM-*co*-St)-CdSeNR nanocomposite obtained by the present SCPD technique, 160 °C for 12 h.

Figure 3 presents the TEM image of the P(AM-*co*-St)-CdSeNR nanocomposite. It was found that the formed CdSe nanorods with widths of 20 nm and lengths up to 250 nm were also well dispersed homogeneously in the P(AM-*co*-St) matrix. The average length and aspect ratio of the resulting CdSe nanorods were 200 nm and 10, respectively. It could be clearly observed that there were some small particles attached to the surface of the CdSe nanorods, as parts of the nanorods. This may indicate that the resulting CdSe nanorods generated from the compact aggregation of smaller CdSe particles.

In summary, the poly(acrylamide-*co*-styrene)-CdE (E = S, Se) nanorod nanocomposites were prepared with a novel so-called in situ simultaneous copolymerization−decomposition (SCPD) route. The formed CdE nanorods were found to be well dispersed homogeneously in the P(AM-*co*-St) matrix. The present SCPD technique may be extended to prepare other 1D nanometer metal chalcogenide−polymer hybrid nanocomposites.

Acknowledgment. This work was supported by the Chinese National Foundation of Natural Science Research (59572031 and 19772049).

CM9904133

---

(19) Yu, S.; Yang, J.; Han, Z.; Zhou, Y.; Yang, R.; Qian, Y.; Zhang, Y. *J. Mater. Chem.*, in press.

(20) Yu, S.; Wu, Y.; Yang, J.; Han, Z.; Xie, Y.; Qian, Y.; Liu, X. *Chem. Mater.* **1998**, *10*, 2309.