



Journal of Applied Sciences

ISSN 1812-5654

science
alert

ANSI*net*
an open access publisher
<http://ansinet.com>

Synthesis of ZnS Nanobelts with Multi Photoluminescence Peaks

Kamal Mahir Sulieman, Xintang Huang and Ming Tang
Department of Physics, Central China Normal University, Wuhan 430079,
People's Republic of China

Abstract: Single-crystalline wurtzite ZnS nanobelts were synthesized using Chemical Vapor Deposition (CVD) method without any catalyst. The selected-area electron diffraction (SAED) and energy-dispersive X-ray spectroscopy (EDS) indicate that the nanobelt is pure single crystal ZnS. The room temperature photoluminescence (PL) spectrum of the products shows that there are three broad emission peaks at 510, 410 and 340 nm, respectively. The broad emission peak at 340 nm is divided into two narrow peaks with full width at half maximum (FWHM) of about 1 nm.

Key words: ZnS, nanobelts, photoluminescence, synthesis

INTRODUCTION

Zinc sulfide, an important semiconductor compound of the IIB-VI groups, has a wide band-gap energy of 3.7 eV (Sooklal *et al.*, 1996) at 300 K. ZnS is a luminescent material well known for its photoluminescence, (Falcony *et al.*, 1992) electroluminescence, (Tang and Cameron, 1996) etc., which enable wide applications in the fields of displays (Bredol and Merikhi, 1998) sensors and lasers (Falcony *et al.*, 1992; Prevenslik, 2000). Moreover, zinc sulfide is also widely used in photocatalysis (Wada *et al.*, 1998; Fujiwara *et al.*, 1998). In recent years, nanocrystalline ZnS attracted much attention because properties in nanoforms differ significantly from those of their bulk counterparts (Dhas *et al.*, 1999). Therefore, much effort has been made to control the size, morphology and crystallinity of the ZnS nanocrystals with a view to tune their physical properties. The recent trend in nanomaterials research is toward onedimensional nanostructured materials because of their wide range of potential applications in nanoscale devices (Frank *et al.*, 1998; Heath *et al.*, 1998; Hu *et al.*, 1999; Xu *et al.*, 1999). Onedimensional ZnS nanostructures such as nanorods, (Chen *et al.*, 2003) nanowires, (Wang *et al.*, 2002a; Meng *et al.*, 2003) nanobelts, (Li and Wang, 2003; Zhu *et al.*, 2003; Jiang *et al.*, 2003) and nanotubes (Wang *et al.*, 2002b) have been produced by different synthesis techniques such as the solvothermal process, (Chen *et al.*, 2003) thermal evaporation of ZnS powder, (Wang *et al.*, 2002; Meng *et al.*, 2003; Li and Wang, 2003; Zhu *et al.*, 2003; Jiang *et al.*, 2003) liquid crystal template method (Jiang *et al.*, 2001) etc. Li and Wang (2003) have reported wurtzite ZnS nanobelts synthesized by thermal evaporation of ZnS powder at 1200°C for 2 h. Two

groups have reported hydrogen-assisted growth of ZnS nanostructures (Zhu *et al.*, 2003; Jiang *et al.*, 2003) by thermal evaporation of ZnS powder at temperature over 1100°C for a time period of 1.5-4 h. All of the above fabrication processes of the ZnS nanobelts were time-catalyst-consuming.

In this study, we report Synthesis of ZnS nanobelts with multi Photoluminescence peaks without any catalyst by thermal evaporation of ZnS powder. The room temperature photoluminescence (PL) spectrum of the products shows that there are three broad emission peaks at 340, 410 and 510 nm respectively. The broad emission peak at 340 nm is divided into two narrow emission peaks.

MATERIALS AND METHODS

In a typical process, ZnS powders were loaded in an alumina boat. And then the boat transferred to the center of a long quartz tube inserted into a horizontal tube furnace. Another empty alumina boat, which existed in the down stream of the furnace, employed as a collector. The furnace temperature was raised to 800°C at a heating rate of 30°C per minute under a constant flow of 95% Ar and 5% H₂. After 30 min the temperature was raised to 1100 °C and held for 2½ h. After the reaction completed, the furnace was allowed to cool down. The deposit cotton like material on the empty boat collected and investigated by X-ray diffraction (Cu K α radiation), Scanning Electron Microscopy (JSM JEOL 6700F), Transmission Electron Microscopy (JEM JEOL 2010) and energy dispersed X-ray spectroscopy (EDS). The Photoluminescence (PL) spectrum (Confocal Laser MicroRaman Spectrometer, He-Cd laser, excitation wavelength 325 nm) was obtained at room temperature.

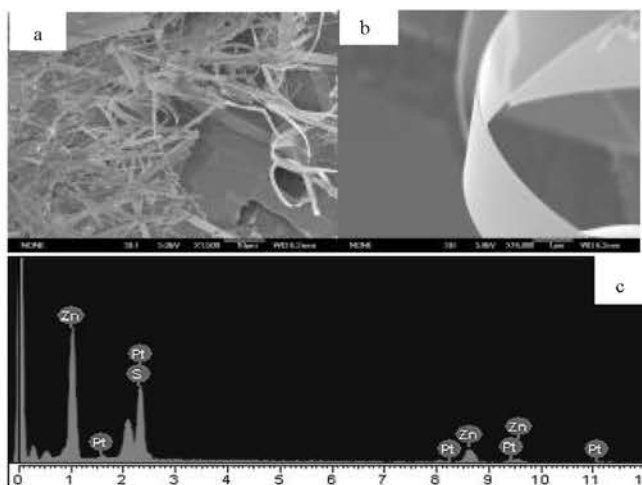


Fig. 1: (a) A typical low magnification SEM image of the belt-like product (b) high magnification SEM image of the belt-like shape (c) EDS analysis

RESULTS AND DISCUSSION

The morphology of the as-synthesized collected product ZnS nanobelts at temperature about 750-800°C grown with evaporated ZnS without any catalyst was firstly examined by SEM. Figure 1a presents a typical SEM image of the cotton-like product. Randomly distributed one-dimensional nanostructures with typical lengths in the range of several tens to several hundreds of micrometers can be observed in the image. Some of them even have lengths on the order of millimeters. The enlarged image Fig. 1b reveals these nanostructures have belt-like shape. The bending and swirling morphologies clearly indicate the typical morphological features of nanobelts. The widths of the belts are in the range of 1.5-2 μm with average thickness of the nanobelts is about 70 nm. The width-to-thickness ratio of the nanobelts is about 5-20 and the widths of the nanobelts were uniform along their entire length. Figure 1c shows the EDS analysis of the nanobelts. The result shows that the atomic ratio of S to Zn is less than 1:1 which demonstrates that in the products there are some vacancies of S.

The X-ray diffraction (XRD) pattern Fig. 2 of the as-prepared samples shows that the samples are well crystallized. All the peaks can be indexed as (100), (002), (101), (110), (103) and (112) crystal planes, which suggests that the samples are pure, wurtzite-phase structured ZnS with lattice parameters $a = 3.820 \text{ \AA}$ and $c = 6.257 \text{ \AA}$.

We now determine if the nanobelts are of the same crystal structure. This analysis relies on Selected-area Electron Diffraction (SAED). For the nanobelts, Fig. 3b is the SAED pattern from a fine nanobelt shown at the

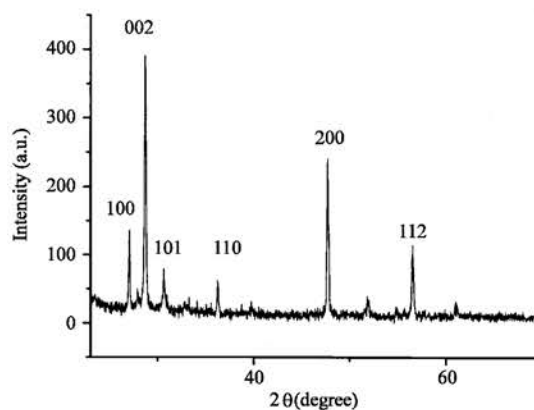


Fig. 2: The X-ray diffraction pattern of collected ZnS nanobelts

center of Fig. 3a. The diffraction pattern revealed that the ZnS nanobelt had a single crystalline hexagonal structure. The nanobelt growth occurred along the (001) direction. We have examined several nanobelts and the same results were obtained in our experiment.

The PL spectrum at room temperature was examined using a Confocal Laser MicroRaman Spectrometer, He-Cd laser, excitation wavelength 325 nm. The PL spectrum of the ZnS nanobelts at room temperature shows in Fig. 4. The spectrum reveals that there are three broad emission peaks at 340, 410, 510 nm, respectively. The 340 nm emission peak is attributed to the spontaneous emission originating from band-to-band transition (Ding *et al.*, 2004). The broad emission peak at 410 nm should be originated from the surface states (Yang *et al.*, 2001). The third broad emission peak is at 510 nm is mainly attributed to the S vacancies in the single crystal ZnS nanobelts

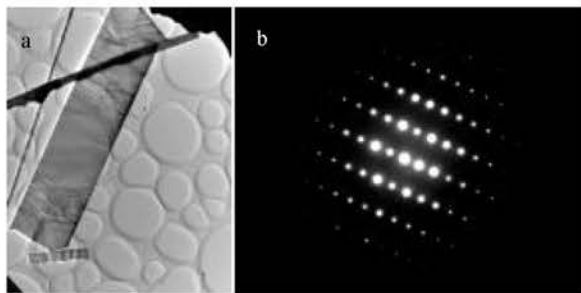


Fig. 3: (a) TEM image of as synthesized ZnS nanobelts (b) the SAED pattern from a fine nanobelt shown at the center of Fig. 3a

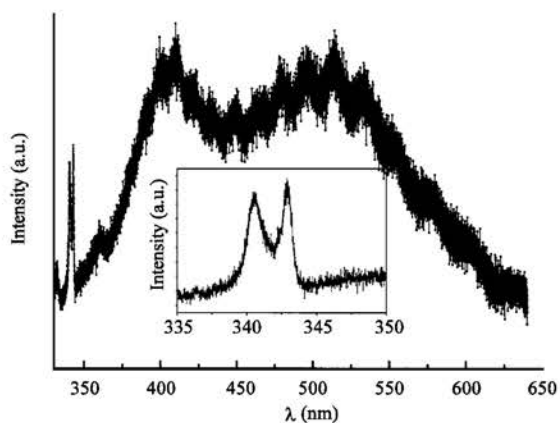


Fig. 4: Room-temperature photoluminescence spectrum of as synthesized ZnS nanobelt

(Qitao *et al.*, 2003; Zhang *et al.*, 2005). From above EDS analysis, we can see that in the ZnS nanobelts there are some S vacancies. Here the PL spectrum also confirms the result. From the PL spectrum, we can also see that the broad emission peak 340 nm is divided into two narrow peaks (338 and 343 nm) with FWHM of about 1 nm. These narrow emission peaks should be lasing emission (Zapien *et al.*, 2004).

CONCLUSIONS

Single-crystalline wurtzite ZnS nanobelts were synthesized using CVD process without any catalyst. The widths of the nanobelts are in the range of 1.5-2 μm , the thickness is about 70 nm and the lengths from several tons to several hundreds of μm . The room temperature PL spectrum of the products shows that there are three broad emission peaks at 340, 410 and 510 nm, respectively. The broad emission peak at 340 nm is divided into two narrow peaks with full width at half maximum (FWHM) of about 1 nm.

REFERENCES

- Bredol, M. and J. Merikhi, 1998. ZnS precipitation: Morphology control. *J. Mater. Sci.*, 33: 471.
- Chen, X., H. Xu, N. Xu and F. Zhao *et al.*, 2003. Kinetically controlled synthesis of wurtzite ZnS nanorods through mild thermolysis of a covalent organic-inorganic network. *Inorg. Chem.*, 42: 3100-3106.
- Dhas, N.A., A. Zaban and A. Gedanken, 1999. Surface synthesis of zinc sulfide nanoparticles on silica microspheres: Sonochemical preparation, characterization and optical properties. *Chem. Mater.*, 11: 806.
- Ding, J.X., J.A. Zapien, W.W. Chen, Y. Lifshitz and T. Lee, 2004. Lasing in ZnS nanowires grown on anodic aluminum oxide templates. *Applied Phys. Lett.*, 85: 2361.
- Falcony, C., M. Garcia, A. Ortiz and J.C. Alonso, 1992. Luminescent properties of ZnS: Mn films deposited by spray pyrolysis. *J. Applied Phys.*, 72: 1525.
- Frank, S., P. Poncharal, Z.L. Wang and W.A. Heer, 1998. Carbon nanotube quantum resistors. *Sci.*, 280: 1744.
- Fujiwara, H., H. Hosokawa, K. Murakoshi, Y. Wada and S. Yanagida, 1998. Surface characteristics of ZnS nanocrystallites relating to their photocatalysis for CO₂ Reduction. *Langmuir*, 14: 5154.
- Heath, J.R., P.J. Kuekes, G.S. Snider and R.S. Williams, 1998. A defect-tolerant computer architecture: Opportunities for Nanotechnology. *Science*, 280: 1716.
- Hu, J., M. Ouyang, P. Yang and C.M. Lieber, 1999. Controlled growth and electrical properties of heterojunctions of carbon nanotubes and silicon nanowires. *Nature*, 399: 48.
- Jiang, X., Y. Xie, J. Lu, L. Zhu, W. He and Y. Qian, 2001. Simultaneous. In situ formation of ZnS nanowires in a liquid crystal template by γ -Irradiation. *Chem. Mater.*, 13: 1213.
- Jiang, Y., X.M. Meng, J. Liu, Z.Y. Xie, C.S. Lee and S.T. Lee, 2003. Hydrogen-assisted thermal evaporation synthesis of ZnS nanoribbons on a large scale. *Adv. Mater.*, 15: 323.
- Li, Q. and C. Wang, 2003. Fabrication of wurtzite ZnS nanobelts via simple thermal evaporation. *Applied Phys. Lett.*, 83: 359.
- Meng, X.M., J. Liu, Y. Jiang and W.W. Chen *et al.*, 2003. Structure and size-controlled ultrafine ZnS nanowires. *Chem. Phys. Lett.*, 382: 434-438.
- Prevenslik, T.V., 2000. Acoustoluminescence and sonoluminescence. *J. Lumin.*, 87-89: 1210.

- Qitao, Z., L. Hou and R. Huang, 2003. Synthesis of ZnS nanorods by a surfactant-assisted soft chemistry method. *Inorg. Chem. Comm.*, 6: 971.
- Sooklal, K., S. Brian, S. Cullum, A. Michael and J.M. Catherine, 1996. Photophysical properties of ZnS nanoclusters with spatially localized Mn²⁺. *J. Phys. Chem.*, 100: 4551.
- Tang, W. and D.C. Cameron, 1996. Electroluminescent zinc sulphide devices produced by sol-gel processing. *Thin Solid Films*, 280: 221.
- Wada, Y., H. Yin, T. Kitamura and S. Yanagida, 1998. Photoreductive dechlorination of chlorinated benzene derivatives catalyzed by ZnS nanocrystallites. *Chem. Commun.*, 24: 2683.
- Wang, X., P. Gao, J. Li, C.J. Summers and Z.L. Wang, 2002a. Rectangular porous ZnO-ZnS nanocables and ZnS nanotubes. *Adv. Mater.*, 14: 1732.
- Wang, Y., L. Zhang, C. Liang, G. Wang and X. Peng, 2002b. Catalytic growth and photoluminescence properties of semiconductor single-crystal ZnS nanowires. *Chem. Phys. Lett.*, 357: 314.
- Xu, D., G. Guo, L. Gui and Y. Tang *et al.*, 1999. Controlling growth and field emission property of aligned carbon nanotubes on porous silicon substrates. *Applied Phys. Lett.*, 75: 481-483.
- Yang, P., M. Lu, D.L. Yuan and G.J. Zhou, 2001. Photoluminescence properties of ZnS nanoparticles co-doped with Pb²⁺ and Cu²⁺. *Chem. Phys. Lett.*, 336: 76.
- Zapien, J.A., Y. Jiang, Y.M. Meng and W. Chen *et al.*, 2004. Room-temperature single nanoribbon laser. *Appl. Phys. Lett.*, 84: 1189-1191.
- Zhang, X., Y. Zhang, Y. Song, Z. Wang and D. Yu, 2005. Optical properties of ZnS nanowires synthesized via simple physical evaporation. *Physica E*, 28: 1.
- Zhu, Y.C., Y. Bando and D.F. Xue, 2003. Spontaneous growth and luminescence of zinc sulfide nanobelts. *Applied Phys. Lett.*, 82: 1769.