The Fabrication of $CuInSe_2$–Polyacrylamide Nanocomposites by a Convenient Simultaneous Polymerization–Decomposition Technique

Yong Zhou,*[†,††] Lingyun Hao,[††] Yuan Hu,[†] Yurui Zhu,[††] and Zuyao Chen[†,††]
[†] *Fire Key Laboratory of State, University of Science and Technology of China, Hefei 230026, Anhui, P. R. China*
[††] *Department of Chemistry, University of Science and Technology of China, Hefei 230026, Anhui, P. R. China*

(Received November 20, 2000; CL-001051)

Either $CuInSe_2$ nanoparticle or $CuInSe_2$ nanorod was in situ dispersed in polyacrylamide (PAM) matrix by a convenient simultaneous polymerization–decomposition (SPD) technique.

During the past decade, considerable interest has focused on the synthesis and characterization of inorganic–organic polymer nanocomposites because of their interesting nonlinearly optical, electrical, catalytic and mechanical properties,[2] and potential applications in microelectronics.[3] Such materials can show not only combination properties of original components, but improved performances not seen in original components.[4] Various techniques have been contributed to fabricate the semiconductor–polymer nanocomposites. The general scheme used was a so called ion-exchanged technique.[5] The technique involves that the polymer matrices and metal ions are mixed in solutions and then exposed to the counter ion (S^{2-}, Se^{2-}) in the form of gas or as ions dissolved in solutions. By this method, many kinds of semiconductor–polymer nanocomposites have been synthesized.[6–11] Recently, Hirai reported the preparation of semiconductor nanoparticle–polyurea composites using a reverse micelle system via in situ diisocyanate polymerization.[12] The use of amphiphilic block copolymer (ABC) opens a doorway to utilize these materials as nanoreactors for synthesis of inorganic-polymer nanocomposites.[13] However, to our knowledge, only binary semiconductor–polymer nanocomposites have been prepared with the present methods reported.

In our previous works, we reported a novel in situ simultaneous polymerization–hydrolysis (SPH) technique for the fabrication of polyacrylamide-semiconductor MS (M = Cd, Zn, Pb) nanocomposites[14] and a novel in situ simultaneous copolymerization –decomposition (SCPD) technique for the preparation of poly(acrylamide-*co*-styrene)–semiconductor CdE (E = S, Se) nanorods nanocomposites.[15] In addition, we also introduced a novel in situ ultraviolet irradiation polymerization–photolysis (UIPP) technique to polyacrylamide (PAM)-semiconductor MS (M = Cd, Pb, Zn) nanocomposites in aqueous systems.[16]

In this letter, we extend the SPH technique and the SCPD technique to encapsulate the $CuInSe_2$ nanocrystal into PAM polymer matrix. It was found that either $CuInSe_2$ nanorod or $CuInSe_2$ nanoparticle could be in situ dispersed in polyacrylamide (PAM) matrix by a so-called convenient simultaneous polymerization –decomposition (SPD) technique. $CuInSe_2$ is an attracting candidate for the anode materials of photochemical devices due to its high performance and high output stability.[17] Besides, $CuInSe_2$ is also a suitable absorber material for polycrystalline thin film solar cell having energy conversion efficiency as high as 17%.[18] Various techniques have been developed to prepare the $CuInSe_2$ thin film[19] and nanocrystal.[20] Encapsulation of $CuInSe_2$ nanocrystal into polymer matrices can provide the necessary stability and processability for its important application.

In a typical preparation procedure of the polyacrylamide–$CuInSe_2$ nanorod (PAM–$CuInSe_2$NR) nanocomposite, a stoichiometric mixture of 1.26 mmol analytical grade $CuCl_2·2H_2O$, 1.29 mmol $InCl_3·4H_2O$, 2.59 mmol Se powder were dissolved in 100 mL ethylenediamine (En). The resulting solution was added to a mixture of 0.5 mol acrylamide (AM) monomer and 0.01 g 2,2'-azobisisobutyronitrile (AIBN) as a radical thermal initiator. The mixture solution was put into a stainless-steel tank with a Teflon inner and heated in an oven at 180 °C for 15 h. The product obtained was washed with distilled water and absolute ethanol, dried at room temperature and ground into powders 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 Rigaku Dmax X-ray diffractometer with high-intensity Cu Kα irradiation (λ = 0.151478 nm) and a graphite monochromator was set at the diffracted irradiation. Figure 1 shows the XRD pattern of the obtained PAM-$CuInSe_2$NR nanocomposite. The broadening peak at about 20° is corresponding with the PAM phase. All other peaks in the XRD pattern can be indexed as the chalcopyrite $CuInSe_2$ phase with a cell parameter a = 0.5778 nm, c = 1.1628 nm, which is well in agreement with the reported JCPDS data (a = 0.5782 nm, c = 1.1619 nm).

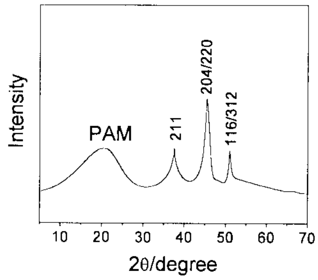

Figure 1. The XRD pattern of the PAM-$CuInSe_2$NR nanocomposite.

The TEM image of the PAM–$CuInSe_2$NR nanocomposite obtained was taken with a Hitachi model H-800 transmission electron microscope, using an accelerating voltage of 200 kV. Figure 2 (a) presents the TEM image of the produced PAM–$CuInSe_2$NR nanocomposite by the present SPD technique. The image shows that the formed $CuInSe_2$ nanorods was indeed in situ dispersed into the PAM matrix. Some of the $CuInSe_2$ nanorods can be seen to extend out of the PAM matrix. The $CuInSe_2$ nanorods was about 5 nm in width.

The formation mechanism of the $CuInSe_2$ nanorods in the PAM–$CuInSe_2$NR nanocomposite using ethylenediamine (En) as reaction medium has been demonstrated by B. Li et al.[20f] It can be formulated as following eqs (1)–(4):

$$2\,\mathrm{InCl_3} + 3\,\mathrm{Se^{2-}} \Rightarrow \mathrm{In_2Se_3} + 6\,\mathrm{Cl^-} \tag{1}$$
$$\mathrm{In_2Se_3} + \mathrm{Se^{2-}} \Leftrightarrow 2(\mathrm{InSe_2})^- \tag{2}$$
$$\mathrm{Cu^+} + 2\,\mathrm{En} \Leftrightarrow [\mathrm{Cu(En)_2}]^+ \tag{3}$$
$$(\mathrm{InSe_2})^- + [\mathrm{Cu(En)_2}]^+ \Rightarrow \mathrm{CuInSe_2}\ \text{nanorods} + \mathrm{En} \tag{4}$$

Here, two points should be noted. One is that Cu^+ was formed by the reduction of Cu^{2+} in the starting materials during the reaction. The other is that the En as solvent plays an important role on the formation of the present $CuInSe_2$ nanorods. With En as solvent, a variety of one-dimensional semiconductor nanometer materials have been synthesized.[21]

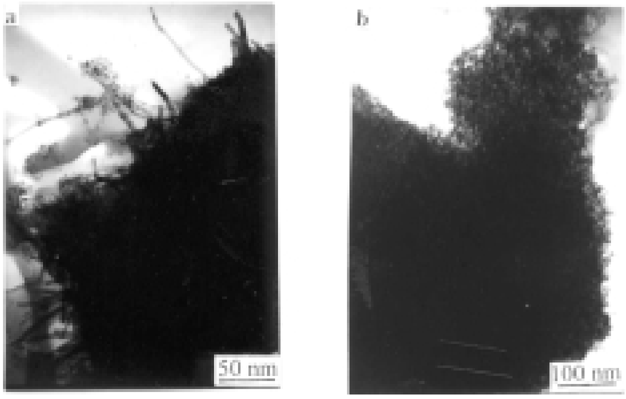

Figure 2. The TEM images of the PAM–$CuInSe_2$NR nanocomposite (a) and the PAM–$CuInSe_2$NP nanocomposite (b).

The optical absorption measurement of the produced PAM–$CuInSe_2$NR nanocomposite was taken with pure PAM as reference by a Shimadzu UV–vis–NIR recording spectrophotometer UV-365. Figure 3 (a) shows that the produced $CuInSe_2$ nanorod in the PAM polymer matrix has an absorption band about 1187 nm, blue-shifted compared with that of bulk $CuInSe_2$ (1252 nm),[22] due to the quantum confinement effect of the $CuInSe_2$ of size in range of nanometer scale.[23] The blue shift was consistent with that of alone one with the same width of nanorod in the absence of PAM.[20f]

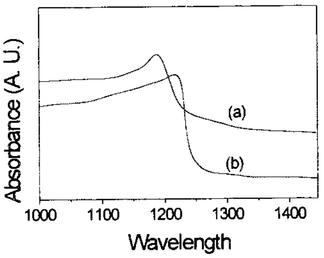

Figure 3. The absorption spectra of the PAM–$CuInSe_2$NR nanocomposite (a) and the PAM–$CuInSe_2$NP nanocomposite (b).

We also prepared the polyacrylamide–$CuInSe_2$ nanoparticle (PAM–$CuInSe_2$NP) nanocomposite by simply substituting En with diethylamine as solvent and extending reaction time from 15 h to 36 h. With the diethylamine as solvent, $CuInSe_2$ can be produced in form of nanoparticle in the present system, which also can be assigned to chalcopyrite $CuInSe_2$ phase by XRD pattern.[20f] Figure 2 (b) shows the TEM image of the PAM–$CuInSe_2$NP nanocomposite. It can be seen that the produced $CuInSe_2$ nanoparticle of average size of 12 nm was in situ dispersed in the PAM matrix. The size of the present $CuInSe_2$ nanoparticle in the nanocomposite was slightly smaller than that of alone one with 15 nm in average size in the absence of PAM.[20f] The reason may be that the producing PAM increased viscosity of the reaction medium, leading to formed $CuInSe_2$ nanoparticle against aggregation and growth. The corresponding absorption band in Figure 3 (b) shows an absorption peak located at about 1221 nm, displaying blue shift compared with the bulk material resulting from the quantum confinement effect of the $CuInSe_2$ of size in range of nanometer scale,[23] also consistent with that of alone one in absence of PAM.[20f]

In summary, either $CuInSe_2$ nanorod or $CuInSe_2$ nanoparticle was in situ dispersed in the polyacrylamide matrices by a convenient simultaneous polymerization–decomposition (SPD) technique. The absorption spectra showed that both $CuInSe_2$ nanorod and $CuInSe_2$ nanoparticle in the nanocomposites displayed blue shift compared to the bulk materials, due to quantum confinement effect of the $CuInSe_2$ of size in range of nanometer scale. Encapsulation of $CuInSe_2$ nanocrystal into polymer matrices can provide the necessary stability and processability for its important application. The technique may be extended to prepare other multinary chalogenide-polymer nanocomposites.

References and Notes

1 M. Antonietti and C. Gölner, *Angew. Chem., Int. Ed. Engl.*, **36**, 910 (1997).
2 D. M. Bigg, *Polym. Composites*, **7**, 125 (1996).
3 G. Schmid, *Chem. Rev.*, **92**, 1709 (1992).
4 a) Z. Pu, J. E. Mark, J. M. Jethmalani, and W. T. Ford, *Chem. Mater.*, **9**, 2442 (1997). b) R. T. Ziolo, E. P. Glannelis, and B. A. Weinstein, *Science,* **257**, 219 (1992). c) M. W. Ellsworth and B. M. Novak, *J. Am. Chem. Soc.*, **113,** 2756 (1991).
5 L. L. Beecroft and C. K. Ober, *Chem. Mater.*, **9,** 1302 (1997).
6 D. Meissner, R. Memming, and B. Kastening, *Chem. Phys. Lett.*, **96**, 34 (1983).
7 J. M. Huang, Y. Yang, B. Yang, S. Y. Liu, and J. C. Shen, *Polym. Bull.*, **36**, 337 (1996).
8 M. Mer, *Synth. Met.*, **41**, 1159 (1991).
9 M. Y. Gao, Y. Yi, B. Yang, F. L. Beng, and J. C. Shen, *J. Chem. Soc., Chem. Commun.*, **1994**, 2777.
10 Y. Wang, A. Suna, W. Mahler, and R. Kasowski, *J. Chem. Phys.*, **87**, 7315 (1987). W. Mahler, *Inorg. Chem.*, **27**, 435 (1988).
11 Y. Wang and N. Herron, *Chem. Phys. Lett.*, **200**, 71 (1992).
12 T. Hirai, T. Watanabe, and I. Komasawa, *J. Phys. Chem. B*, **103**, 10120 (1999).
13 a) M. Antonietti and C. Göltner, *Angew. Chem., Int. Ed. Engl.*, **36**, 910 (1997). b) A. Roesch and M. Möller, *Adv. Mater.*, **7**, 151 (1995).
14 Y. Zhou, S. H. Yu, C. Y. Wang, X. G. Li, Y. R. Zhu, and Z. Y. Chen, *Chem. Commun.*, **1999,** 1229.
15 Y. Zhou, L. Y. Hao, S. H. Yu, M. You, Y. R. Zhu, and Z. Y. Chen, *Chem. Mater.*, **11**, 3411 (1999).
16 Y. Zhou, L. Y. Hao, Y. Hu, Y. R. Zhu, and Z. Y. Chen, *Chem. Lett.*, **2000**, 1308.
17 Cahen, G. Dagan, Y. Mirovsky, G. Hodes, W. Giriat, and M. Lubke, *J. Electrochem. Soc.*, **132,** 1065 (1985).
18 L. C. Yang, H. Z. Xiao, W. N. Shafarman, and R. W. Birkmire, *Sol. Energy Mater. Sol. Cells*, **36**, 445 (1995).
19 a) S. Kohiki, M. Nishitani, K. Nishikura, T. Negami, M. Terauchi, and T. Hirao, *Thin Solid Film*, **207,** 265 (1992). b) J. Vedel, *Adv. Mater.*, **6**, 379 (1994).
20 a) D. Duonghong and J. Ramsden, , *J. Am. Chem. Soc.*, **104**, 2977 (1982). b) A. Henglein, *Chem. Rev.*, **89,** 1861 (1989). c) H. Weller, *Adv. Mater.*, **5,** 88 (1993). d) A. Hagfeldt and M. Gratzell, *Chem. Rev.*, **95,** 49 (1995). e) T. Trindade and P. O`Brien, *Adv. Mater.*, **8,** 161 (1996). f) B. Li, Y. Xie, J. X. Huang, and Y. T. Qian, *Adv. Mater.*, **11**, 1101 (1999).
21 W. Wang, Y. Geng, Y. Qian, M. Ji, and X. Liu, *Adv. Mater.*, **10**, 1479 (1998); Y. D. Li, H. W. Liao, Y. Ding, Y. T. Qian, L. Yang, and G. E. Zhou, *Chem. Mater.*, **10**, 2301 (1998).
22 N. Kavcar, *Sol. Energy Mater. Sol. Cells*, **52**, 183 (1998).
23 L. E. Brus, *J. Phys. Chem.*, **80**, 4403 (1984); L. E. Brus, *J. Phys. Chem.*, **89**, 2555 (1986).