ACADEMIC PRESS

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Solid State Chemistry 172 (2003) 480–484

JOURNAL OF SOLID STATE CHEMISTRY

http://elsevier.com/locate/jssc

Synthesis of beltlike CdS nanocrystals via solvothermal route

Shuhong Liu, Haiwei Lu, Xuefeng Qian,* Jie Yin, and Zikang Zhu

School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China

Received 21 August 2002; received in revised form 17 December 2002; accepted 18 December 2002

Abstract

CdS nanocrystals with a beltlike morphology were prepared via a low-temperature solvothermal route in ethylenediamine. The obtained nanocrystals were characterized by X-ray powder diffraction, transmission electron microscopic, ultraviolet-visible and fluorescence spectroscopy. In the mixed solvents of ethylenediamine and distilled water, CdS nanocrystals with various morphologies were obtained with the change of the volume ratio of the two constituents.

Keywords: Nanocrystals; Solvothermal; Ethylenediamine

1. Introduction

In the nanoscale regime, the size and shape of inorganic crystals strongly influence their physical properties [1–3]. In particular, one-dimensional (1-D) nanostructured materials, such as nanotubes, nanorods and nanowires, not only exhibit novel optical and magnetic properties, but also are key components in the fabrication of nanodevices [4].

Over the past few years, considerable efforts have been placed on the synthesis of 1-D nanostructured materials. For example, Li et al. synthesized bismuth nanotubes through a low-temperature hydrothermal reduction method [5]. Qian et al. synthesized ternary semiconductor $CuInE_2$ ($E = S$, Se) nanorods from elements under a solvothermal process [6]. Zhang et al. reported the synthesis of silver nanowires in aqueous solutions of a double-hydrophilic block copolymer [7]. In geometrical structures, the nanostructures mentioned above have a common characteristic of cylindrical symmetric cross section. Recently, Pan et al. reported another group of distinctly different semiconducting oxide nanostructures that have a rectangular cross section, in correspondence to a beltlike (or ribbonlike) morphology [8]. Due to the potential applications of beltlike materials, research activities were then significantly stimulated into the synthesis and characterization of nanobelts, such as Ga_2O_3 [9], SnO_2 [10], and Al_4C_3 [11]. However, all reported methods need vigorous conditions such as high temperature, and the synthesis of nanobelts at low temperature has not been reported yet.

Herein, we reported the synthesis of beltlike CdS nanocrystals via a low-temperature solvothermal route in ethylenediamine (EN). Using EN as the liquid media, a variety of II–VI semiconductor nanorods have been successfully prepared and a solvent coordination molecular template (SCMT) mechanism has been proposed [12–14]. However, to our knowledge, nanostructured CdS with a beltlike morphology formed in the SCMT process has not been reported before. In this work, we prepared beltlike CdS nanocrystals in pure EN, and when the mixtures of EN and water in different volume radios (v/v) were served as the solvents, CdS nanocrystals with various morphologies were obtained.

2. Experimental

All the reactants and solvents used in this study were analytical grade and used without any further purification. In a typical preparation process, $Cd(Ac)_2 \cdot 2H_2O$ (0.001 mol) and thioacetamide (0.002 mol) were added into a Teflon-lined stainless steel autoclave which had been filled with solvents to 80% of its capacity. EN, distilled water (DW), as well as their mixtures in different volume ratios (v/v) were served as the solvents.

---

*Corresponding author. Fax: +86-21-54741297.
E-mail address: xfqian@mail.sjtu.edu.cn (X. Qian).

0022-4596/03/$ - see front matter © 2003 Elsevier Science (USA). All rights reserved.
doi:10.1016/S0022-4596(03)00046-X

The autoclaves were maintained at 130°C for 10 h and then cooled to room temperature naturally. The precipitates were filtered and washed several times with DW and absolute ethanol to remove excessive thioacetamide and other by-products. The samples were then dried in vacuum at 60°C for 2 h and collected for further characterization.

The X-ray powder diffraction (XRD) patterns were recorded at a scanning rate of $4^\circ\ \mathrm{min}^{-1}$ in the 2θ range of 20–60° using a Rigaku D/max γA X-ray diffractometer with Cu$K\alpha$ radiation ($\lambda = 1.54178$ Å). Transmission electron microscopic (TEM) photographs of the samples were taken on a Hitachi S-530 TEM. Samples for TEM analysis were prepared by dispersing the product in DW by ultrasonic stirring and adding a drop of the dispersion on carbon-coated Cu grids. Ultraviolet-visible (UV-Vis) spectra were measured on a Perkin–Elmer Lambda 20 UV-Vis spectrophotometer. Room-temperature fluorescence spectra were recorded on a Perkin–Elmer LS 50B fluorescence spectrophotometer. Samples for UV-Vis and fluorescence spectra were prepared by dispersing the product in ethanol by ultrasonic stirring.

3. Results and discussion

3.1. XRD analysis

Fig. 1a showed the XRD pattern of the sample synthesized in EN. All diffraction peaks could be indexed to wurtzite structure CdS with cell constants $a_0 = 4.12$ Å, $c_0 = 6.68$ Å, which are very close to those in the JCPDS card (card No. 41-1049). Besides, it was noted that the diffraction peak of (002) was stronger and narrower than those of others, which indicated a preferential orientation along the c-axis [13,15]. When the mixtures of EN and DW in different volume ratios were used as the solvents, their XRD patterns were quite similar to that in Fig. 1a, which showed the unusual diffraction peak of (002). In contrast, when pure DW was served as the solvent, no preferential orientation was indicated in its XRD pattern (Fig. 1b). Therefore, it was conceivable that EN really played a key role in the formation of 1-D nanostructured CdS nanocrystals.

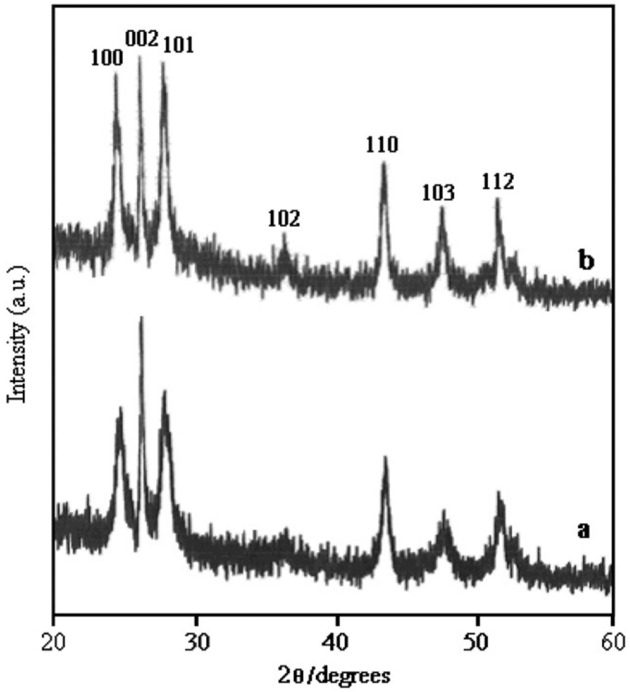

Fig. 1. XRD patterns of the products obtained in different solvents: (a) EN; (b) DW.

3.2. TEM analysis

The TEM analysis (Fig. 2a) revealed a beltlike geometry for CdS prepared in pure EN. As can be seen from the length and width distribution graphs (Fig. 3a and b), the short nanobelts have a typical width of about 32 nm and an average length of 280 nm. No particle was observed at the end of the nanobelts. To further verify the morphological characteristics of the beltlike CdS nanocrystals, a cross-sectional TEM image was given in the inset of Fig. 2a, which exhibits a rectangular-like cross section. The typical thickness and width-to-thickness ratio are about 7 nm and 4, respectively.

Till now, two mechanisms have been proposed to account for the growth of 2-D nanobelts, the vapor–solid process [8] and the catalytic-assisted self-assembly process [11]. In our case, the reaction took place in the liquid medium and no catalyst was added to the reaction medium, so the obtained short nanobelts may not be dominated by the above two processes. Besides, we have carried out the experiments under various conditions, such as different reaction temperatures (from 80°C to 140°C), different reaction time (4–48 h), and different sulfur source (thioacetamide or thiourea). The results indicated that the above factors did not have much impact on the shape of the cross section. Yang et al. have found that the CdS 1-D nanostructure was obtained through the process of folding and then breaking of the initial formed lamellar structure, and EN played a key role in the formation of 1-D nanostructure [14]. However, the factors that determined the shape of the cross section were still not very clear. We considered that kinetic factors, such as the transformation rate from the lamellar to the obtained nanostructures, probably had a significant impact, but we still had not enough evidence to confirm this.

When the mixtures of EN and DW in different volume ratios (v/v) were served as the solvents, CdS

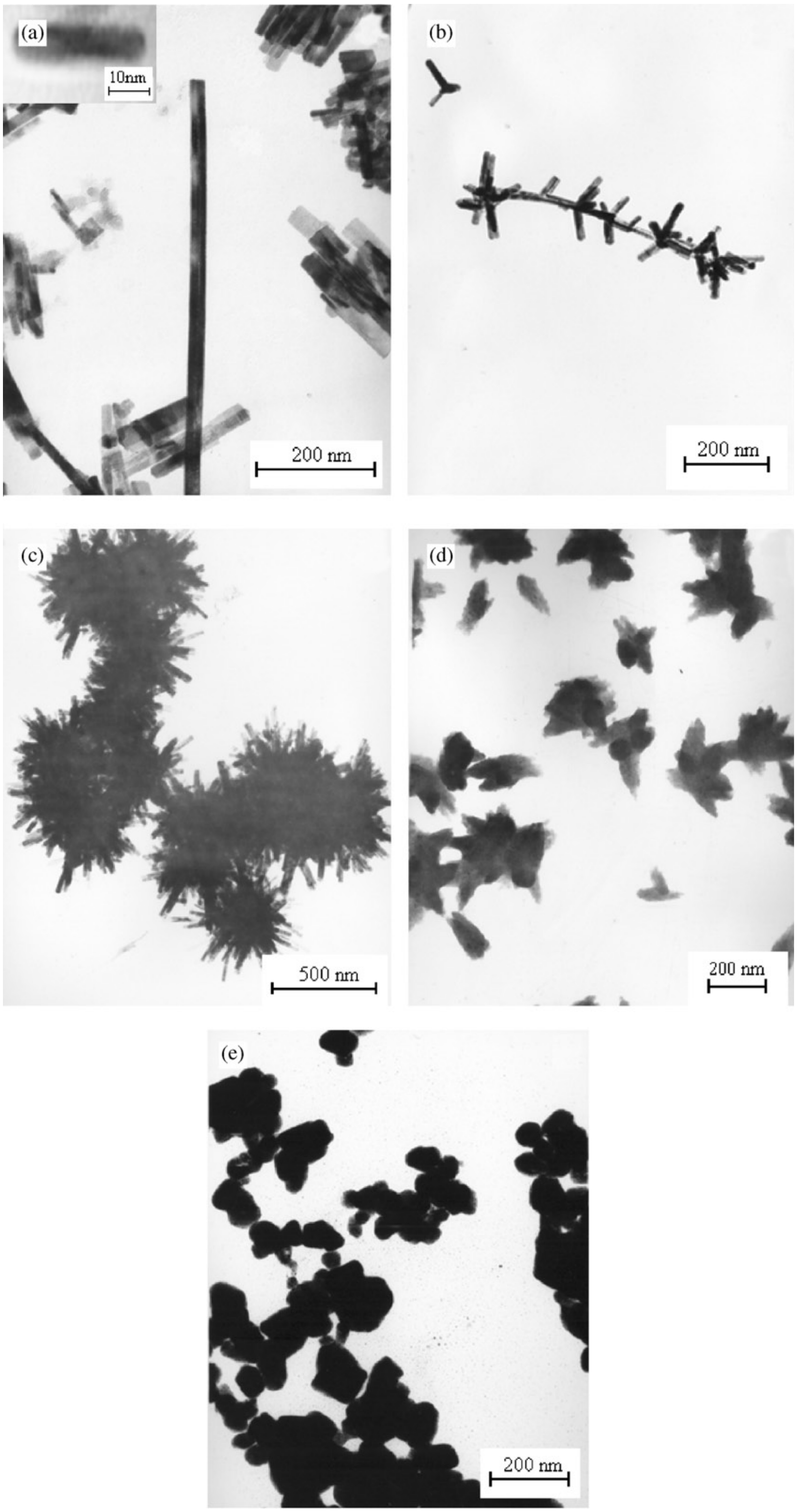

Fig. 2. TEM images of the products obtained in different solvents: (a) EN; (b) EN + DW, 3:1; (c) EN + DW, 1:1; (d) EN + DW, 1:3; (e) DW. The inset of (a) showed the cross-sectional TEM image of a CdS short nanobelt. The cross-sectional TEM specimen was prepared by slicing nanobelts embedded in epoxy with an ultramicrotone.

nanocrystals with various morphologies were obtained (Fig. 2). The different coordination ability of EN and water may account for the various morphologies. Compared with EN, the coordination ability of water was quite weak, so the coordination ability of the mixtures decreased with the increase of the volume

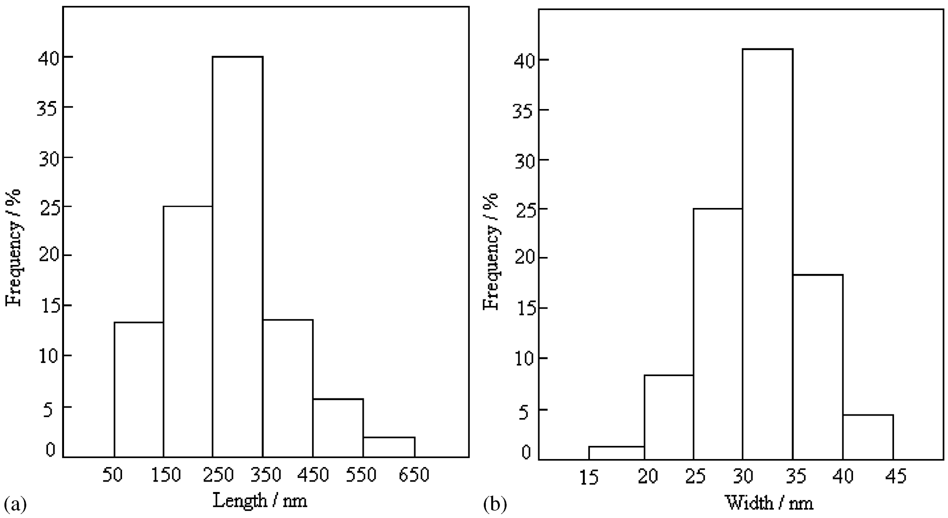

Fig. 3. Length (a) and width (b) distribution of the product obtained in EN.

ratio (DW:EN). As could be seen in Fig. 2, the 2-D nanostructure was more and more unobvious with the volume ratio (DW:EN) being increased. When the ratio was increased to 3, the ‘beltlike’ structures (Fig. 2b and c) changed into the ‘petallike’ structures (Fig. 2d), and when pure DW was used as the solvent, the 2-D nanostructure disappeared (Fig. 2e). These different morphologies could further confirm the role of EN in determining the preferential orientation along the *c*-axis.

In other way, it was also interesting to find that the obtained nanocrystals self-assembled to different morphologies while changing the volume ratio (DW:EN). In pure EN, the obtained nanobelts were nearly parallel to each other when they aggregated (Fig. 2a). While in the mixed solvents, as could be seen in Fig. 2b and c, the obtained nanocrystals self-assembled into the ‘dendritic’ and the ‘starlike’ morphologies, respectively. And when pure DW was used as the solvent, CdS nanocrystals only aggregated randomly (Fig. 2e).

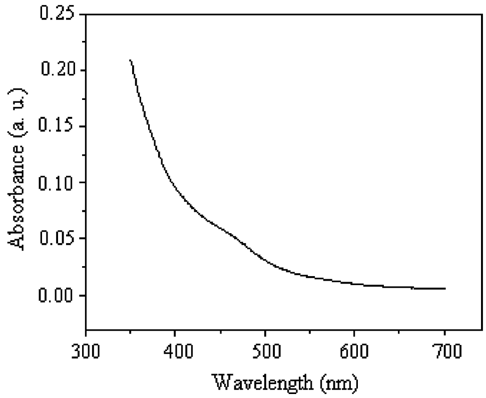

Fig. 4. UV-Vis absorption spectrum of the product obtained in EN.

3.3. UV-Vis spectrum

The formation of CdS nanocrystals could be identified from both the color change and the UV-Vis spectrum of the as-prepared product. After the reaction, yellow CdS precipitated from the solution. The formation process of CdS nanocrystals includes the decomposition of thioacetamide in basic media to release S^{2-}, which bonded with $[Cd(en)_3]^{2+}$ in the solution, and the loss of volatile EN molecules at a certain temperature to form CdS crystals [16]. The process may be expressed in Eqs. (1) and (3) when pure EN is used as the solvent [17], and may be expressed in Eqs. (2) and (3) when there is water present in the reaction mixture [18]:

$$CH_3CSNH_2 \rightarrow CH_3CN + H_2S(\leftrightarrow CH_3CN + 2H^+ + S^{2-}), \quad (1)$$

$$CH_3CSNH_2 + 2OH^- \rightarrow CH_3COO^- + NH_4^+ + S^{2-}, \quad (2)$$

$$Cd(en)_3^{2+} + S^{2-} \rightarrow CdS(en)_m \leftrightarrow CdS(en)_{m-n} + n(en). \quad (3)$$

Fig. 4 presented the UV-Vis absorption spectrum of the obtained CdS short nanobelts. This featured spectrum showed that the onset of the optical absorption (480 nm) was blue-shifted compared with that of bulk CdS (512 nm). This blue shift was caused by strong quantum confinement effect, due to the decrease in particle size [19].

To determine the band gap, we fitted the absorption data to Eq. (3) by extrapolating the linear portion of the curve to absorption equal zero [20].

$$\alpha h\nu = A(h\nu - E_g)^{1/2}, \quad (4)$$

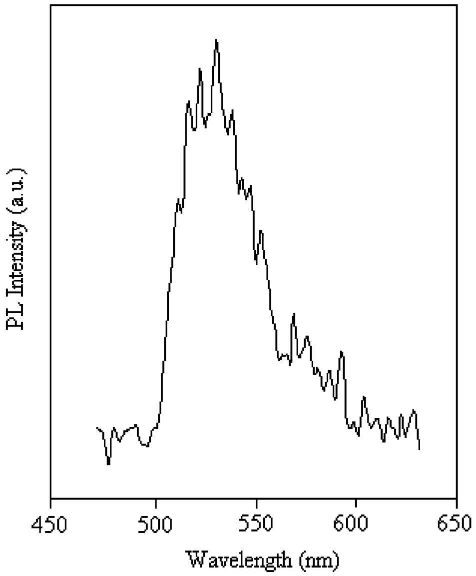

Fig. 5. Room-temperature fluorescence spectrum of the product obtained in EN. The excitation wavelength was 480 nm.

where α is the absorption coefficient, $h\nu$ is the photo energy, E_g is the direct band gap, and A is a constant. The band gap of CdS nanobelts was calculated to be about 2.6 eV, greater than that of the bulk CdS (2.5 eV) [21].

3.4. PL spectrum

It has been reported that CdS is typically sulfur deficient, and the sulfur vacancies which are located at the surface of the material might be important in mediating low-energy emissions [22]. The PL spectrum of the CdS short nanobelts, which was recorded with the excitation wavelength of 480 nm, was shown in Fig. 5. The emission peak was at 530 nm, which was assigned to the surface-trap-induced fluorescence. The PL emission involved the recombination of electrons trapped inside a sulfur vacancy with a hole in the valence band of the CdS nanostructures [23,24].

4. Conclusions

This work showed that it was possible to prepare CdS short nanobelts via a low-temperature solvothermal route in EN. The obtained nanocrystals have a rectangular-like cross section with a width of about 32 nm, a width-to-thickness ratio of about 4, and an average length of 280 nm. XRD analysis showed that the CdS short nanobelts had a wurtzite structure, with a preferential orientation along the *c*-axis. When the mixtures of EN and water in different volume ratios (v/v) were served as solvents, CdS nanocrystals with various morphologies were obtained, which indicated that EN played a key role in the growth of 2-D nanostructures.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (50103006), the Shanghai Shu Guang Project, and the Shanghai Nanomaterials Project.

References

[1] C.M. Lieber, Solid State Commun. 107 (1998) 607–616.
[2] R.E. Smalley, B.I. Yakobson, Solid State Commun. 107 (1998) 597–606.
[3] A.P. Alivisatos, Science 271 (1996) 933–937.
[4] Y.W. Jun, Y.Y. Jung, J. Cheon, J. Am. Chem. Soc. 124 (2002) 615–619.
[5] Y.D. Li, J.W. Wang, Z.X. Deng, Y.Y. Wu, X.M. Sun, D.P. Yu, P.D. Yang, J. Am. Chem. Soc. 123 (2001) 9904–9905.
[6] Y. Jiang, Y. Wu, X. Mo, W.C. Yu, Y. Xie, Y.T. Qian, Inorg. Chem. 39 (2000) 2964–2965.
[7] D.B. Zhang, L.M. Qi, J.M. Ma, H.M. Cheng, Chem. Mater. 13 (2001) 2753–2755.
[8] Z.W. Pan, Z.R. Dai, Z.L. Wang, Science 291 (2001) 1947–1949.
[9] G. Gundiah, A. Govindaraj, C.N.R. Rao, Chem. Phys. Lett. 351 (2002) 189–194.
[10] Z.R. Dai, Z.W. Pan, Z.L. Wang, Solid State Commun. 118 (2001) 351–354.
[11] H.F. Zhang, A.C. Dohnalkova, C.M. Wang, J.S. Young, E.C. Buck, L.S. Wang, Nano Lett. 2 (2002) 105–108.
[12] Y.D. Li, H.W. Liao, Y. Ding, Y.T. Qian, Chem. Mater. 10 (1998) 2301–2303.
[13] Y.D. Li, H.W. Liao, Y. Ding, Y. Fan, Y. Zhang, Y.T. Qian, Inorg. Chem. 38 (1999) 1382–1387.
[14] J. Yang, J.H. Zeng, S.H. Yu, L. Yang, G.E. Zhou, Y.T. Qian, Chem. Mater. 12 (2000) 3259–3263.
[15] P. Yan, Y. Xie, Y.T. Qian, X.M. Liu, Chem. Commun. (1999) 1293–1294.
[16] S.H. Yu, M. Yoshimura, J.M.C. Moreno, T. Fujiwara, T. Fujino, R. Teranishi, Langmuir 17 (2001) 1700–1707.
[17] C.Y. Wang, X. Mo, Y. Zhou, Y.R. Zhu, H.T. Liu, Z.Y. Chen, J. Mater. Chem. 10 (2000) 607–608.
[18] J.H. Zeng, J. Yang, Y. Zhu, Y.F. Liu, Y.T. Qian, H.G. Zheng, Chem. Commun. (2001) 1332–1333.
[19] L.E. Brus, J. Chem. Phys. 80 (1984) 4403–4409.
[20] Y. Wang, A. Sunna, W. Mahler, R. Kasowski, J. Chem. Phys. 87 (1987) 7315–7322.
[21] P.E. Lippens, M. Lannoo, Phys. Rev. B 39 (1989) 10935–10944.
[22] O.B. Paul, L.P. Nigel, Chem. Mater. 13 (2001) 3843–3850.
[23] Y. Wang, N.J. Herron, J. Phys. Chem. 92 (1988) 4988–4993.
[24] J. Kuczynski, J.K. Thomas, J. Phys. Chem. 89 (1985) 2720–2725.