六方相 ZnS 单晶纳米线束的合成及其光学性质研究

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摘要: 利用丙烯酸和丙烯酸锌的共聚物作为前驱体,硫脲作为硫源,在溶剂热条件下于 170 ℃反应 96 h 得到了 ZnS 纳米线束。透射电子显微镜(TEM),选区电子衍射(SAED)和高分辨透射电子显微镜(HRTEM)测试表明这些线束是由单晶纳米线组装而成。该纳米结构具有很好的光学性质。傅立叶变换红外光谱(FTIR)结果证明纳米线被聚合物包裹。此外,对纳米线束的生长机理进行了简要讨论。

关键词: ZnS；纳米线；纳米线束；六方相
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Synthesis and Optical Properties of α-ZnS Single Crystalline Nanowire Bundles

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Abstract: ZnS nanowire bundles have been successfully synthesized by solvothermal method at a low temperature of 170 ℃ using a copolymer of acrylic acid (AA) and zinc acrylic acid (ZnAA) as the precursor. Transmission Electron Microscope (TEM), Selected Area Electron Diffraction (SAED) and High Resolution Transmission Electron Microscope (HRTEM) measurements show that these ZnS nanowire bundles are composed of single crystalline nanowires and the synthesized ZnS is of hexagonal wurtzite structure. The individual nanowire was encapsulated by polymer. This novel structure exhibits excellent optical properties. Furthermore, the formation mechanism has been proposed.

Key words: ZnS; nanowire bundle; wurtzite

0　Introduction

One-dimensional semiconductor nanostructures, such as nanowires, nanobelts and nanotubes, offer a high degree of interest due to their potential applica-tions, ranging from nanoscale electronic devices to tools for biomedical applications[1]. Among them, semicon-ductor nanowires (NWs) have been used as nanoscale building blocks to assemble into a range of electronic and photonic structures, including light emitting

diodes[2], thin film transistors[3], photodetectors[4], and lasers[5]. Due to these potential applications, it is necessary to develop a controllable approach to prepare those important NWs building blocks. Among various semiconductors, ZnS is a wide band-gap (3.66 eV at 300 K) semiconductor, which makes it transparent in the visible region and has attractive photonic properties. Therefore, it can be used in phosphors[6], solar cell[7], infrared window[8], and fuel cell[9] etc. Especially, when the size of the ZnS particles is reduced to nanometer scale, they can display novel optical, electronic, and structural properties different from those of the bulk ZnS, and make the ZnS nanoparticls suitable for non-linear optical devices[10], photocatalysis[11], and gas sensitive sensors[12]. Recently, various methods including pulsed laser vaporization[13] and thermal evaporation methods[14] have been used to synthesize ZnS NWs. Xie and co-workers prepared ZnS NWs in a liquid crystal template by γ-irradiation [15]. The high quality ZnS NWs can be obtained by the above methods, but high energy or temperature higher than 300 ℃ (mostly 900~1 500 ℃) is needed. The micelle template method[16] and anodic aluminum oxide (AAO) template[17] by electrochemically method were also employed to prepare ZnS NWs. These reaction conditions are mild and the size of the product can be controlled, but the yield is low. In order to overcome those limitations, we designed a copolymer of acrylate zinc (ZnAA) and acrylic acid (AA) as precursor to prepare ZnS NWs at a low temperature of 170 ℃ by solvothermal method. The results show that ZnS NWs are oriented into bundles and the ZnS NWs in the bundle are encapsulated with polymer. Otherwise, ZnS exists in two crystal forms: blende (cubic phase) and wurtzite (hexagonal phase), and the phase transition from blende to wurtzite takes place at 1 020 ℃. In our experiment, the polymer serves as the template and capping agent, and promotes the formation of hexagonal phase ZnS structure at such a low temperature. What's more, these nanowire bundles (NWBs) exhibit excellent optical properties.

1 Experimental

1.1 Preparation of copolymer precursor

ZnCl$_2$ (2.5 g, 0.018 mol) was dissolved into 30 mL (in excess, ρ=1.05 g·mL^{-1}, 0.44 mol) acrylic acid at 85 ℃ with stirring in a flask for 30 min and a strong stimulus gas (HCl) was evolved as the reaction proceeded. After ZnCl$_2$ was completely dissolved, a small amount of (NH$_4$)$_2$S$_2$O$_8$ (~10 mg) was added to the above solution to induce the polymerization reaction. The product was washed with absolute ethanol and distilled water, then dried as precursor for further reaction.

1.2 Preparation of ZnS NWBs

(NH$_2$)$_2$C=S (0.57 g, 0.075 mol) was dissolved in 25 mL of ethylenediamine under ultrasonic, in which 1.5 g of precursor was added, then the resulting solution was put into a Teflon-lined stainless-steel autoclave. The reactor was maintained at 170 ℃ for 96 h and then cooled to ambient temperature. The product was centrifugated from the solvent at 8 000 r·min^{-1} for 0.5 h and washed with absolute ethanol and distilled water, respectively, to remove starting materials and by-products. The final product was dried in vacuum for 4 h at ambient temperature. A white product was obtained.

1.3 Preparation of ZnS nanorods (NRs)

ZnCl$_2$ (35 g, 0.26 mol) was put into 30 mL (0.44 mol) of acrylic acid at 85 ℃ with stirring for 30 min accompanied with a strong stimulus gas (HCl) evolution. The undissolved ZnCl$_2$ was separated by centrifugation. The subsequent procedures were the same as above.

1.4 Instruments and characterizations

The samples obtained were characterized with X-ray powder diffraction (XRD). The XRD patterns were recorded with a Japan Rigaku D/max-r A rotating anode X-ray diffractometer using Ni-filtered Cu $K\alpha$ radiation (λ =0.154 18 nm). Transmission electron microscope (TEM) images were taken with a JEM-200CX instrument (Japan) operating at 200 kV. Selected area electron diffraction (SAED) pattern and high resolution transmission electron microscope (HRTEM) image were obtained on JEOL-2010 at an accelerating voltage of 200 kV. Absorption spectra were collected at room temperature on a Shimadzu UV-Vis absorption diode array spectrometer. Samples were prepared by

pressing ZnS NWBs on the surface of the spectral grade magnesium oxide sheet. Photoluminescence spectrum was recorded on American AB-2 fluorescence spectrophotometer.

2 Results and discussion

2.1 Morphology and structure characterization

The typical TEM image of the as-prepared ZnS NWBs is shown in the Fig.1a. The diameter and length of the ZnS NWBs are ~25~180 nm and ~1 μm, respectively. The single bundle is composed of many thin nanowires. To the best of our knowledge, this novel structure is very rare[14i]. Corresponding selected area electron diffraction (SAED) of the single ZnS NW (Fig.1b) shows clear spots, indicating that ZnS NW is single crystal. Those spots can be indexed to {002},

{004}, {100}, {102}, {104} and {202} reflections from ZnS wurtzite structure. In addition, the high-resolution TEM image (Fig.1c) reveals good crystallinity and clear lattice fringes with a 0.316 nm distance between planes corresponding to the (002) d-spacing of ZnS wurtzite structure and the direction of [002] is a preferable growth direction of the NWs. Fig.2 is the FTIR spectrum of the sample. The characteristic vibration bands of $-NH_2$ at 3 239 cm^{-1}, 3 171 cm^{-1}, 1 566 cm^{-1}; -NH- at 3 116 cm^{-1}; -C=O at 1 635 cm^{-1} and $-CH_2-$ at 2 933 cm^{-1} confirm the existence of the polymer, demonstrating that the thin ZnS nanowires are encapsulated with the polymer to form bundles. The polymer here is not only the capping agent, but also serves as the link agent beneficial to the formation of bundles.
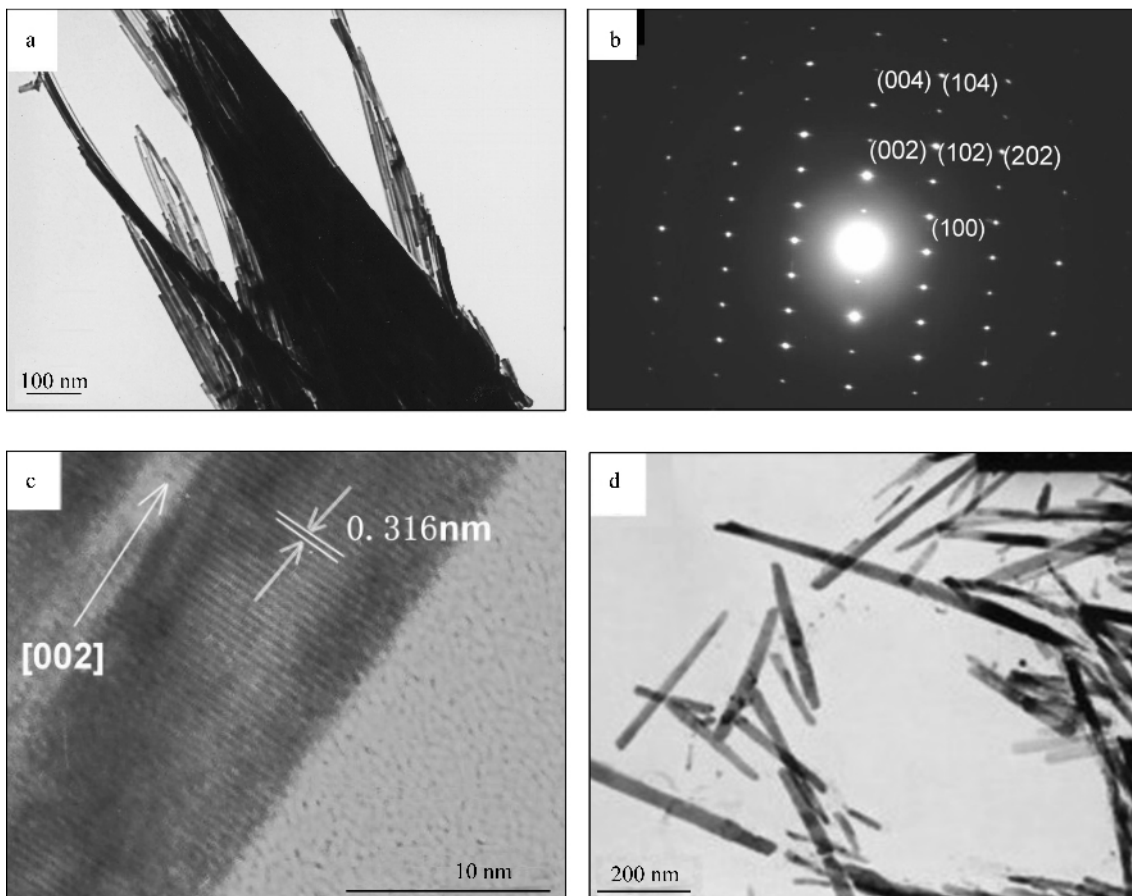
(a) typical NWBs of ZnS;

(b) a selected area electron diffraction pattern (SAED);

(c) high-resolution TEM (HRTEM) image;

(d) TEM image of ZnS NRs when the amount of $ZnCl_2$ is in excess
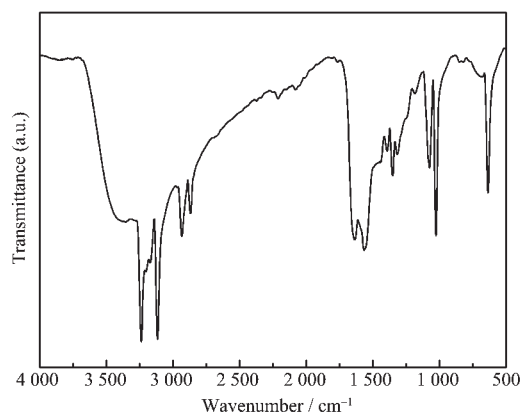
Fig.1 TEM micrographs of ZnS NWBs

Fig.2　FTIR spectrum of the ZnS NWBs: 3 238.79 cm^{-1},
3 170.63 cm^{-1} ($\nu_{\text{N-H}}$); 3 115.74 cm^{-1} ($\nu_{\text{-NH-}}$);
2 932.61 cm^{-1} ($\nu_{\text{-(CH}_2)_n\text{-}}$); 2 868.32 cm^{-1} ($\nu_{\text{-CH-}}$);
2 211.92 cm^{-1}, 2 079.39 cm^{-1} ($\nu_{\text{as-N-C=O}}$);
1 635.30 cm^{-1} ($\nu_{\text{C=O}}$); 1 566.45 cm^{-1} ($\delta_{\text{N-H}}$);
1 393.35 cm^{-1}, 1 352.05 cm^{-1} ($\delta_{\text{-C-H}}$);
821.97 cm^{-1} ($\rho_{\text{-(CH}_2)_n\text{-}}$)

2.2　Optical properties

The optical absorption spectrum of ZnS NWBs is shown in Fig.3a. A weak and broad absorption band at around 550 nm can be attributed to the transition from the surface state of ZnS NWBs because it lies below the absorption edge of the particles, i.e., the absorption energy is lower than the band gap of the particles[18]. It is reasonable that the polymer envelope saturated dangling bonds partially and weakened the surface states. A similar absorption peak at 610 nm has been reported[19], which is 60 nm red-shifted compared with our result. The narrow absorption band centred at 330 nm corresponds to interband transition, which is due to the quantum size effect, blue-shifted about 10 nm as compared with absorption edge of the bulk ZnS. It should be mentioned that due to lamp switching at 368 nm, the corresponding curve appears discontinuous there.

The photoluminescence spectrum of ZnS NWBs is shown in Fig.3b. For most semiconductor nanocrystals, two emissions arising from excitonic and trapped luminescence can be observed. The former is sharp and locates at the absorption edge, while the latter is broad and has a Stokes-shift[20]. Because the excitation wavelength （355 nm) is longer than that of the absorption edge, the excitonic luminescence can not be

observed and only trapped luminescence at 410 nm appears in Fig.3b, which is blue-shifted about 10 nm compared with the previous data and may be attributed to the quantum size effect[19]. The blue emission lies in the spectral region associated with luminescence from self-activated centres, which have often been attributed to crystal lattice vacancies[21].
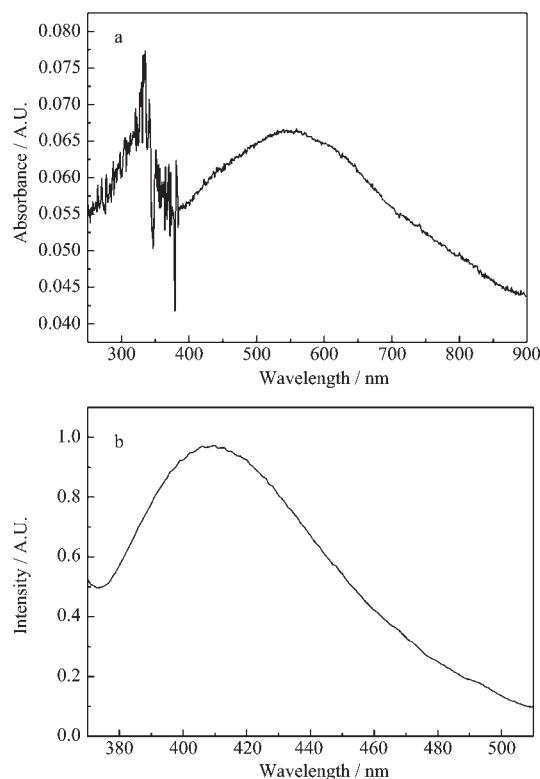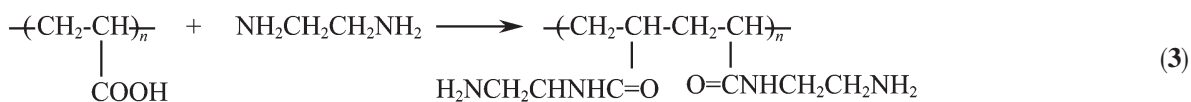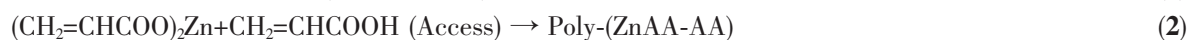

Fig.3　(a) UV-Vis absorption spectrum of ZnS NWBs;
(b) Photoluminescence spectrum of ZnS NWBs

2.3　Mechanism discussion

Generally, ZnS with wurtzite structure (hexagonal phase) is prepared at high temperature (900~1070 ℃)[22]. However, single crystal ZnS NWs with this wurtzite structure have been synthesized in this work at low temperature (170 ℃), attributed to the good dispersion of Zn^{2+} and the solvothermal conditions. Scheme 1 shows the corresponding reactions. The metal ions react with the monomer of the polymer firstly, and then in situ polymerize to form a copolymer precursor with uniformly disperse metal ions. According to reaction (3), the PAA can react with ethylenediamine to form the dangling coordinating group binding Zn^{2+} on the polymer chain. The interaction between Zn^{2+} and the polymer induces the polymer chains taking an extend-

ed conformation. Also, the reaction (**3**) promotes ethylenediamine dissolution in the polymer to form many parallel channels[23]. Due to the physical confinement of the channels, ZnS NWs are formed and embedded in the polymer to form the bundles. When the amount of $ZnCl_2$ is in excess, acrylic acid completely reacts with Zn^{2+} to form ZnAA and there is no free -COOH group in the poly-(ZnAA), which can not react with ethylenediamine to form a dangling coordination group on the polymer chain. Therefore, Zn^{2+} can only react with ethylenediamine to form $[Zn(NH_2 CH_2CH_2NH_2)_2]^{2+}$ in bulk ethylenediamine solvent and reacts with H_2S to form ZnS nanorods (Fig.1d). It is also found that the polymer envelope of ZnS NWs dis-

appeared and the nanowires became individual one instead of the bundles while the reaction time was lasted to more than 120 h because the polymer was hydrolysed under acidic condition. Furthermore, increasing reaction time, the diameters of the products are enlarged and the ratios of length to diameter are decreased. To obtain an insight into the role played by poly-(ZnAA-AA), Zn^{2+} ions were added into the poly-acrylic acid solution for a period of time and then repeated the same procedures as above mentioned, only small amount of ZnS nanorods with blende structure were obtained. It indicates that the polymer precursor plays an important role in the growth of ZnS NWBs with wurtzite structure.

$$ZnCl_2 + CH_2\!=\!CHCOOH \rightarrow (CH_2\!=\!CHCOO)_2Zn + HCl \tag{1}$$

$$(CH_2\!=\!CHCOO)_2Zn+CH_2\!=\!CHCOOH\ (Access) \rightarrow Poly\text{-}(ZnAA\text{-}AA) \tag{2}$$

$$\underset{\underset{COOH}{|}}{-\!\!(CH_2\text{-}CH)_n} \ + \ NH_2CH_2CH_2NH_2 \longrightarrow \underset{\underset{H_2NCH_2CHNHC=O \quad O=CNHCH_2CH_2NH_2}{|\qquad\qquad |}}{-\!\!(CH_2\text{-}CH\text{-}CH_2\text{-}CH)_n} \tag{3}$$

$$(NH_2)_2C\!=\!S + 2H_2O \rightarrow H_2S + 2NH_3 + CO_2 \tag{4}$$

$$Poly\text{-}(ZnAA\text{-}AA) + H_2S \rightarrow ZnS + PAA \tag{5}$$

Scheme 1　Related chemical reactions in this work

3　Conclusion

Novel ZnS nanowire bundles composed of many thin nanowires with wurtzite structure have been successfully prepared with high yields at lower temperature (170 ℃) by solvothermal method. In our method, Zn^{2+} ions are introduced via ZnAA and AA co-polymerization. The UV-Vis spectrum showed the surface state absorption at 550 nm. The photoluminescence spectrum of the sample showed a strong blue emitted-light at 410 nm belonging to the trapped luminescence, which has often been attributed to crystal lattice vacancies.

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