

水热法制备 ZnS 纳米线

李国平* 罗运军

(北京理工大学材料科学与工程学院, 北京 100081)

摘要: 以十六烷基三甲基溴化铵(CTAB)为表面活性剂,利用水热法通过二吡啶硫氰酸锌分解制备了 ZnS 纳米线,并用 SEM、XRD、EDX 和 HR-TEM 等方法对其纳米结构进行了表征。实验结果表明,反应时间和表面活性剂浓度是决定纳米 ZnS 最终形貌的关键因素,CTAB 起到了纳米线生长的分子-诱导模板作用。

关键词: ZnS 纳米线; 水热法; CTAB; 二吡啶硫氰酸锌

中图分类号: O614.122 **文献标识码:** A **文章编号:** 1001-4861(2007)11-1864-05

Hydrothermal Preparation of ZnS Nanowires

LI Guo-Ping* LUO Yun-Jun

(School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081)

Abstract: Nanowires of ZnS were synthesised by using a surfactant assisted hydrothermal approach. The synthesis is based on decomposition of dipyrizylzinc thiocyanate with cetyl trimethyl ammonium bromide (CTAB) as a surfactant. The nanostructure was characterized by SEM, XRD and EDX, HR-TEM. The experimental results indicate that the reaction time and concentration of surfactant play key roles in determining the final morphologies of nano-ZnS, and CTAB acts as a molecule-directing template for the growth of nanowires.

Key words: ZnS nanowires, hydrothermal approach, CTAB, dipyrizylzinc thiocyanate

Nanostructure has arose tremendous interest among the researchers working in all fields including physics to bioscience, from basic science to technologists for their improved physical and chemical properties and applications superior to their bulk counterparts^[1,2]. Since the first discovery of carbon nanotubes, one-dimensional (1D) semiconductor materials such as nanorods, nanowires, nanotubes and nanobelts/nanoribbons have attracted extensive interest because of their fundamental physical, chemical, optical, electrical and magnetic properties, and their potential applications in nano-scale devices^[3,4]. It is well known that 1D nanostructure can play an important role both as interconnect and functional units in fabricating electronic, optoelec-

tronic, electrochemical and electromechanical devices with nanoscale dimension. 1D nanostructure have been synthesized through a variety of synthesis technique such as template-directed synthesis^[5], Vapor-solid growth^[6], vapor-liquid-solid (VLS) growth^[7], solution-liquid-solid (SLS) growth^[8] etc. A variety of metal^[9], semiconducting oxides^[10] in different 1D nanoforms have been reported so far.

Out of these materials, zinc sulfide, a II-VI semiconductor, is one of the most studied materials for its wide range of technologically important properties. Zinc Sulfide (ZnS) has a wide band gap of 3.72 eV for cubic phase^[11] and 3.77 eV for the hexagonal Wurtzite phase^[12] at room temperature. It is a key material for ultraviolet

收稿日期:2007-06-01。收修改稿日期:2007-09-11。

北京理工大学优秀青年基金资助计划(No.000Y04-18)。

*通讯联系人。E-mail:girlping3114@bit.edu.cn; Tel:010-68913698

第一作者:李国平,女,29岁,讲师;研究方向:纳米材料和高分子材料。

light-emitting diodes, injection lasers, cathode ray tubes, flat panel displays and IR windows. ZnS is also important for photoluminescence, electroluminescence, etc. Recently, optical wave confining and lasing has been demonstrated in ZnS nanoribbons^[13]. In recent years, nanocrystalline ZnS has attracted much attention because properties in nanoforms differ significantly from those of their bulk counterparts. Therefore, much effort has been devoted to control the size, morphology and crystallinity of the ZnS nanocrystals with a view to tune their physical properties.

In this study, we present a relatively simple and effective procedure for synthesis of 1-D ZnS via hydrothermal reaction at 200 °C using a dipyrizylzinc thiocyanate colloidal solution, cetyl trimethyl ammonium bromide (CTAB) as a surfactant. The influence of surfactant and reaction time on the morphology has been investigated.

1 Experimental

1.1 Hydrothermal reaction of ZnS nanowire with surfactant CTAB

All reagents were analytical grade. CTAB (0, 0.12, 0.24 or 1.44 mmol·L⁻¹) and 3 mL of methoxy ethanol solution of dipyrizylzinc thiocyanate (0.24 mmol·L⁻¹) were put into Teflon-lined autoclave of 50 mL capacity, and then was filled with double distilled water up to 80% of the total volume. After being sealed, the autoclave was heated to 200 °C and maintained for 2 h, and then cooled to room temperature. The resulting black solid fraction was washed with deionized water and then with absolute ethanol. Finally the products were dried under vacuum at 40 °C.

1.2 Characterization

High resolution transmission electron microscopy (HRTEM) observations were done on Hitachi modes

H700A-2 apparatus equipped with an EDAX EDS detector with an accelerated voltage of 200 kV. High resolution scanning electron microscopy (HR-SEM) images were obtained by OPTON CSM-950 with an accelerated voltage of 160 kV. UV-Vis spectra were recorded on a Unico UV-2201 UV-Vis spectrometer with measured wavelength range from 900 nm to 200 nm and slit of 1 nm and scan speed of 300 nm·min⁻¹. X-ray diffraction (XRD) patterns were obtained on a Rigaku D/Max-2550X with Cu K α radiation (40 kV, 200 mA, λ = 0.154 186 nm) and 2 θ range of 20°~80° and scan speed of 0.02°·s⁻¹. PL study was performed on Hitachi F-2500 with slit of 1nm and scan speed of 300 nm·min⁻¹.

2 Results and discussion

2.1 Effect of the concentration of CTAB on the morphology of nano-ZnS

Figs.1a~d show SEM images of the ZnS nanostructure synthesized with varied amounts of CTAB surfactant. These images clearly reveal that the morphology of ZnS nanostructure varies significantly with the amount of CTAB. The shape of ZnS nanostructure varies from spherical at the ratio of Zn:CTAB=1:0 (Fig.1a) to high-yield wires like at the ratio of Zn:CTAB=1:6 (Fig.1d) with the reaction time of 2 h.

The similar phenomena were observed from UV-Vis spectra of ZnS nanostructure (Fig.2). Curve a in Fig.2 shows the absorption of ZnS nanostructure prepared without CTAB and there is a peak at about 337 nm corresponding to a band gap of 3.68 eV, a bulk cubic ZnS reported in reference^[14]. With the increase of CTAB, the absorption peak shifts shorter (blue) to 330 nm (Curve b), 325 nm (Curve c) and 289 nm (Curve d), respectively, which corresponds to a band gap of hexagonal ZnS. The band gap of bulk hexagonal ZnS is 3.80 eV^[14], so it suggests that the presence of CTAB

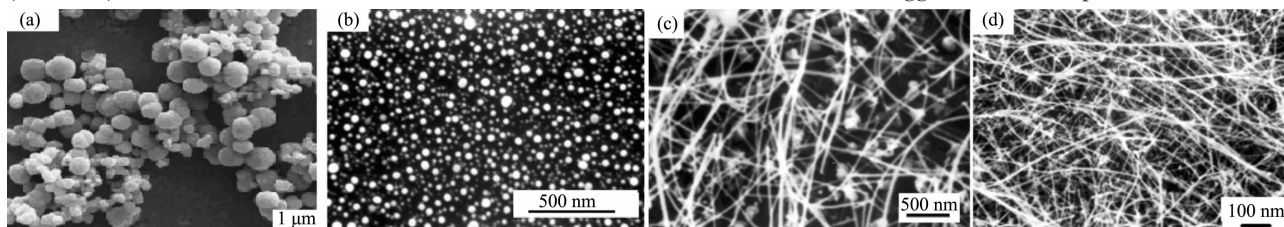


Fig.1 SEM of ZnS nanostructure prepared using 0 mmol·L⁻¹ (a), 0.12 mmol·L⁻¹ (b), 0.24 mmol·L⁻¹ (c) and 1.44 mmol·L⁻¹ (d) of CTAB with the reaction time of 2 h

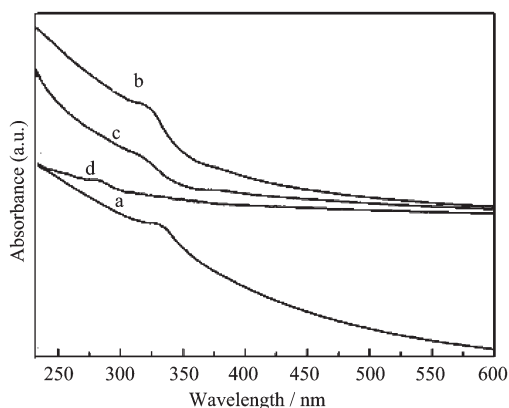


Fig.2 UV-Vis spectrum of ZnS nanostructure prepared using $0 \text{ mmol}\cdot\text{L}^{-1}$ (a), $0.12 \text{ mmol}\cdot\text{L}^{-1}$ (b), $0.24 \text{ mmol}\cdot\text{L}^{-1}$ (c) and $1.44 \text{ mmol}\cdot\text{L}^{-1}$ (d) of CTAB, respectively, with the reaction time of 2 h

makes the absorption peak considerably blue-shifted from 345 nm for hexagonal ZnS.

2.2 Effect of reaction time on the morphology of nano-ZnS

In addition to the effect of CTAB concentration, reaction time is another important factor that influences the shape and size of ZnS nanostructure. A comparison between the images of ZnS nanostructures, prepared with the same CTAB concentration and with various (0.5 and 2 h) reaction times, shows the time-related shape evolution process of ZnS nanostructure. As mentioned above, the nanowires obtained with $1.44 \text{ mmol}\cdot\text{L}^{-1}$ of CTAB with a reaction time up to 0.5 h consist only of a few individual wire-like structures with a width of 40 nm and a length of 150 nm as well as the spherically shaped ZnS (60 nm in diameter) (Fig.3a). After 2 h of synthesis, the yield of wire-shaped ZnS increases; wire-like structures with a width of 60 nm and a length of 2 000 nm are seen (Fig.3b). In all the cases described (reactions with surfactant), at the shorter reaction time duration

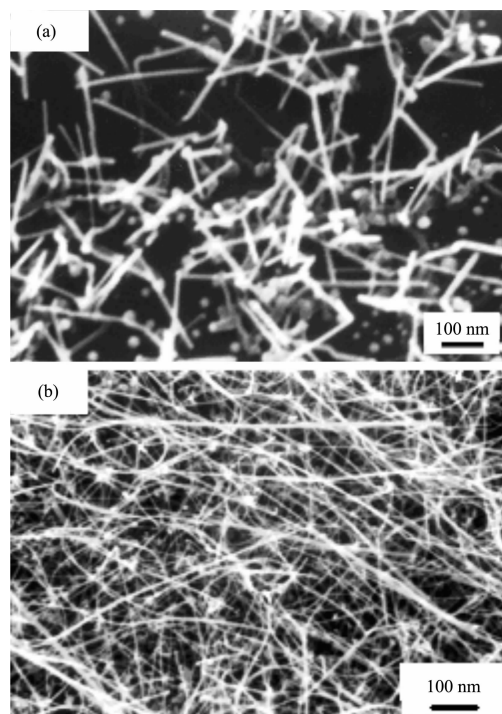


Fig.3 SEM of ZnS nanostructure prepared using $1.44 \text{ mmol}\cdot\text{L}^{-1}$ of CTAB with the reaction time of 0.5 h (Fig.3a) and 2h (Fig.3b), respectively

(0.5 h) we see only the beginning of the evolution of ZnS from cubic shaped wire-like morphological assemblies, while after 2 h of synthesis, the ZnS nanowires yield increases with increasing sizes of ZnS crystal. From the time-related shape-evolution process, it seems that increasing the reaction duration to 2 h, using various CTAB concentrations leads to a high yield of wire-like structures.

2.3 Further characterization of ZnS nanostructure

Fig.4a, b and c are the XRD patterns of the synthesized ZnS nanostructure prepared without CTAB and in presence of $0.24 \text{ mmol}\cdot\text{L}^{-1}$, $1.44 \text{ mmol}\cdot\text{L}^{-1}$ of CTAB with the reaction time of 2 h, respectively. All the

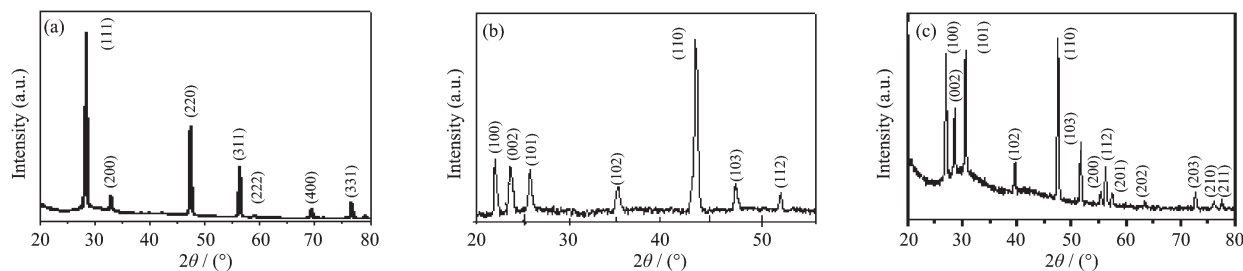


Fig.4 XRD patterns of ZnS nanostructure prepared without CTAB (a) and in presence of $0.24 \text{ mmol}\cdot\text{L}^{-1}$ (b), $1.44 \text{ mmol}\cdot\text{L}^{-1}$ (c) of CTAB with the reaction time of 2 h, respectively

diffraction peaks in Fig 4a can be indexed to cubic ZnS (PDF Card No.5-566) and in Fig.4b,c can be indexed to hexagonal phase ZnS (PDF Card No.12-688), which is in good agreement with the results obtained from UV-Vis spectra (Fig.2). No impurities such as Zn, NiO or intermediary phase zinc sulfides are detected in the XRD patterns of Fig.4b and c. But the characteristic diffraction peaks in Fig.4b is less obvious than those in Fig.4c, which indicates that the concentration of CTAB affects the crystal integrality.

Typical EDX pattern of as-obtained ZnS sample is shown in Fig.5. The results show that the ZnS nanowires are composed of Zn and S and the ratio of Zn to S is 1.08:1, in agreement with the expected value.

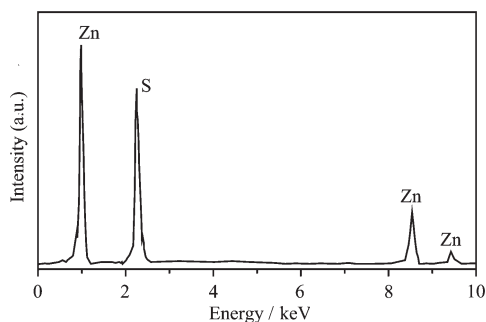


Fig.5 EDAX spectrum of a representative ZnS nanowires prepared using $1.44 \text{ mmol} \cdot \text{L}^{-1}$ of CTAB with the reaction time of 2 h

In Fig.6, HR-TEM image of ZnS shows that they are composed of about 7 nm ZnS nanocrystals assem-

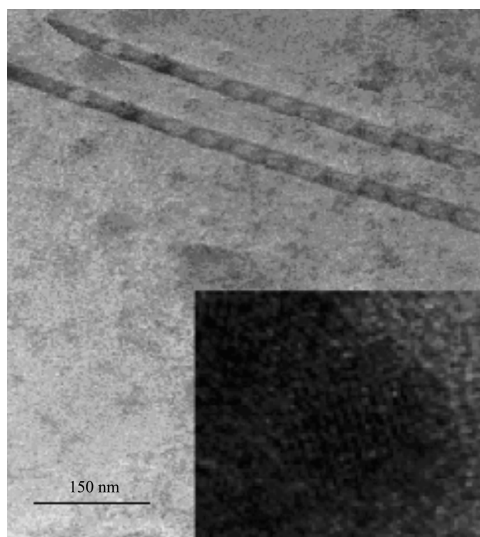


Fig.6 TEM image of ZnS nanowire and HR-TEM image of the ZnS nanowire(inset) prepared using $1.44 \text{ mmol} \cdot \text{L}^{-1}$ of CTAB with the reaction time of 2 h

blies because neck-like connections among the adjacent nanocrystals are clearly observed. The lattice planes of ZnS nanocrystals are clearly visible in the inset of Fig.6.

Fig.7 illustrates the photoluminescence (PL) spectrum of ZnS nanowires with an excitation wavelength of 335 nm. The appearance of a narrow emission peak at about 452 nm is weak. A broad band at about 520 nm is also observed, which can be divided into two peaks at 523 nm and 533 nm, respectively, demonstrating that these nanowires may have potential applications in optoelectronic devices.

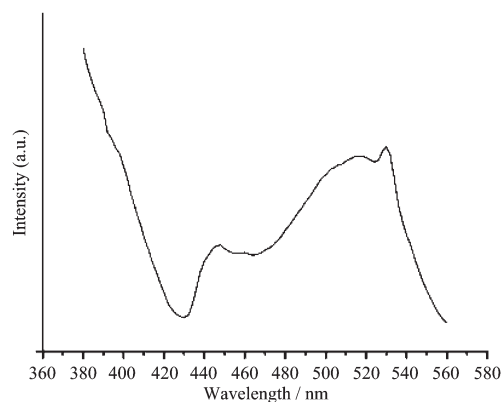


Fig.7 PL of the ZnS nanowires prepared using $1.44 \text{ mmol} \cdot \text{L}^{-1}$ of CTAB with the reaction time of 2 h

2.4 Role of CTAB on the morphology of nano-ZnS

The nucleation and growth conditions of nano-ZnS were examined without and with various concentrations of cationic surfactant CTAB. This growth process could be related to the interaction of oriented surfactant chains and formatted ZnS nanowires. Uniform and ordered chain structure (16 carbon atoms) is easily adsorbed on the surface of ZnS colloidal particles. When the surface of the colloidal ZnS adsorbs CTAB, the activities of colloid greatly decrease and the growth rate of the colloid in some certain direction will be confined. The addition of more CTAB in the colloidal solution modifies the growth kinetics of the growing colloids, which finally leads to anisotropic growth of nanocrystals. Investigations have been done with different concentrations of CTAB (under the same conditions) for the synthesis of nanowires. From the

time related-shape evolution process throughout the paper, it can be assumed that the presence of CTAB micelle-forming surfactant induces the sphere to wires transition of micelles in aqueous solution (Fig.3). Thus CTAB acts as a molecule-directing template for the growth of nanowires.

3 Conclusions

The relatively simple and effective procedure for synthesis and evolution of ZnS was developed from spherical-shaped to wire-like morphological assemblies via a hydrothermal reaction at 200 °C using CTAB as surfactant. ZnS nanowires were prepared with high yield. It was observed that the surfactant concentration and reaction duration influenced the morphology of ZnS. During the preparation of ZnS nanowires, the CTAB acts as a molecule-directing template for the growth of nanowires.

References:

- [1] Jiang C, Zhang W, Zou G, et al. *Mater. Chem. Phys.*, **2007**, **103**:24~27
- [2] Gao G. *Nanostructures and Nanomaterials: Synthesis, Properties and Applications*, London: Imperial College Press, **2004**,219
- [3] Huang Y, Duan X, Cui Y, et al. *Science*, **2001**,**294**:1313~1316.
- [4] Johnson J C, Knutsen K P, Yan H, et al. *Nanoletters*, **2004**, **4**:197~202
- [5] Liang Y, Zhen C, Zou D, et al. *J. Am. Chem. Soc.*, **2004**, **126**:16338~16342
- [6] Pan Z W, Dai Z R, Wang Z L. *Science*, **2001**,**291**:1947~1952
- [7] Morales A M, Lieber C M. *Science*, **1998**,**279**:208~212
- [8] Trentler T J, Hickman K M, Goel S C, et al. *Science*, **1995**, **270**:1791~1795
- [9] Qu L, Shi G, Wu X, et al. *Adv. Mater.*, **2004**,**16**:1200~1205
- [10] Guha P, Kar S, Chaudhuria S. *Appl. Phys. Lett.*, **2004**,**85**: 3851~3858
- [11] Tran T K, Park W, Tong W, et al. *J. Appl. Phys.*, **1997**,**81**: 2803~2811
- [12] Cong H, Chang R P. *Appl. Phys. Lett.*, **2001**,**79**:3612~3615
- [13] Zapien J A, Jiang Y, Meng X M, et al. *Appl. Phys. Lett.*, **2004**,**84**:1189~1192
- [14] Xiong Q, Chen Q. *Acord Nano. Lett.*, **2004**,**4**:1663~1668