Template Synthesis and Characterization of $Zn_xCd_{1-x}S$ Nanorod

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$Zn_xCd_{1-x}S$ nanorods were hydrothermally synthesized by a template reaction of CdS nanorods with $ZnCl_2 \cdot H_2O$ and thiourea at 180 °C. Through changing the molar ratio of Zn to Cd in the reactants, $Zn_xCd_{1-x}S$ nanorods ($0<x<0.55$) were obtained. XRD, ICP-AES, TEM and UV–vis were used to characterize the samples.

$Zn_xCd_{1-x}S$, which has considerable technological interest due to its semiconducting, optical and mechanical properties, is a promising material for optoelectronic applications in the blue and UV spectral region and for energy transferring application in solar cell device.[1–4] Over the past years, much attention has been paid to $Zn_xCd_{1-x}S$ films and extensive researches about synthesis and applications have been carried out. $Zn_xCd_{1-x}S$ films can be prepared by the solution growth technique,[5] spray pyrolysis,[6] electrodeposition,[7] successive ionic layer adsorption and reaction process[8] and chemosorption,[9] vacuum evaporation,[10] sputtering,[11] MOVPE,[12] MBE[13] and solid-state diffusion from vapor phase.[14] Recently, nanocrystalline $Zn_xCd_{1-x}S$ was also paid attention, and the studies of synthesis, photophysical properties and potential application were carried out.[15–18]

In this paper, $Zn_xCd_{1-x}S$ nanorods were hydrothermally synthesized through a template reaction of CdS nanorods with $ZnCl_2 \cdot H_2O$ and thiourea at 180 °C. The CdS nanorods were prepared using a mild one-step solvothermal route reported by our laboratory.[19] Through changing the molar ratio of Zn to Cd in the reactants, $Zn_xCd_{1-x}S$ nanorods ($0<x<0.55$) were obtained.

A typical procedure is as follows. All of the used reagents are analytical pure. Different molar ratios of $ZnCl_2 \cdot H_2O$ to CdS with appropriate amount of thiourea were put in Teflon-lined stainless steel autoclaves. Then they were filled with distilled water up to 90% of the capacity (50 mL). The autoclaves were maintained at 180 °C for 10 h, and then were cooled to room temperature naturally. The precipitates were filtered, washed with distilled water and ethanol successively. The final yellow products were dried in a vacuum at 80 °C for 2 h.

All the products were characterized by X-ray powder diffraction patterns (XRD)[20] and inductively coupled plasma-atomic emission spectra (ICP-AES)[21]. The molar ratio of Zn to Cd in the reactants and the results were listed in Table 1. The results of ICP indicated that the value of x in the products increased slower than the increasing of the molar ratio of Zn to Cd in the reactants. The value of x was only 0.52 when Zn was three times more than Cd in the reactants, which indicated that Zn^{2+} ions did not fully react to form $Zn_xCd_{1-x}S$. Figure 1 shows the XRD patterns of $Zn_{0.28}Cd_{0.72}S$ and $Zn_{0.52}Cd_{0.48}S$. All peaks in Figures 1a and 1b can be indexed to hexagonal phase, which indicates that no cubic $Zn_xCd_{1-x}S$ or ZnS was formed when the molar ratio range of Zn to Cd in the reactants was 1–3. But when the Zn/Cd molar ratio in the reactants was 6 : 1, cubic ZnS was produced besides hexagonal $Zn_xCd_{1-x}S$. Due to broadening of the peaks, the lattice parameters of $Zn_xCd_{1-x}S$ could not be accurately calculated. But it is obvious that the peaks shifted to high degrees with the increasing of x, which indicated the decreasing of the lattice parameters.[22]

Table 1. The molar ratio of Zn to Cd in the reactants and the results

Molar ratio of Zn to Cd	Products	Phase
1 : 1	$Zn_{0.28}Cd_{0.72}S$	Hexagonal
2 : 1	$Zn_{0.49}Cd_{0.51}S$	Hexagonal
3 : 1	$Zn_{0.52}Cd_{0.48}S$	Hexagonal
6 : 1	$Zn_xCd_{1-x}S$, ZnS	

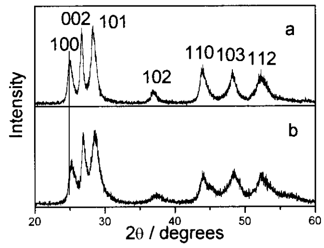
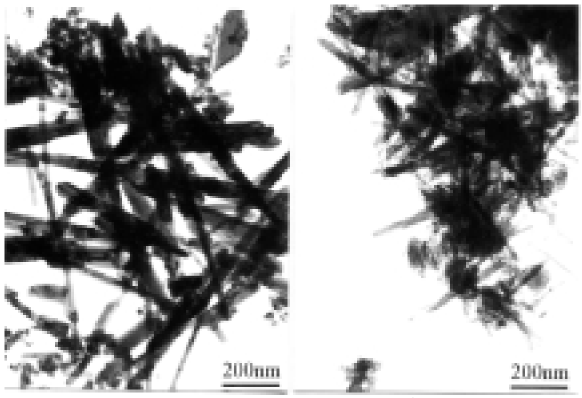


Figure 1. XRD patterns of nanocrystalline (a) $Zn_{0.28}Cd_{0.72}S$, (b) $Zn_{0.52}Cd_{0.48}S$.

Figure 2 shows TEM[23] images of $Zn_{0.28}Cd_{0.72}S$ and $Zn_{0.52}Cd_{0.48}S$, both of them are composed of nanorods. EDX analysis of the nanorods gave similar values of ICP. The diameter of the two kinds of nanorods are similar (20–50 nm), but their lengths differs greatly, the average length of the nanorods of $Zn_{0.28}Cd_{0.72}S$ is about 800 nm, and that for $Zn_{0.52}Cd_{0.48}S$ is about 300 nm. The morphology of the nanorods in Figure 1a is much better than that in Figure 1b. These differences may be due to bad crystallization of $Zn_xCd_{1-x}S$ when $x>0.5$.[13]



(a) (b)

Figure 2. TEM images of (a) $Zn_{0.28}Cd_{0.72}S$, (b) $Zn_{0.52}Cd_{0.48}S$ nanorods.

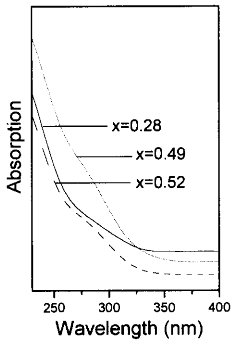


Figure 3. UV–vis absorption spectra of nanocrystalline Zn$_x$Cd$_{1-x}$S.

Figure 3 shows the UV–vis absorption spectra of Zn$_x$Cd$_{1-x}$S with different x. It can be found that the onset of absorption is shifted toward shorter wavelength with increasing Zn : Cd ratio. Compared with the bulk Zn$_x$Cd$_{1-x}$S (x = 0.25, 2.64 eV; x = 0.5, 2.88 eV),[21] the energy band gap of the so-prepared Zn$_x$Cd$_{1-x}$S was 3.8–3.9 eV, which is larger than that of bulk Zn$_x$Cd$_{1-x}$S due to the quantum size effect.[15,24]

In this reaction, the morphology of Zn$_x$Cd$_{1-x}$S products is almost the same as that of the rod-like CdS precursor. And it is found that if CdS is not nanorods but irregular nanoparticles, the obtained Zn$_x$Cd$_{1-x}$S has irregular morphology. It is believed that CdS nanorods acted as a template in the process, and Zn$_x$Cd$_{1-x}$S nanorods were formed through an ionic exchange and absorption process. Figure 2 shows that the rod-like Zn$_{0.52}$Cd$_{0.48}$S is collapsed to some extent compared with the Zn$_{0.28}$Cd$_{0.72}$S nanorods. The decreasing of crystal quality when Zn content is high (x>0.4) is due to the increased mismatch of ZnS to CdS lattice, which is consistent with previous report.[13] The experiments showed that only hexagonal Zn$_x$Cd$_{1-x}$S was formed when the Zn/Cd molar ratio was not too large, which indicated that ZnS was not easy to form under the experimental conditions though there existed a competition in the formation of Zn$_x$Cd$_{1-x}$S and ZnS.

In summary, through changing the molar ratio of Zn to Cd in the reactants, Zn$_x$Cd$_{1-x}$S (0<x<0.55) nanorods were hydrothermally prepared by the template reaction of CdS nanorods with $ZnCl_2 \cdot H_2O$ and thiourea at 180 °C.

References and Notes

1 H. H. L. Kwok, M. Y. Leung, and Y. M. Lam, *J. Cryst. Growth*, **59**, 421 (1982).

2 S. A. Al Kuhaimi and S. Bahammam, *Jpn. J. Appl. Phys.*, **29**, 1499 (1990).

3 Zelayla-Angel, J. J. Alvarado-Gil, R. Lozado-Morales, H. Vargas, and A. Ferreira de Silva, *Appl. Phys. Lett.*, **64**, 291 (1994).

4 K. C. Park and H. B. Im, *J. Electrochem. Soc.*, **135**, 793 (1988).

5 G. K. Padam, G. L. Malhotra, and S. U. M. Rao, *J. Appl. Phys.*, **63**, 770 (1988).

6 R. S. Feigelson, A. N Diaye, S. Y. Yin, and R. H. Bube, *J. Appl. Phys.*, **48**, 3162 (1977).

7 C. D. Lokhande, V. S. Yermune, and S. H. Pawar, *J. Electrochem. Soc.*, **138**, 624 (1991).

8 Y. F. Nicolau, M. Dupuy, and M. Brunel, *J. Electrochem. Soc.*, **137**, 2915 (1990).

9 V. V. Klechkovskaya, V. N. Maslov, M. B. Muradov, and S. A. Semiletov, *Kristallografiya*, **34**, 182 (1989).

10 V. D. Vankar, S. R. Das, P. Nath, and K. L. Chopra, *Phys. Status Solid A*, **45**, 665 (1978).

11 P. Aguihotri and B. K. Gupta, *Jpn. J. Appl. Phys.*, **18**, 317 (1979).

12 S. Yamaga, A. Yoshikawa, and H. Kasai, *J. Cryst. Growth*, **99**, 432 (1990).

13 M. Hetterich, S. Petillon, W. Petri, A. Dinger, M. Grün, and C. Klingshrin, *J. Cryst. Growth*, **159**, 81 (1996).

14 E. Nebauer, *Phys. Status Solidi A*, **19**, K183 (1973).

15 B. Balamurugan, B. R. Mehta, and S. K. Sharma, *Nanostruct. Mater.*, **12**, 151 (1999).

16 E. Cordoncillo, J. B. Carda, M. A. Tena, G. Monros, and P. Escribano, *J. Sol. -Gel Sci. Technol.*, **8**, 1043 (1997).

17 J. Huang, P. Lianos, Y. Yang, and J. C. Shen, *Langmuir*, **14**, 4342 (1998).

18 J. H. Fendler and F. C. Meldrum, *Adv. Mater.*, **7**, 607 (1995).

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

20 XRD were taken on a MAX 18 AHF X-ray diffractometer (MAC Science Co. Ltd) with Cu Kα_1 radiation (λ = 1.54056 Å).

21 Elemental analysis was carried out on an Atomscan Advantage spectrometer (Therma Jarrell Ash Cop).

22 C. B. Murray, D. J. Norris, and M. G. Bawendi, *J. Am. Chem. Soc.*, **115**, 8706 (1993).

23 TEM images were made on a Hitachi H-800 transmission electron microscope with an accelerating voltage of 200 KV.

24 P. E. Lippen and M. Lannoo, *Phys. Rev.B*, **39**, 10935 (1989).