Polymer Bulletin 37, 679-682 (1996)

Polymer Bulletin

Preparation and characterization of $Cu_2S/CdS/ZnS$ nanocomposite in polymeric networks

Jinman Huang [1], **Yi Yang** [2], **Bai Yang** [1], **Shiyong Liu** [2], **Jiacong Shen** [1]

[1] Department of Chemistry, Jilin University, Changchun 130023,
People's Republic of China
[2] National Key Lab of Integrated Optoelectronics, Jilin University, Changchun 130023,
People's Republic of China

Received: 22 March 1996/Revised version: 8 July 1996/Accepted: 16 July 1996

SUMMARY

A novel inorganic semiconductor nanocomposite($Cu_2S/CdS/ZnS$) were prepared in polymeric networks. The XPS data show that the mass content of Cu, Cd and Zn ions in polymeric networks were roughly 1.4%, 6.7% and 7.7% respectively. The particle sizes of Cu_2S, CdS and ZnS were about 2.8nm, 5.3nm and 7.1nm respectively determined by XRD, and they have monoclinic, hexagonal and hexagonal structures. Considering the densities, molar ratio and solubilities of these metal sulfides and compared with the TEM photograph, we can deduce that these three kinds of metal sulfides in polymeric networks formed a three-layered structure.

INTRODUCTION

Over the past ten years extensive research has been carried out in the field of nanometer-sized semiconductor particles(1-5) due to their special physical and chemical properties which are intermediate between the molecular and bulk limits. Most of the studies have focused on the spectroscopic, photochemical and nonlinear optical properties of these materials(6-9). Recently some papers on CdS/ZnS(10), ZnS/CdSe(11), CdS/PbS(12) and CdS/HgS(13) composite or coated nanoparticles have been reported. One of the most striking features of these nanoclusters is the strong size-quantivity effect, thus a synthesis which controls particles size and its distribution are of importance. Polymer is expected to provide good mechanical and optical properties, conferring high kinetic stability on nanometer-sized semiconductor particles. More recently, PbS(14), PbI_2(15), Fe_2O_3(16) have been synthesized in polymer matrices in our group using a variety of methods. As the band gap energies of Cu_2S, CdS and ZnS nanoparticles change from narrow to wide, the difference in energy levels of these semiconductor systems plays an important role in achieving charge separation. So these metal sulfides composites have potential application in nonlinear optical. In this paper, the $Cu_2S/CdS/ZnS$ nanocomposite was successfully prepared in polystyrene system by ion exchange, which can be easily prepared the transparent thin film material for optical measurements. In comparison with those of the previously works(14-16), it is a good method to synthesize the multi-semiconductor nanocomposite in polymer matrices.

EXPERIMENTAL

Materials

Styrene, $K_2S_2O_8$, sodium oleate, DMF(dimethylformamide), methanol, cupric acetate,cadmium chloride, zinc chloride were all analytical grade agents; Styrene was distilled under reduction of pressure.

Preparation of $Cu_2S/CdS/ZnS$ nanocomposite

The synthesis of polymer networks called BS has been reported before(17). The sulphonation reaction of BS was similar to the reference(17), but this time, the reaction time was much longer than that(about 6hrs), and the degree of sulfonation was about 19.4% estimated by XPS data. The sulphonated product was also called BSS.

5g of BSS immersed into the solution which contained 1g of cupric acetate, 3g of cadmium chloride and 5g of zinc chloride in 100ml of distilled water for 100hrs. Then these metal ions exchanged with H^+ of $-SO_3H$ groups were adsorbed into the BSS networks. The polymer networks containing metal ions was briefly named BSSM, and the XPS was used to measure these metal ions' content.

0.02g of BSSM was dissolved in 4ml of DMF, and then treated with H_2S gas from zero to 10ml gradually in a sealed container after which the solution turned yellow, but with no precipitation.

RESULTS AND DISCUSSION

XPS was used to estimate the metal ions content in BSSM(see Table1). From that, we can estimate that the mass percents of Cu, Cd and Zn ions were roughly 1.4%, 6.7% and 7.7% respectively. According to these data, the atomic ratio of these three metal ions was about 1/ 2.85/5.56.

Table 1. Observed elemental composition determined by XPS

Element	Binding energy	Atomic%
S 2p	170.4eV	10.44
C 1s	285.1eV	53.83
Cd 3d5	306.8eV	1.11
O 1s	533.4eV	32.06
Cu 2p3	937.1eV	0.39
Zn 2p3	1023.6eV	2.17

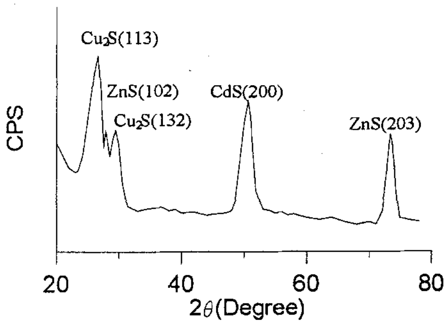

Fig.1 X-ray diffraction pattern of nanocomposite

Fig.1 was the x-ray diffraction(XRD) pattern of the casting film of nanocomposite. We determined the average particle size from the line width of the diffraction peaks using Scherrer's equation(18):

$$D(\text{particle diameter})=kl/\beta\cos\theta \qquad (1)$$

where β is the half width of the diffraction peak, l is the x-ray wavelength(0.1542nm) and k is geometric factor taken to be 0.9. So the average particle sizes of Cu_2S, CdS and ZnS were about 2.8nm, 5.3nm and 7.1nm respectively. Fig.2 was the absorption spectrum of

$Cu_2S/CdS/ZnS$ nanocomposite dissolved in DMF solution. With decreasing particle size, the absorption edge will shift to higher energies, and the particle sizes of this nanocomposite can be estimated from the shifts in the absorption edge according to the reference(9,19),which. correspond well with the data obtained by XRD(see Table2).

Table2. Particle sizes of the nanocomposite measured by different methods

	XRD	UV	TEM
Cu_2S	2.8nm		~2.9nm
CdS	5.3nm	5.2nm	
ZnS	7.1nm	6.9nm	~7.2nm

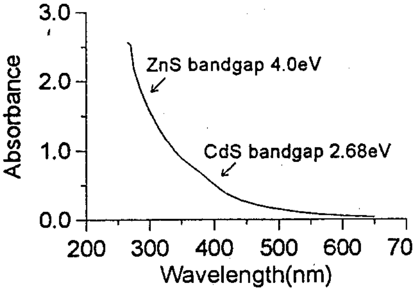

Fig.2 UV spectrum of nanocomposite in DMF solution

However, From TEM micrograph(Fig.3) we could observe that the average particle size was only about 7.2nm, and many nanocomposite particles had core-shell structures whose core diameter was roughly 2.9nm. (Here, we think the core may be Cu_2S particles, as its color is much deeper than those of CdS and ZnS.) How to explain this phenomena? We suppose that these three metal sulfides may form a layered structure. Bearing in mind that the solubility product of Cu_2S is at least 21 and 24 orders of magnitude smaller compared to those of CdS and ZnS respectively. As we added H_2S gas little by little into the DMF solution which contains BSSM, the Cu_2S crystals must form firstly, then CdS and ZnS could appear sequentially. Similar to the reference(20), if one assumes that the entire amount of metal sulfides formed a three layered structure consisting of Cu_2S acting as core and a layer of CdS on the surface of this core covered by, furthermore, ZnS as the outermost shell, the molar ratio of Cu_2S,CdS and ZnS should be about 1/2.74/5.53 according to their diameters(2.8nm, 5.3nm and 7.1nm) and their densities(5.6, 4.82 and 3.98 respectively)(21), which was similar to the XPS data(1/2.85/5.56). So we deduced that the layered structure of this nanocomposite could be formed.

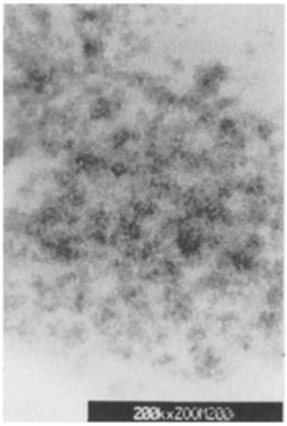

Fig.3 TEM photograph of the nanocomposite in polymeric networks

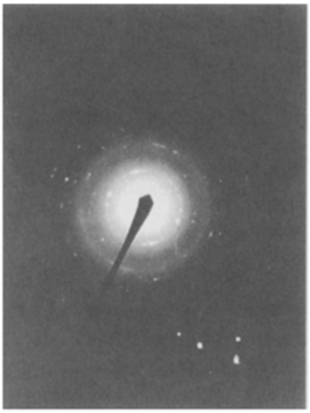

Fig.4 Electron diffraction image of the nanocomposite shown in **Fig.3**

Data obtained from the electron diffraction(ED) pattern(Fig.4) and XRD are given in Table3 which both indicate that the Cu_2S, CdS and ZnS in nanocomposite have monoclinic, hexagonal and hexagonal structures respectively compared with their standard data(22).

Table3. Diffraction data(*d*) for nanocomposite measured by ED and XRD

Metal Sulfide	ED	XRD	Standard value
Cu_2S		0.3344nm	0.3336nm
ZnS		0.3208nm	0.3200nm
Cu_2S		0.3028nm	0.3054nm
Cu_2S	0.2869nm		0.2869nm
Cu_2S	0.2335nm		0.2330nm
CdS	0.1793nm	0.1802nm	0.1791nm
CdS	0.1462nm		0.1462nm
ZnS		0.1289nm	0.1296nm
ZnS	0.1250nm		0.1251nm
CdS	0.1124nm		0.1125nm
ZnS	0.0956nm		0.0955nm

Reference

1. Henglein•A(1984) Pure Appl Chem 56: 1215.
2. Brus L E(1986) J Phys Chem 90: 2555.
3. Wang Y, Herron N(1991) J Phys Chem 95:525.
4. Weller H(1993) Angew Chem 105:43.
5. Weller H(1993) Adv Mater 5:88.
6. Fox M A(1983) Acc Chem Res 16:314.
7. HilinskicE F, Lucas P A, and Wang Y(1988) J Chem Phys 89(6): 3435.
8. Sphanhel L, Haase M, Weller H, Henglein A(1987) J Am Chem Soc 109:5649.
9. Rossetti R, Hull R, Gibson J M and Brus L E(1985) J Chem Phys 82(1): 552.
10. Youn H C, Baral S, Fendler J H(1988) J Phys Chem 92:6320.
11. Kortan A R, Hull R, Opila R L, Bawendi M G, Steigerwald M L, Carroll R J, Brus L E(1990) J Am Chem Soc 112:1327.
12. Zhou H S, Honma I, Komiyama H and Haus J W(1993) J Phys Chem 97:895.
13. Mews A, Eychmüller, Giersig M, Schooss D, Weller H(1994) J Phys Chem 98:934.
14. Mingyuan G, Yi Y, Bai Y, Fenglan B, Jiacong S(1994) J Chem Soc, Chem Commun 2777.
15. Mingyuan G, Xi Z, Bai Y, Jiacong S(1994) J Chem Soc, Chem Commun 2229.
16. Mingyuan G, Xiaogang P, Jiacong S(1994) Thin Solid Films 248:106.
17. Jinman H, Yi Y, Bai Y, Shiyong L, Jiacong S(1996) Polym Bull 36:337.
18. Klug H P and Alexander L E(1954) X-ray diffraction procedures, John Wiley, New York.
19. Rama Krishna M V, Friesener R A(1991) J Chem Phys 95: 8309.
20. Hässelbarth A, Eychmüller A, Eichberger R, Giersig M, Mews A, and Weller H(1993) J Phys Chem 97:5333.
21. David R Lide(1992-1993) CRC Handbook of Chemistry and Physics, 73rd, Boca Raton, Ann Arbor, London Tokyo.
22. Berry L G, Post B, Weissmann S(1967) Powder diffraction file, Inorganic Volume, Philadelphia.