

Hydrothermal Synthesis and Luminescent Properties of Microtubes Constructed by Fluffy ZnS:Mn²⁺ with Nanostructures

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Tubular micrometer-sized ZnS:Mn²⁺ constructed by fluffy nanostructures were fabricated in the mixed solutions of water and ethanol in a fixed volume ratio with the aid of ethylenediamine. In the X-ray diffraction pattern, the products obtained in the presence and absence of ethylenediamine show the wurtzite and sphalerite phases, respectively. Field-emission scanning electron microscopic images reveal the evolution process from nanowires to fluffy ZnS:Mn²⁺ to microtubes with the reaction times of 2, 4, and 8 hours at 100 °C, and the basal nanowires are below 10 nm in diameter. Photoluminescence and photoluminescence excitation spectra were investigated. The results suggest that the wurtzite phase, instead of the sphalerite phase ZnS:Mn²⁺ is luminescence-active for the ⁴T₁–⁶A₁ transition of the Mn²⁺ in the ZnS host. The excitation spectra monitored at orange emission bands exhibit sharp peaks at 320, 326 and 327 nm with increasing reaction times of 2, 4, and 8 hours, respectively, indicating the energy transfer from ZnS host to Mn²⁺ ions, and the blue-shifts compared with the band gap absorption of the bulk counterpart (344 nm) are also observed due to the quantum confinement effects. The formation mechanism of the wurtzite one-dimensional nanostructures at such a low temperature is proposed based on a molecular template mechanism involving the bidentate coordinating ligand, ethylenediamine, and the possible formation mechanism of novel tubular structure are also discussed.

Keywords: Hydrothermal Synthesis, Semiconductor, ZnS:Mn²⁺ Nanowires, Microtubes, Photoluminescence, Energy Transfer.

1. INTRODUCTION

One dimensional (1D) nanostructures such as nanowires and nanotubes are emerging as versatile building blocks for a “bottom-up” paradigm, pursuing the controllable synthesis of nanomaterials at the atomic level and hence, the widespread applications in both fundamental science and technology. In recent years, such 1D nanostructures have attracted intensive research because of their fascinating properties and promising future applications in optoelectronic devices and sensors.^{1–4} Many efforts have been focused on achieving 1D structures such as the thermal evaporation process⁵ and the hydrothermal technique, involving wet chemical methodologies^{3,6} at relative low temperature. As an important II–VI group semiconductor with wide band gap (3.6 eV), zinc sulfide

adopts two structure polymorphs: one is cubic sphalerite, the most stable phase under ambient conditions, and the other hexagonal wurtzite, a thermodynamically stable phase. The bulk cubic ZnS can transform to the hexagonal phase conversely at the high temperature of 1,020 °C. Because the wurtzite phase is much more desirable for its optical properties than the sphalerite structure, to synthesize wurtzite-phase ZnS at low temperatures is becoming extremely crucial and practical. Li's group⁷ reported the successful preparation of pure wurtzite-phase ZnS and ZnSe with 1D nanostructures via the solvothermal route using ethylenediamine (EN) as liquid media and proposed a reasonable solvent coordinating molecular template mechanism to explain the formation process of 1D materials.⁸ Novel wurtzite ZnS with hierarchical architectures has been synthesized by Qi's group⁹ and explained by the Ostwald-ripening involved formation mechanism.^{10,11}

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ZnS doped with transition-metal ions such as manganese or rare earth ions like terbium ions is one kind of important luminescent material used in displays and electroluminescent devices, and its zero-dimensional (0D) nanostructures are well documented,^{12-15,19} however, 1D nanosized counterparts have rarely been reported to the best of our knowledge. Lieber's group reported the synthesis of Mn²⁺-doped ZnS and GaN nanowires through chemical vapor deposition technology.¹ ZnS:Mn²⁺ nanorods prepared by the solvothermal method have been reported¹⁶ with an interesting finding that the doped Mn²⁺ ions in the ZnS host prefer to be inside the cubic phase rather than the hexagonal phase. In this work, by means of hydrothermal methodology, tubular micrometer-sized ZnS:Mn²⁺ constructed by fluffy nanostructures are fabricated in mixed solutions of water and ethanol in a fixed volume ratio with the assistance of EN. The morphology evolution process from nanowires to fluffy structures to ZnS:Mn²⁺ microtubes is investigated through time-dependent experiments by prolonging the reaction time from 2 to 4 to 8 hours at 100 °C. The photoluminescence (PL) and PL excitation spectra are measured to investigate the optical properties of the samples. The formation mechanism of the wurtzite 1D nanostructures in such mild and low-temperature conditions is also discussed.

2. EXPERIMENTAL DETAILS

All the starting chemical reagents were analytical grade, purchased from Beijing Chemicals Co. Ltd., and are used as received without further purification. Appropriate amounts of zinc acetate [Zn(CH₃COO)₂ · 2H₂O], manganese acetate [Mn(CH₃COO)₂ · 4H₂O] and thiourea (NH₂CSNH₂) were dissolved into a mixed solvent of water and ethanol with a fixed volume ratio as stock solutions. In the typical synthesis procedure, 20 ml solutions containing Zn²⁺ and Mn²⁺ ions with a molar ratio of 50:1 and 10 ml thiourea solutions were stirred with a magnetic stirrer at room temperature for a few minutes. Thiourea was used in stoichiometric ratio. Then, ethylenediamine and 10 ml ethanol were added to the mixture followed by simultaneously stirring for another 10 minutes to homogenize the mixture. Three resultant mixtures were transferred into six 50-ml Teflon-lined stainless steel autoclaves on average keeping the left volume ratio to be 40%. The sealed chambers were placed in an electric oven and maintained at 100 °C for 2, 4 and 8 hours respectively. After the reaction, the autoclaves were cooled to room temperature naturally. The resulting precipitate was collected and washed several times with deionized water and ethanol to remove the possible residues. The final product was then dried in a vacuum at 70 °C for 8 hours to obtain the white powder.

The data of X-ray diffraction (XRD) patterns were obtained on a Rigaku D/Max 2500V PC diffractometer operated at 18 kW with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Field-emission scanning electron microscopy (FE-SEM)

images were measured on a Hitachi S-4800. PL and PL excitation spectra were recorded on a Hitachi F-4500 Spectra-fluorometer equipped with a 150 W Xe-arc lamp at room temperature.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the prepared ZnS:Mn²⁺ in the absence (Fig. 1(d)) and presence of EN at 2, 4 and 8 hours (Figs. 1(a, b, and c)). It can be seen in Figure 1(d) that the diffraction peaks are indexed as sphalerite ZnS in agreement with the standard JCPDS card No. 05-0566. The broadening of the diffraction peaks suggests the existence of nanostructures. When EN is introduced into the reaction precursor, the wurtzite phase is observed in the product as demonstrated in Figures 1(a, b, and c). The diffraction peaks can be indexed as wurtzite-phase zinc sulfide with (100), (002), (101), (110), (103), and (112) diffraction peaks in the literature data (JCPDS card No. 36-1450). The sharp and dominated intensity nature of the (002) peaks indicates that the 1D nanostructures grow along the *c* axis. With the prolonged reaction time, the (100), (101), and (103) character peaks of wurtzite ZnS are manifest due to the gradually improving crystallinity of the samples. No peaks of impurities were detected indicating high purity of the product. The result revealed that EN plays an important role in the formation of hexagonal structures and will be discussed later based on the fact that wurtzite ZnS can be obtained with the assistance of EN in such preparation conditions where the cubic phase is formed in the absence of EN.

The morphology and dimensions of the samples prepared with various reaction times from 2 to 8 hours were examined by FE-SEM, and the typical images are shown in Figure 2. As can be seen in Figure 2, the morphology evolution from nanowires to fluffy structures to microtubes

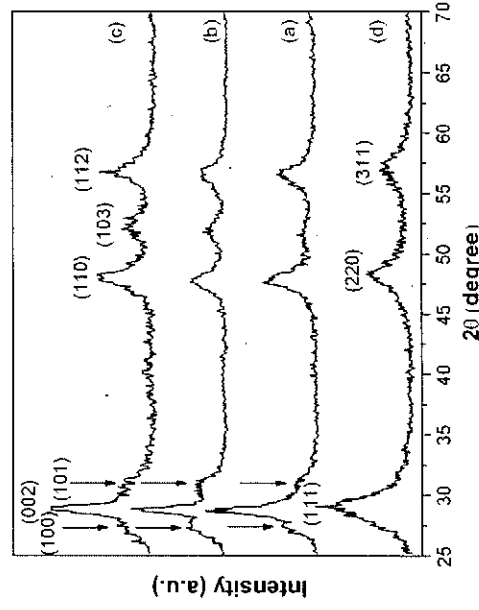


Fig. 1. XRD patterns of obtained sample prepared with different reaction times (h: hours) in the presence [(a) 2 h; (b) 4 h; (c) 8 h] and absence (d) of ethylenediamine.

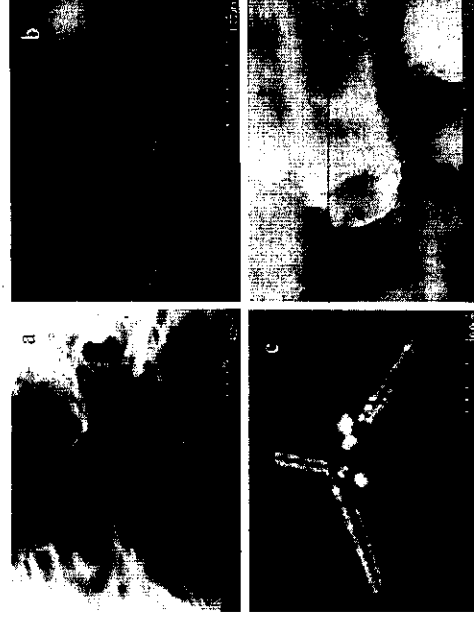
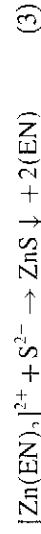
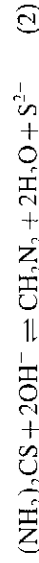
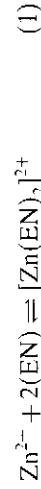


Fig. 2. FE-SEM images of products prepared in different reaction times from (a) 2 h, (b) 4 h, to (c) 8 h. (d) is one typical magnified section of tubular ZnS:Mn²⁺.

is clearly presented. The nanowires were below 10 nm in diameter and over 500 nm in length (Fig. 2(a)) when the reaction was carried out within 2 hours, a relatively shorter time span. With the reaction time prolonged to 4 hours, the nanowires get tangled and aggregated to generate the fluffy ZnS:Mn²⁺ (Fig. 2(b)), and these fluffy spheres show the tendency of self-organizing along a 1D direction followed by the formation of microtubes (Fig. 2(c)). Figure 2(d) shows one typical magnified section of a hollow tubular ZnS:Mn²⁺ structure with an inner diameter of about 500 nm and a robust, smooth shell indicating the improved crystallinity. This is also evidenced by the sharp diffraction peak (002) and more apparent peak (103) when the XRD patterns in Figures 1(a) and (c) are compared.

To elucidate the mechanism of wurtzite structure formation and 1D growth process, the molecular soft template role of EN should be considered. In our synthesis system, EN as a strong bidentate coordinating ligand, tended to form relatively stable Zn²⁺ complexes with $\log\beta$ of Zn(EN)₃ to be 14.11.⁷ The thiourea as the sulfur source was ready to decompose and generate S²⁻ as described in the following equations at current temperature (100 °C) accompanied by alkaline conditions:



It has been reported that smaller wurtzite ZnS in vacuum is more thermodynamically stable than sphalerite phase and the transition temperature from sphalerite to wurtzite decreases dramatically as the particle size decreases below 20 nm due to the surface free energy effects.¹⁷ In our current work, EN plays the crucial role of strong coordinating ligand, resulting in very small nanoparticles with the thermodynamically stable wurtzite phase, and hence,

aggregating to larger cell stacks. Moreover, the initial addition of thiourea into the Zn²⁺ solution is expected to form [Zn(TU)₂]²⁺ (TU = thiourea molecule) complexes providing another strengthened coordinating effect. With the reaction time prolonged, more and more nanoparticles are produced and subsequently the wurtzite structure appears due to the free energy effects. In contrast to the preparation condition in the presence of EN, the cubic phase is reasonably formed in the EN-free synthesizing system.

EN has been found to be helpful in forming 1D structures of ZnS and CdS due to its chelating properties in a solvothermal process adopting EN as the solvent.^{6–8} Under this synthesis condition, EN molecules are expected to adsorb on the formed nanowires, which prevents them from coagulating as shown in Figure 2(a). The growth of the 1D nanostructures is ascribed to the highly anisotropic crystal structure and the structure-directing coordination template effects of EN. With the reaction time increasing, EN is evacuated gradually, the resultant nanowires tangle with each other, and the fluffy structure occurs via the Ostwald ripening process.^{10,11} It is worth noting that these fluffy ZnS:Mn²⁺ with wurtzite phases can be self-assembled to form the 1D microtubes. The formation mechanism of this tubular architecture is still unclear; however, a plausible explanation is proposed as follows. First, the relatively stable wurtzite phase nanowires are formed within a short reaction time (2 hours in this work) with the adsorption of EN molecules on the surface. After the occurrence of fluffy ZnS:Mn²⁺, the surface of the fluffy sphere is still capped with large amounts of EN molecules due to the decreased surface free energy. With the reaction duration increased, the EN is removed and the Ostwald ripening process becomes dominant. The steric hindrance of the EN molecules between the [Zn(EN)]²⁺ complexes may play a crucial role in the formation of hollow tubular structures.

PL and PL excitation spectra (upper in Fig. 3) are measured to investigate the optical properties of the nanowires and fluffy and tubular ZnS:Mn²⁺ compared with the sample prepared in the absence of ethylenediamine (lower in Fig. 3). Two emission bands appear in the PL spectrum of the tubular sample when under the excitation of 327 nm. One is a band-to-band emission peaking at around 340 nm, and the other is characterized by the ⁴T₁–⁶A₁ transition of the Mn²⁺ ion in T_d symmetry, which is located at 566 nm. The PL excitation spectra monitored at the orange emission bands exhibit sharp peaks at 320, 326, and 327 nm with increasing reaction times from 2 to 8 hours, which are blue-shifted compared with the band gap absorption of the bulk counterpart (344 nm) due to the quantum confinement effects. These UV excitation peaks are attributed to the ZnS host, indicating the energy transfer process between the host and Mn²⁺ impurities. The longer the reaction time, the stronger the orange Mn²⁺ emission is. One can deduce that the crystallinity

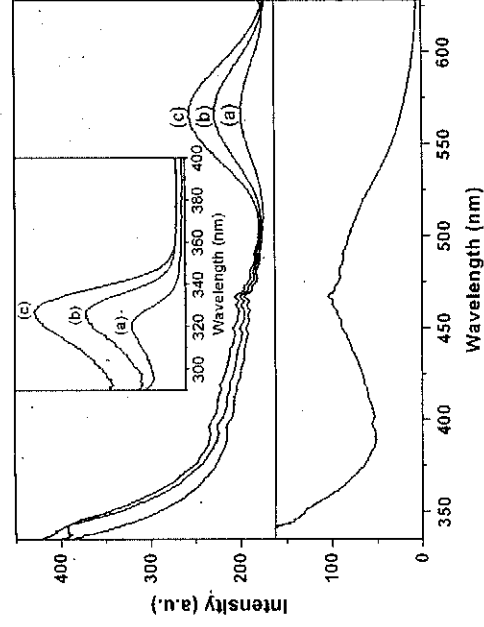


Fig. 3. PL spectra (a: λ_{ex} = 320 nm; b: λ_{ex} = 326 nm; c: λ_{ex} = 327 nm) of microtubes of ZnS:Mn²⁺ in the presence (upper) and absence (lower) of ethylenediamine. Inset is the PL excitation spectra of (λ_{em} = 566 nm) of samples obtained with different reaction times (a: 2 h; b: 4 h; c: 8 h).

is remarkably improved with the prolonged time, which is in agreement with the results from the XRD and FE-SEM images. With respect to the EN-free condition, a broad green band centered at about 470 nm with a shoulder at around 350 nm is observed in the PL spectrum (lower Fig. 3). The former is originated from self-activated defect centers formed by zinc/sulfur vacancies,^{18,19} in the ZnS host lattice, and the latter is from the band-edge (or excitonic) emission. In the absence of EN, Mn²⁺ ions do not occupy the sites that favor the orange emission. These results reveal that the wurtzite phase is desirable and luminescence-active for Mn²⁺ ⁴T₁–⁶A₁ orange emission rather than the sphalerite phase.

In summary, ZnS:Mn²⁺ microtubes constructed by fluffy spheres with nanowires are fabricated using hydrothermal techniques with the aid of ethylenediamine. X-ray diffraction analysis indicates that the product obtained in the presence of ethylenediamine shows the wurtzite phase and the product obtained in the absence of EN shows the sphalerite phase. The wurtzite phase, instead of the sphalerite phase ZnS:Mn²⁺ is luminescence-active for the ⁴T₁–⁶A₁ transition of Mn²⁺ in the ZnS host. The formation mechanism of the wurtzite ID nanostructures in such a mild and low-temperature condition is proposed based

on a molecular template mechanism involved the bidentate coordinating ligand, ethylenediamine, and the possible formation mechanism of novel tubular structure evolved from ZnS:Mn²⁺ nanowires and fluffy structures is also put forward to be related to the steric hindrance of EN molecules between [Zn(EN)]²⁺ complexes and Ostwald-ripening effects.

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