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SOLVOTHERMAL SYNTHESIS AND OPTICAL PROPERTIES OF WURTZITE-TYPE CdS NANORODS

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Cadmium sulfide (CdS) nanorods were synthesized by simple solvothermal reactions at 200 °C for 12-24 h using $Cd(NO_3)_2·4H_2O$ and NH_2CSNH_2 as starting materials and $(C_2H_5)_2NH$ as solvent. XRD and TEM analysis show a hexagonal-phase single crystalline CdS nanorods with diameter of 20 nm and length of 100-200 µm. UV-visible absorption of as-prepared CdS nanorods presented an absorption peak of around 482 nm. The PL spectrum exhibited an emission band at 403 nm due to electron–hole recombination of CdS.

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1. Introduction

One-dimensional semiconductors have attracted a great deal of attention because of their novel properties. They have promising applications in optoelectronic nanodevices due to their important non-linear photonic properties, luminescent properties, quantum size effects and other important physical and chemical properties [1-3]. As a well-known direct-band gap II-VI semiconductor, CdS has primary band gap of 2.4 eV and exhibits a number of remarkable characteristics, including good thermal, mechanical and size-dependent optical properties, which has potential applications in laser light-emitting diodes and optical devices [4-7]. One-dimensional CdS nanostructured material with different morphologies including nanorods [2, 4, 6], nanowires [5, 8, 9], nanobelts [10-12], and nanotubes [13-15] has already been synthesized by a variety of processes, such as solvothermal methods [2, 4, 5, 13], thermal evaporation [10], chemical vapor deposition (CVD) [11, 12], chemical bath deposition [14] and electrochemical synthesis [15].

In this research, we report a simple approach for the synthesis of CdS nanorods by solvothermal reaction. The phase, morphologies and optical properties of the as-synthesized CdS solids were investigated.

2. Experiment

All of the chemicals are analytical-grade and were used without any further purification. In a typical procedure, appropriate amount of $Cd(NO_3)_2·4H_2O$ and NH_2CSNH_2 with 1:2 molar ratio was dissolved in 20 ml diethylamine ($(C_2H_5)_2NH$) and followed by the addition of 0.1 g

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polyvinylpyrrolidone (PVP) into these solutions under 30 min stirring. The precursor was transferred into a Teflon-lined stainless steel autoclave which was filled with $(C_2H_5)_2NH$ to 80% of its capacity. The stainless steel autoclave was heated by an electric oven at 200 °C for 12-24 h. Then, they were cooled to room temperature. The precipitates were filtered, washed by deionized water and ethanol several times, dried in an oven at 70 °C for 12 h, and collected for further characterization.

XRD patterns were collected by a Philips X'Pert MPD X-ray diffractometer equipped with graphite monochromatized Cu K_α radiation, employing a scanning rate of 0.02 deg/s in the 2θ range from 10 deg to 80 deg. Raman spectroscopy (T64000 HORIBA Jobin Yvon) was operated using 50 mW Ar green laser with 514.5 nm wavelength. TEM images and SAED pattern were taken by a TEM, JEOL JEM-2010 transmission electron microscope at an accelerating voltage of 200 kV. The samples for these measurements were dispersed in absolute ethanol by ultrasonic vibration. Then, the solutions were dropped onto Cu grids coated with amorphous carbon films. UV-visible absorption was carried out on a Lambda 25 PerkinElmer spectrometer, using 450 W Xe-lamp with the resolution of 0.2 nm. The photoluminescence was studied by a fluorescence spectrophotometer (LS50B PerkinElmer) using 208 nm excitation wavelength at room temperature.

3. Results and discussion

Fig. 1 shows XRD patterns of the as-synthesized CdS samples prepared by solvothermal at 200 °C for 12-24 h. All XRD patterns can be consistently indexed to be hexagonal wurtzite-type CdS of the JCPDS No. 41-1049 [16]. The reflection peaks at 2θ = 25.09°, 26.75°, 28.43°, 36.89°, 43.97°, 48.11°, 51.34°, 52.13°, 53.07°, 54.89°, 58.63°, 67.11°, 69.52°, 71.17°, 72.72° and 75.85° corresponded to the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), (202), (203), (210), (211), (114) and (105) planes, respectively. The distinctive reflection peaks at 2θ = 28.43° and 53.07° are the evidence of hexagonal CdS phase. The absence of a reflection peak at 2θ = 31.5° is the specification of no incorporation of the cubic zinc blende phase of CdS. Nevertheless, the intensities of diffraction peaks were relatively enhanced with an increase in the lengths of the reaction time from 12 to 24 h which confirmed the increasing in the crystalline degree of these products as well.

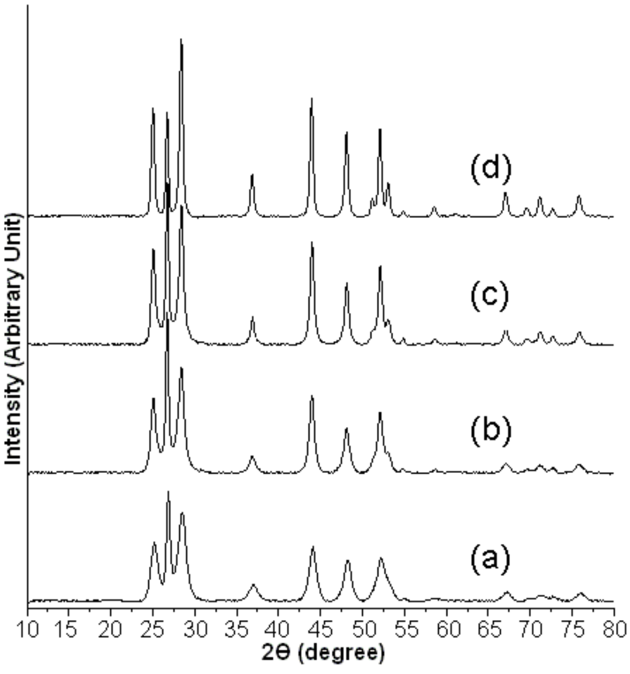

Fig. 1 XRD patterns of the as-synthesized CdS samples prepared by solvothermal reaction at 200 °C for (a) 12 h without PVP, (b) 12 h with PVP, (c) 18 h with PVP, and (d) 24 h with PVP.

The hexagonal wurtzite CdS has C^4_{6v} space group. The different vibrations were assigned to be the $1A_1 + 1E_1 + 2E_2$ (E_{2H} and E_{2L}) Raman active modes and the $2B_2$ silent modes. The A_1 branch was the phonon polarization in the z direction, including the doubly degenerate E_1 and E_2 branches in the x-y plane. Both of A_1 and E_1 modes were split into longitudinal optical (LO) and transverse optical (TO) components, because the wurtzite CdS structure is noncentrosymmetric [16-18]. Raman spectra of the products showed at the same vibrations of 1LO and 2LO belonging to the A_1 modes at 299 and 600 cm^{-1}, which were polarized in the x-z face and strongly coupled to the excitons along the c axis [16-18].

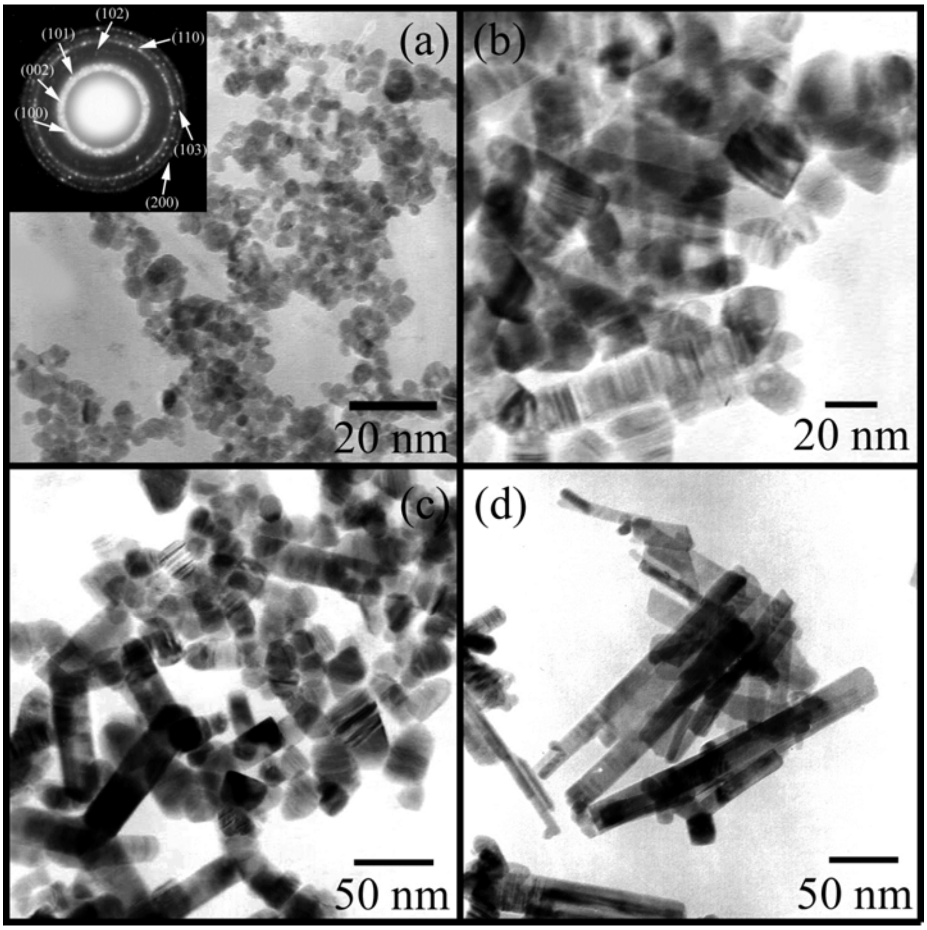

Fig. 2 TEM images and SAED pattern of the as-synthesized CdS samples prepared by solvothermal reaction at 200 °C for (a) 12 h without PVP, (b) 12 h with PVP, (c) 18 h with PVP, and (d) 24 h with PVP.

The morphologies of products were examined by TEM. Fig. 2 displays the TEM images representing the morphology evolution of the CdS nanoparticles into nanorods. The as-synthesized CdS sample by the solvothermal reaction at 200 °C for 12 h without PVP adding was detected only nanoparticles in shape with below 5-10 nm in diameter. No other morphologies were detected in the system without PVP adding. The SAED pattern indicated the (100), (002), (101), (102), (110), (103) and (200) planes corresponding to the JCPDS No. 41-1049 [16]. Comparing to PVP-added solution at 200 °C for 12 h, the morphology of the product was transformed from nanoparticles into nanorods, which confirmed the functionality of PVP as a template to control the formation of CdS nanorods. In the solution without PVP adding, the nanoparticles were free to grow, and a number of nanoparticles with different orientations were synthesized. Fig. 2d reveals that the CdS product was straight and uniform nanorods with 100-200 nm long and 20 nm in diameter. The SAED pattern shows a brightness spot pattern, revealing that each nanorod was wurtzite CdS single crystal. The SAED confirms that the growth direction of the nanorods was in the [001] direction parallel to their axial lengths. High resolution TEM (HRTEM) image presents the lattice fringes of nanocrytallites with a spacing of 0.34 nm, corresponding to the interplanar distance of the (002) plane of hexagonal CdS phase. The plane is normal to the growth direction of the nanorod which confirms that CdS nanorods have the [001] growth direction. Composition of the products was analyzed by EDX technique. They showed the presence of Cd and S elements at the 23.11 keV $K_{\alpha1,2}$ line for Cd and 2.31 keV $K_{\alpha1,2}$ line for S. The atomic ratio of Cd to S is 1.03, very close to the CdS chemical formula. However, the C and Cu peaks were also detected, resulting from the TEM grid used for the TEM analysis.

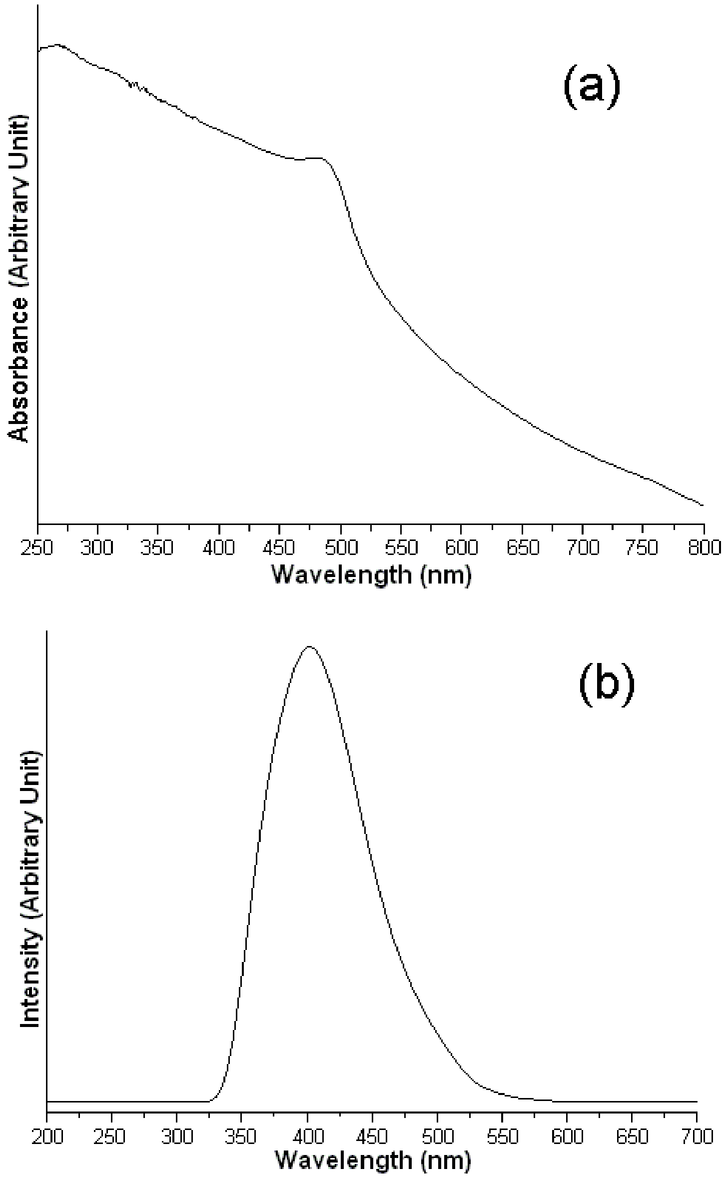

Fig. 3 (a) UV-visible and (b) photoluminescence spectra of CdS nanorods.

The UV-visible absorption spectrum of as-synthesized CdS nanorods dispersed in ethanol is shown in Fig. 3a. The absorption spectrum of CdS nanorods exhibited an absorption peak of around 482 nm, assigned to be the first excitation of CdS [5]. The band gap of the CdS nanorods is estimated to be 2.57 eV from the UV-visible absorption spectrum. They are blue shift as compared to the characteristic absorption of bulk CdS material (515 nm) due to the quantum size effect [2, 5, 16, 19].

The photoluminescence (PL) spectrum of the as-synthesized CdS nanorods dispersed in ethanol is shown in Fig. 3b. The PL of CdS nanorods exhibited a broad band emission wavelength ranging from 325 nm to 584 nm with the emission centered at 403 nm in the violet wavelength range. The result indicates that the PL emission comes from the electron–hole recombination of CdS [18].

4. Conclusions

The crystalline CdS nanorods have been synthesized in the presence of PVP through a solvothermal route. The product shows a hexagonal wurtzite CdS structure with 100-200 nm in length and 20 nm in diameter. The UV-visible absorption spectrum of CdS nanorods presents an absorption peak of around 482 nm, blue shift relative to its bulk, due to the quantum size effect.

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References

[1] X. Wang, B. Zou, Q. Zhang, A. Lei, W. Zhang and P. Ren, J. Alloy. Compd. **509**, 9959 (2011).
[2] P. Dalvand and M. R. Mohammadi, J. Nanopart. Res. **13**, 3011(2011).
[3] J.F.A. Oliveira, T.M. Milao, V.D. Araujo, M.L. Moreira, E. Longo and M.I.B. Bernardi, J. Alloy. Compd. **509**, 6880 (2011).
[4] J. Zhou, G. Zhao, J. Yang and G. Han, J. Alloy. Compd. **509**, 6731 (2011).
[5] S. Yan, D. Hu, J. Wu, J. Qian, Y. Wang and Z. Xiao, Solid State Sci. **12**, 1507 (2010).
[6] P. Dalvand, M.R. Mohammadi and D.J. Fray, Mater. Lett. **65**, 1291 (2011).
[7] K. Pal, U.N. Maiti, T.P. Majumder and S.C. Debnath, Appl. Surf. Sci. **258**, 163 (2011).
[8] T. Thongtem, A. Phuruangrat and S. Thongtem, Ceram. Int. **35**, 2817 (2009).
[9] A. Phuruangrat, T. Thongtem and S. Thongtem, Curr. Appl. Phys. **9**, S201 (2009).
[10] L. Xu, Y. Su, D. Cai, Y. Chen and Y. Feng, Mater. Lett. **60**, 1420 (2006).
[11] Y. Wang, C.Y. To and D.H.L. Ng, Mater. Lett. **60**, 1151 (2006).
[12] W. Liu, C. Jia, C. Jin, L. Yao, W. Cai and X. Li, J. Cryst. Growth **269**, 304 (2004).
[13] X. Li, H. Chu and Y. Li, J. Solid State Chem. **179**, 96 (2006).
[14] H. Zhang, X. Ma, J. Xu and D. Yang, J. Cryst. Growth **263**, 372 (2004).
[15] D. Mo, J. Liu, H.J. Yao, J.L. Duan, M.D. Hou, Y.M. Sun, Y.F. Chen, Z.H. Xue and L. Zhang, J. Cryst. Growth **310**, 612 (2008).
[16] A. Phuruangrat, N. Ekthammathat, T. Thongtem and S. Thongtem, J. Alloy. Compd. **509**, 10150 (2011).
[17] A. Phuruangrat, T. Thongtem and S. Thongtem, J. Exper. Nanosci. **4**, 47 (2009).
[18] H. Wang, P. Fang , Z. Chen and S. Wang, J. Alloy. Compd. **461**, 418 (2008).
[19] S. Suwanboon, R. Tanattha, R. Tanakorn, Songklanakarin J. Sci. Technol. **30**, 65 (2008).