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# Growth and Photoluminescence of Single Crystal ZnS Nanowires

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**Abstract:** Single crystal ZnS nanowires, with diameters around 80 nm and lengths up to several tens micronmeters, were successfully synthesized. The morphology and size of the as-synthesized products were determined using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The room temperature photoluminescence (PL) spectrum of the products shows that there are three broad emission peaks at 336, 410 and 515 nm, respectively. The broad emission peak at 336 nm is composed of three narrow peaks with Full Width at Half Maximum (FWHM) of about 0.3 nm and the intervals between the narrow peaks are about 4 nm.

**Key words:** ZnS, nanowires, AAO template, optical properties

## INTRODUCTION

In recent years, much progress has been made in the preparation of one-dimensional (1D) nanomaterials such as nanowires (Zheng *et al*., 2002), nanorods (Li *et al*., 1998; Zhang *et al*., 2002) and nanotubes (Wang *et al*., 2002), because their functions are much more interesting than the bulk counterparts and different from the isolated atoms or molecules. Among the 1D nanostructures, semiconductor nanowires or nanorods, such as CdSe, CDs, ZnS, ZnO, etc., have been attracting much attention due to their size-dependent optical, nonlinear optical or optoelectronic functionalities. Hence, a lot of methods have been developed to fabricate these wide-band gap semiconductor nanomaterials (Wang *et al*., 1999; Wu *et al*., 2002). Recently, lasing, an exciting application of nanostructures has been demonstrated in nanowires (Huang *et al*., 2001; Johnson *et al*., 2001; Duan *et al*., 2003).

ZnS, as an important wide band-gap semiconductor, has attracted much attention owing to its wide applications, including UV-light-emitting diodes, efficient phosphors in flat-panel displays and photo catalysis (Nicolau *et al*., 1990). Low-dimensional ZnS nanostructures, such as nanorods, nanowires and nanobelts, are expected to exhibit excellent optical and optoelectronic performances, which differ much from the bulk ZnS material (Ma *et al*., 2003; Denzler *et al*., 1998). In this study, we report the large-scale synthesis of single crystal ZnS nanowires on an Anodic Aluminum Oxide (AAO) template coated with Au, by evaporation of ZnS powder using Chemical Vapor Deposition (CVD) method and their room temperature photoluminescence (PL) spectrum. The room temperature PL spectrum of the ZnS nanowires was excited with wavelength of 325 nm laser beam with a power density about 70 kW $cm^{-2}$. The PL spectrum is composed of three broad emission peaks at 336, 410 and 515 nm, respectively and at the 336 nm peak there are three narrow emission peaks with Full Width at Half Maximum (FWHM) of about 0.3 nm and the intervals between the narrow emission peaks are about 4 nm. These narrow emission peaks should be the lasing emission (Zapien *et al*., 2004).

## MATERIALS AND METHODS

The synthesis of single crystal ZnS nanowires was carried out in a horizontal alumina tube furnace. Pure commercial ZnS powder was placed in the middle of a quartz tube and Au coated the AAO template was placed next to the center along the down stream. The quartz tube was inserted into the furnace which heated to 800°C within 15 min under a flow of 95% Ar mixed with 5 % $H_2$ as a carrier gas at a rate 80 and 16 sc cm $m^{-1}$ (standard cubic centimeter per minute), respectively. Then the temperature raised to 1100°C after 30 min and fixed at that degree of temperature for 150 min. ZnS was evaporated and then the quartz tube was drawn out of the furnace when it was cooled down to 400°C under the flow of Ar gas. White product was founded on the template and single crystal ZnS nanowires were obtained on the whole area of the AAO template. The as-synthesized products were characterized and analyzed by scanning electron microscopy (SEM, JSM, JEOL 6700F), Energy Depresive

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Spectroscopy (EDS), transmission electron microscopy (TEM, JEM, JEOL, 2010) and PL spectrometer (Confocal Laser MicroRaman Spectrometer, He-Cd laser, excitation wavelength 325 nm) at room temperature.

## RESULTS AND DISCUSSION

The SEM images of the as-synthesized product (Fig. 1) shows that the product consists of nanowires, with uniform diameters can grow in a large-scale on the AAO template. The nanowires have high aspect ratio, with diameters of around 80 nm and lengths of about several tens micrometers, as it is shown clearly in the Fig. 1a However, several hundred micrometers nanowires can also be observed on the SEM image. Figure 1c the EDS image shows that the product is pure ZnS (O and Al are the AAO template elements, Au is the catalyze coated AAO template, Pt is the cover layer on the nanowires for SEM). Figure 1b shows that enlarged SEM image of the synthesis ZnS nanowires, the nanowires are linear single crystal ZnS with uniform diameters.

TEM image of the ZnS nanowire and select area diffraction patterns shown in Fig. 2a. The image reveals a typical image of single crystal ZnS nanowires with diameter about 80 nm. A nanoparticle of Au catalyst could be found at the end of the nanowire, which was the evidence of a VLS mechanism. The Selected-area electron diffraction pattern (SAED) corresponding to Fig. 2a reveals that the ZnS nanowires are structurally uniform and single crystalline. The recorded SAED pattern perpendicular to the nanowire long axis could be indexed for the [001] zone axis of single crystalline ZnS as shown in Fig. 2a. TEM observation also reveals that the ZnS nanowires terminate in a nanoparticle at one end as shown in Fig. 2b. The nanoparticle of ZnS and Au at the tip of the nanowire generally appears dark and have high contrast compared with the nanowire.

The EDS analysis in Fig. 1c shows that each of the nanowires has the same composition, the atomic ratio of Zn to S for the nanowires is 36:28, which material reacted with $H_2$ vapor in the carrier gas in the high temperature zone, forming Zn and $H_2S$ vapors. The Zn vapor was carried along with the carrier gas to the low-temperature zone, where it deposited on the substrate, reacted with gold film and formed the Au (Zn) solid solution droplets with diameters dictated by the Au film thickness. The Au (Zn) liquid droplets would continuously absorb more Zn and $H_2S$ vapors from the carrier gas. Inside the droplets,

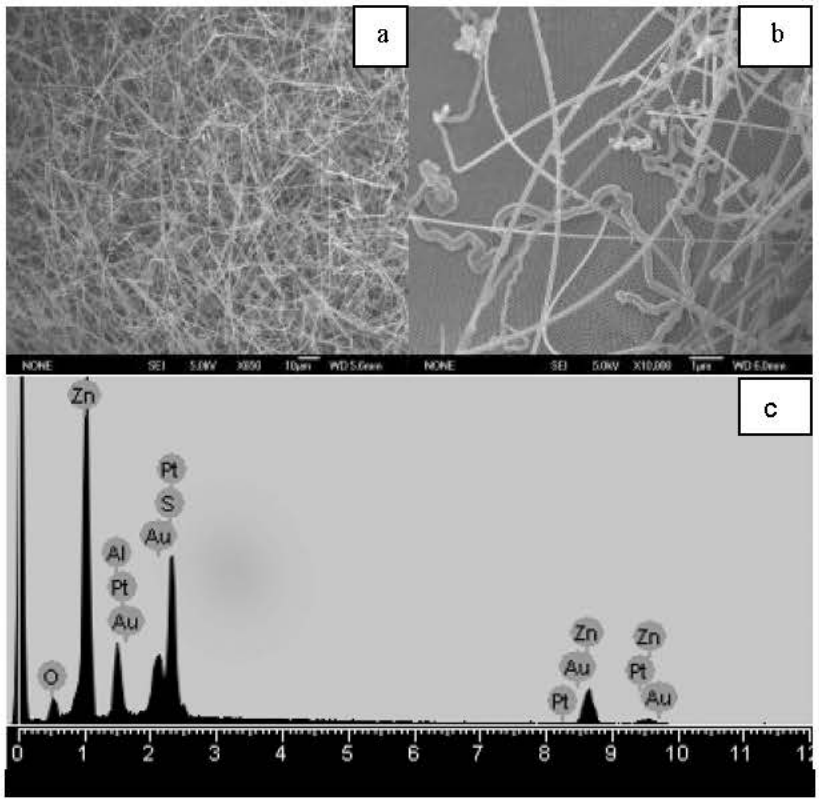


Fig. 1: (a) SEM image of as synthesis ZnS nanowires on AAO (low magnification), (b) Enlarged SEM image of the synthesis ZnS nanowires and (c) EDS of the ZnS nanowires

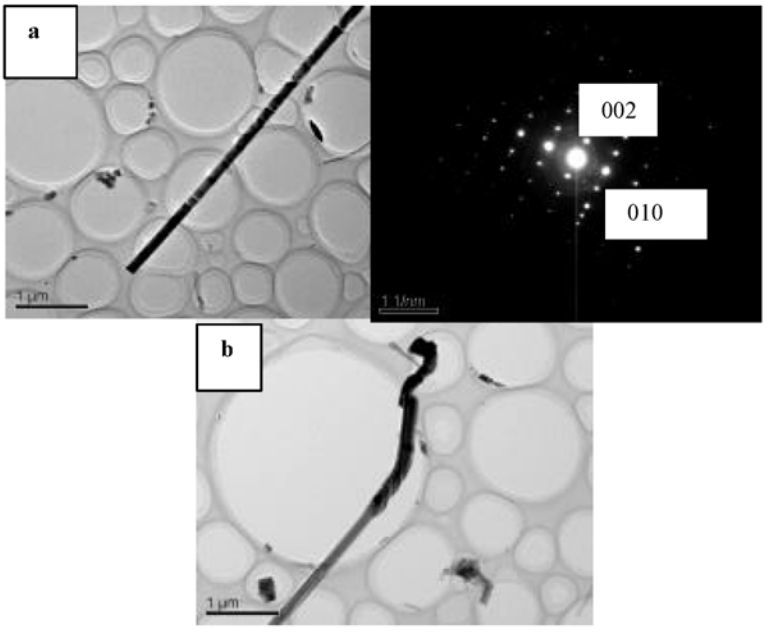


Fig. 2: (a) TEM image of an individual ZnS nanowire and (b) Nanoparticles of ZnS and Au in the tip of a nanowire

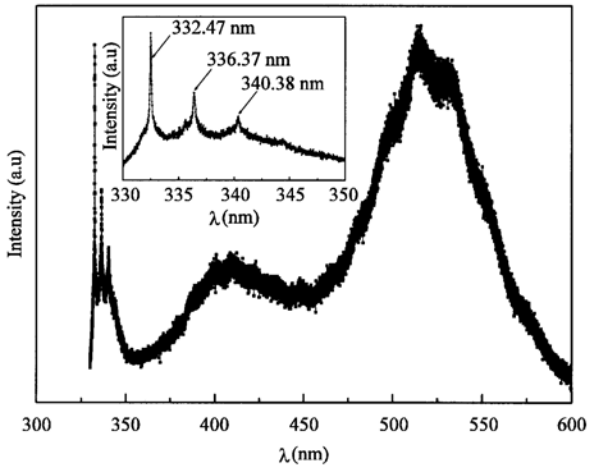


Fig 3: Room-temperature photoluminescence spectrum of the as synthesized ZnS nanowires

Zn and $H_2S$ reacted and formed ZnS and $H_2$. The $H_2$ would evaporate leaving ZnS/Au in the liquid droplets. As the concentration of ZnS reached super-saturation at the substrate temperature, the ZnS phase would then separate out from the droplet and form the ZnS nanowires, during the growth process, Zn and $H_2S$ vapors are continuously absorbed into the liquid droplet; ZnS would separate out continuously to form the ZnS nanowire with the Au particle at the tip. Consequently, the diameter of ZnS nanowires is controlled by the size of the Au (Zn) solid solution droplet and nanoholes of AAO template as it was suggested that the AAO itself serves as a catalyst in cracking the carbon feed stock for the graphite layer synthesis on the surface of the alumina (Gao *et al*., 2003; Jee *et al*., 2001). Also we point out that the formation temperature and the thickness of template are very important factors in controlling the structure of the product according to those ZnS nanowires grown on Si substrate (Meng *et al*., 2003).

The room temperature PL spectrum in Fig. 3, lasing has been observed in photoluminescence (PL) measurements. Which were obtained using a Confocal Laser Microraman Spectrometer (He-Cd laser, excitation wavelength 325 nm), indicates that the single crystal ZnS nanowires display three main broad emission peaks at 336 nm, 410 and 515 nm around 330-600 nm. The 336 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 (Spanhel *et al*., 1987; Yang *et al*., 2001). The third broad emission peak is at 515 nm. This emission is mainly attributed to the Au nanoparticles doping and the S vacancies in the single crystal ZnS nanowires (Yang *et al*., 2001; Zhao *et al*., 2003; Zhang *et al*., 2005). From above, we can see that the single crystal ZnS nanowire is ended with Au nanoparticle at one end, so the Au ions nanoparticle is doped in the single crystal ZnS nanowire. Otherwise from the EDS pattern, we can see that the atomic ratio of Zn to S in the ZnS nanowires is 36:28, so we can believe that in the ZnS nanowires there are some S vacancies. From the PL spectrum, we can also see that the broad emission

peak 336 nm is composed of three narrow peaks at about 332, 336 and 340 nm with full width at half maximum (FWHM) of about 0.3 nm and the intervals between the narrow peaks are about 4 nm. The narrowing of the PL peak and the concurrent super linear increase of peak intensity with excitation power indicates lasing action. The increasing red shift of the PL peak with power is typical for semiconductor lasers and is attributed to band-gap renormalization. So we suggest that, these narrow emission peaks in our work should be the lasing emission. (Zapien *et al*., 2004; Ding *et al*., 2004).

## CONCLUSIONS

Large-scale ZnS nanowires with diameter about 80 nm and length of several tens micrometers were successfully synthesized via a chemical vapor deposition process onto anodic aluminum oxide template in the presence of an Au catalyst. The room temperature PL spectrum of the products shows that there are three broad emission peaks at 336, 410 and 515 nm, respectively and the broad emission peak 336 nm is composed of three narrow peaks with full width at half maximum (FWHM) of about 0.3 nm and the intervals between the narrow peaks are about 4 nm.

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