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Synthesis of the CdS nanoparticles in polymer networks

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

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

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SUMMARY

CdS nanoparticles were synthesized in polymer networks. EDAX data show that the content of Cd^{2+} was about 3%wt. The particles size can be controlled by varying the amount of H_2S, and the absorption spectra indicated that the band edge shifts toward blue with decreasing the particles size. TEM and diffraction data show that the CdS nanoparticles with narrow size distribution were well assembled in polymer networks, and it has a hexagonal structure .

INTRODUCTION

Nanometer-sized semiconductor clusters have attached growing interest during the last decade(1,2). Besides their extensive utilization as catalysts for photoinduced charge transfer reactions(3), semiconductor microcrystallites possess properties which are intermediate between the molecular and bulk limits and, thus, show a number of striking effects such as size quantization(4), nonlinear optical behaviors(5), or unusual fluorescence(6). One of the most striking features of these clusters is the strong size-quantivity effect, thus a synthesis which controls particles size and its distribution are of importance. In general, the cluster size of the semiconductor particles formed in polymer systems(7-10) is controlled by varying the effective concentration of metal cations within the polymers prior to cluster formation. Polymer is expected to provide good mechanical and optical properties, conferring high kinetic stability on nanometer-sized semiconductor particles. Recently, PbS(11), PbI_2 (12)and Fe_2O_3 (13)have been synthesized in polymer matrices in our group using a variety of methods. In this paper, the synthesis of CdS nanoparticles in polymer networks is described, which can disperse well in styrene monomer to form the transparent bulk materials easily.

EXPERIMENTAL

Materials

Styrene, $K_2S_2O_8$, sodium oleate, DMF(dimethylformamide), 1,2-dichloroethane and methanol used in the present work were all analytical grade agents; Styrene was distilled under reduced pressure. The synthesis of bisvinyl-A(1a)was as reference(14).

Formation of the polymer networks

1.6g of bisvinyl-A which works as cross-linking agent and 110ml of styrene were dispersed by sodium oleate in distilled water. 0.2g of $K_2S_2O_8$ was added as initiator and began to polymerize at 85^{0}C under the atmosphere of N_2 for 5 hrs. Then the polymerisate(called BS network) precipitated by methanol was dried in vacuum for 48hrs at 60^{0}C, the yield was about 90%.

Sulphonation reaction

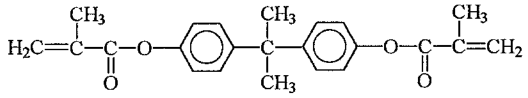
5g of BS was swelled in 100ml of 1,2-dichloroethane solvent and 20ml of sulfuric acid was dripped and reacted with BS at 50^{0}C for 3hrs. The sulphonated product was called BSS briefly, its ion exchange capacity was about 0.78mmol/g, the degree of sulphonation was roughly 8.6% and the proposed equation is as follow.

$$BS + H_2SO_4 \xrightarrow[50^{o}C,\ 3hrs]{ClCH_2CH_2Cl} BS\text{—}(SO_3H)_n \ ,\ \text{[called BSS]} \qquad (1)$$

Preparation of CdS nanoparticles

5g of BSS immersed into the solution which contained 10g of $CdCl_2$ in 100ml of water for 24hrs. The Cd^{2+} ions were adsorbed into the BSS networks in exchange with $H^+$of $-SO_3H$ groups. The polymer networks containing Cd^{2+} was briefly named BSSCd. EDAX data show that the mass percent of Cd^{2+} in BSS was roughly 3%wt.

0.08g of BSSCd was dissolved in 10ml of DMF, and then treated with H_2S gas in a sealed container after which the solution turned yellow, but with no precipitation.The preparation procedure is described as follow.



1 a

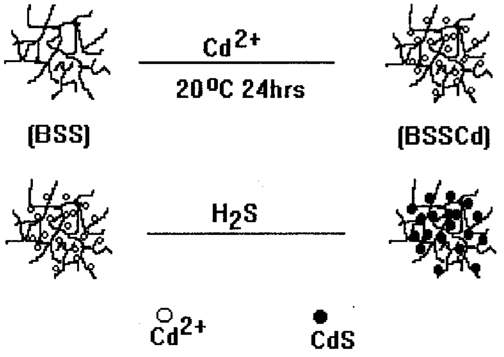


Fig.1 Scheme for the synthesis of CdS nanoparticles in polymer networks

RESULTS AND DISCUSSION

The absorption spectra of CdS nanoparticles in polymer networks are shown in Fig.2. The absorption characteristics were dependent on the amount of H_2S injected in system. A blue-shift in the absorption edge of CdS nanoparticles in polymer networks indicated that the particles size of the CdS nanoparticles decreased with reducing the amount of H_2S. As reference(15-18), decreasing particles size in the quantum size regime(CdS nanoparticle diameter was less than 5nm) increases the bandgap of the semiconductor which results in a blue-shift in the absorption spectra. From this shift in the absorption edge we can estimate the particle size(Table.1) according to the reference(19).

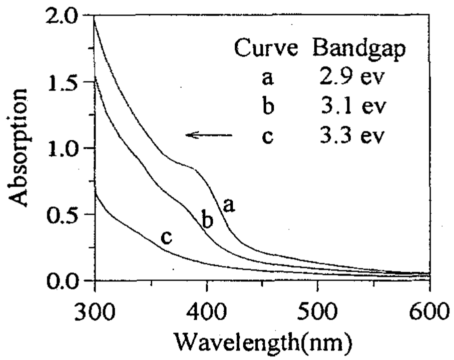


Table 1. CdS particle size measured by UV and TEM

Bandgap(ev)		UV	TEM
a	2.9	2.7 nm	2.4 nm
b	3.1	2.0 nm	1.6 nm
c	3.3	1.3 nm	1.0 nm

Fig.2 UV spectra of CdS nanoparticles in DMF solution. 0.08g of BSSCd treated with different amount of H_2S respectively, a. 2.0ml, b. 1.5ml, c. 1.0ml

TEM was used to observe CdS nanoparticles in polymer networks. A drop of the solution which contains the polymer networks with CdS nanoparticles was dripped onto a copper grid for TEM detection. From the photograph(Fig.3), it can be seen that the CdS nanoparticles are well dispersed, and the average size was found to be 2.4 nm. The result fits well with that obtained from the absorption spectra. The histogram of the nanoparticles(Fig.4) shows a narrow distribution of particles size. All these indicated that the polymer networks could effectively prevent the particles from growing and aggregating further.

Fig.3 TEM photograph(100 000) of CdS nanoparticles in polymer networks

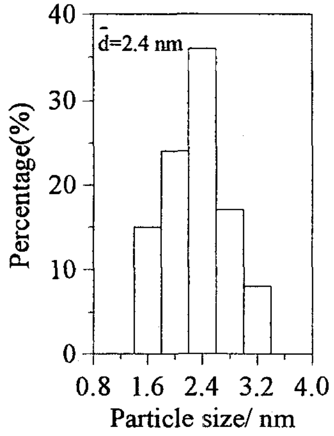


Fig.4 Histogram of particle size of the CdS nanoparticles shown in **Fig.3**

Data obtained from the diffraction pattern(Fig.5) are given in Table2 which establishes a hexagonal structure for the CdS nanoparticles compared with the standard data(20).

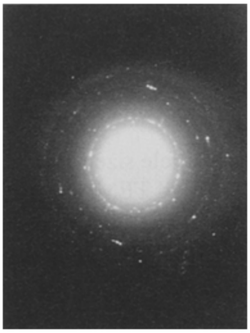


Fig.5 Electron diffraction image of the CdS nanoparticles shown in **Fig.3**.

Table 2. Diffraction data for CdS nanoparticles

nd	d/Å
1	2.510 (2.450)
2	2.114 (2.068)
3	1.731(1.731)
4	1.521(1.520)
5	1.304(1.303)

data for standard CdS given in parentheses

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