

## *In situ* synthesis of $Zn_xCd_{1-x}S$ nanorod by a hydrothermal route

QIULIN NIE

Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China; Hangzhou Institute of Electronic Engineering, Hangzhou 310018, People's Republic of China

QIULI YUAN

Hangzhou Institute of Electronic Engineering, Hangzhou 310018, People's Republic of China

QINGSHENG WANG, ZHUDE XU

Department of Chemistry, Zhejiang University, Hangzhou 310027, People's Republic of China  
E-mail: nqlzju@163.com

$Zn_xCd_{1-x}S$ , whose physical and chemical properties can be tuned by changing the constituent stoichiometries [1], is a promising material for optoelectronic applications in the blue and UV spectral region as well as for energy-transfer applications in solar cell devices [2–4]. Over the past years, much attention has been paid to  $Zn_xCd_{1-x}S$  films and extensive research on the synthesis and applications has been carried out.  $Zn_xCd_{1-x}S$  films can be prepared by various methods such as the solution growth technique [5], spray pyrolysis [6], electrodeposition [7], successive ionic layer adsorption and reaction process [8], chemisorption [9], vacuum evaporation [10], sputtering [11], MOVPE [12], MBE [13], and solid-state diffusion from vapor phase [14]. Recently, nanocrystalline  $Zn_xCd_{1-x}S$  has also attracted great interest. Studies on the synthesis of nanocrystalline  $Zn_xCd_{1-x}S$  and on its photophysical property and potential applications have been reported [15–18].

In this paper,  $Zn_xCd_{1-x}S$  nanorods were hydrothermally synthesized through an *in situ* reaction of  $CdCl_2 \cdot 2.5H_2O$ ,  $ZnCl_2$  and  $(NH_4)_2S$  with 20 wt% ethylenediamine aqueous solution as the solvent at 180 °C. Through changing the molar ratio of Zn/Cd in the reactants,  $Zn_xCd_{1-x}S$  nanorods with different composition, namely the different stoichiometric coefficient  $x$ , were successfully prepared.

In our experiment, all of the reagents used were of analytical purity.  $ZnCl_2$  and  $CdCl_2 \cdot 2.5H_2O$  with different molar ratios were put into Teflon-lined stainless steel autoclaves together with appropriate amount of  $(NH_4)_2S$ . Then the autoclaves were filled with 20 wt% ethylenediamine aqueous solution up to 80% of the capacity (50 mL). The autoclaves were maintained at 180 °C for 48 hr and then cooled down naturally to room temperature. The precipitates were filtered and washed with distilled water and ethanol successively. The final products were dried in vacuum at 80 °C for 2 hr.

X-ray powder diffraction (XRD) analysis was carried out on an X'pert MPD Philips X-ray diffractometer using  $Cu K_\alpha$  radiation. Inductively coupled plasma-atomic emission spectra (ICP) were determined to discover the composition of  $Zn_xCd_{1-x}S$ . Data were recorded on an Atomscan Advantage spectrom-

eter (Therma Jarrell Ash Corp.). The morphology and size were characterized by transmission electron microscopy (TEM) on a JEM-200cx transmission electron microscope, using an accelerating voltage of 160 kV. Photoluminescence experiments were carried out on a Hitachi F-4500 fluorescence spectrometer, using photons of 300 nm wavelength from a xenon lamp for excitation.

The ICP results have revealed that the as-prepared products were  $Zn_{0.24}Cd_{0.76}S$ ,  $Zn_{0.48}Cd_{0.52}S$ , and  $Zn_{0.72}Cd_{0.28}S$ , respectively. The XRD patterns of the three samples are shown in Fig. 1 which can be all assigned to the wurtzite hexagonal structure. However, owing to the increasing mismatch of ZnS to CdS lattice, the crystal quality of  $Zn_xCd_{1-x}S$  decreases with increasing Zn content, which is consistent with a previous report [13].

Fig. 2 has TEM images of  $Zn_{0.24}Cd_{0.76}S$ ,  $Zn_{0.48}Cd_{0.52}S$ , and  $Zn_{0.72}Cd_{0.28}S$  samples, which all show nanorods structures. The diameter of these nanorods is almost the same (about 20 nm) for the three compositions, but the lengths differ slightly and decrease with increasing Zn content. The typical length is about 250 nm for  $Zn_{0.24}Cd_{0.76}S$ , 160 nm for  $Zn_{0.48}Cd_{0.52}S$ , and 100 nm for  $Zn_{0.72}Cd_{0.28}S$ .

In Fig. 3, the PL spectra of  $Zn_xCd_{1-x}S$  are illustrated along with the ZnS and CdS PL spectra. The PL peak position of  $Zn_xCd_{1-x}S$  changes gradually with increasing concentration of Cd, a progressive red shift from 500 nm for pure ZnS to about 580 nm for pure CdS. Besides, the profile of the PL curves of  $Zn_xCd_{1-x}S$  can not be simulated by a superposition of the corresponding ZnS and CdS PL spectra, indicating that the  $Zn_xCd_{1-x}S$  products are complex compounds rather than a simple mixture of ZnS and CdS.

In the formation of  $Zn_xCd_{1-x}S$  nanorods, template ethylenediamine played an important role. When the concentration of ethylenediamine was lower than 10 wt%, or other reagents such as ammonia and pyridine were used instead, the final  $Zn_xCd_{1-x}S$  products were spherical particles even when other experimental conditions were kept all the same. In addition, the proper molar ratio of Zn/Cd in the reactants is also a key factor. It was found that hexagonal-structured  $Zn_xCd_{1-x}S$

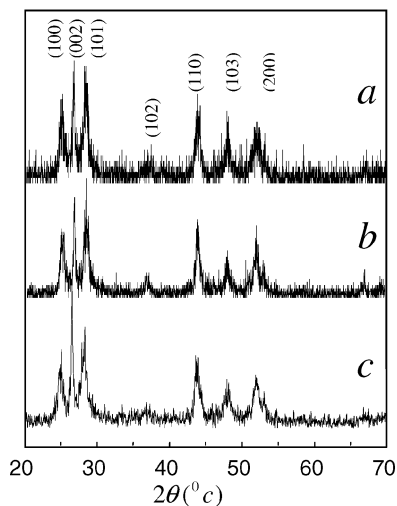


Figure 1 XRD pattern of  $Zn_xCd_{1-x}S$ . (a)  $Zn_{0.72}Cd_{0.28}S$ , (b)  $Zn_{0.48}Cd_{0.52}S$  and (c)  $Zn_{0.24}Cd_{0.76}S$ .

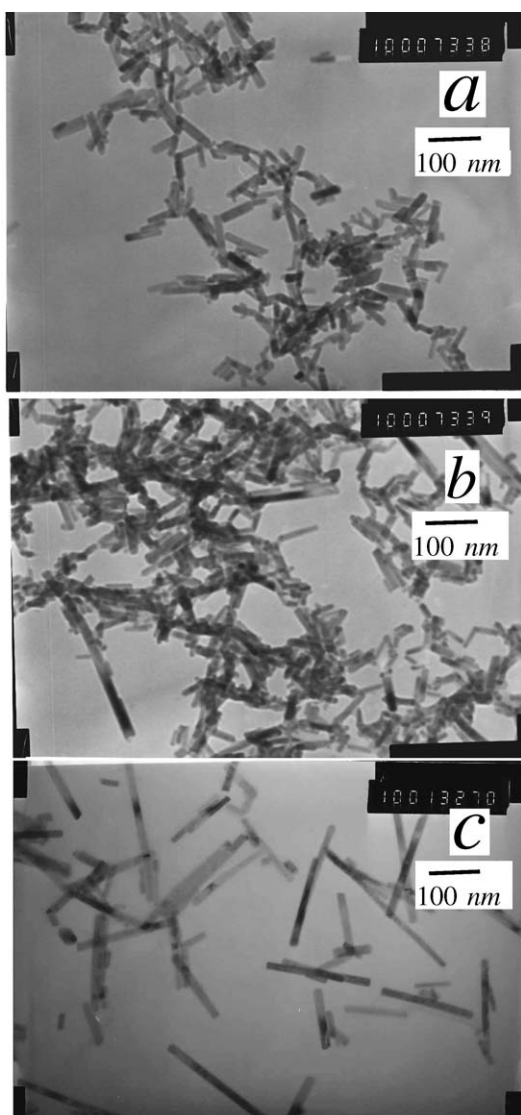


Figure 2 TEM images of as-obtained products. (a)  $Zn_{0.72}Cd_{0.28}S$ , (b)  $Zn_{0.48}Cd_{0.52}S$  and (c)  $Zn_{0.24}Cd_{0.76}S$ .

nanorods could only be formed when the Zn/Cd molar ratio was less than 9. If the Zn/Cd molar ratio exceeded 9, the formed  $Zn_xCd_{1-x}S$  nanocrystallite was spherical with cubic structure, similar to the case of pure ZnS crystallizing.

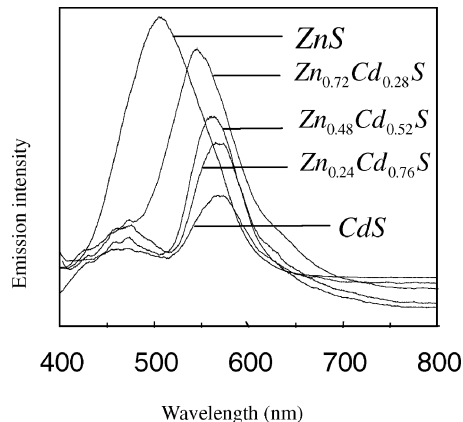


Figure 3 Photoluminescence spectra of  $Zn_xCd_{1-x}S$ .

In summary, through changing the molar ratio of Zn to Cd in the reactants,  $Zn_xCd_{1-x}S$  nanorods with different compositions such as  $Zn_{0.24}Cd_{0.76}S$ ,  $Zn_{0.48}Cd_{0.52}S$ , and  $Zn_{0.72}Cd_{0.28}S$  were hydrothermally synthesized by an *in situ* reaction of  $CdCl_2$ ,  $ZnCl_2$ , and  $(NH_4)_2S$  with 20 wt% ethylenediamine aqueous solution as the solvent at  $180^\circ C$ .

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