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Preparation and photoluminescence of single-crystal zinc selenide nanowires

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Abstract

Single-crystal ZnSe nanowires have been synthesized via a thermochemical method in a N_2 atmosphere with CO and H_2 gases. The as-prepared ZnSe nanowires have a mean diameter of 40 nm and a length of 1 μm. The nanowires are single crystals with a hexagonal structure growing along the [0 0 1] direction. A self-catalyzed vapor–liquid–solid process is proposed for the formation of such nanowires. The as-prepared nanowires show two emission bands at ca. 447 and 617 nm.

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1. Introduction

Selenides as wide-band-gap II–VI semiconductor materials have been studied extensively due to their wide applications in the fields of light-emitting devices, solar cells, sensors, and optical recording materials [1–4]. ZnSe is one of the promising materials for fabrication of light-emitting devices, such as blue–green laser diodes [1,2], and turnable mid-IR laser sources for remote-sensing applications [5]. ZnSe also has potential application in optically controlled switching due to its giant photoresistivity [6].

Nanoscale semiconductor materials represent an area of ever-increasing research interest, due to the unique optical and electronic properties demonstrated by these quantum-confined nanostructures such as quantum dots (0D), quantum wires (1D), and quantum sheets (2D) [7]. 1D semiconductor nanostructures are of special interest in the assembly of nanodevices, such as logic circuits, nanosensors, nanolasers etc. [8–10]. 1D nanoscale materials have been shaped into various morphologies, such as nanotubes, nanocables, nanowires, and nanobelts [11–13]. Many attempts have been made to prepare ZnSe nanostructures and study their optical and electronic properties. ZnSe nanocrystallites have been synthesized using surfactant-assisted chemistry methods [14,15], a sonochemical method [16], solvothermal routes [17], and a vapor-phase synthesis etc. [18]. Most of these researches are focused on ZnSe nanoparticles, while there are few reports on the preparation and characterization

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of one-dimensional ZnSe nanostructures [6,19,20]. ZnSe nanowires or rods have been synthesized by using a template method [6], a solvothermal method [19] and vapor phase growth method [20]. In this Letter, we report the preparation, structural characterization, and the photoluminescence (PL) property of zinc selenide nanowires by using zinc selenide powders as precursors via a thermochemical process. This process involves a self-catalyzed vapor–liquid–solid (VLS) mechanism without using additional catalysts such as gold etc. [20], which means a low cost and high purity of the products.

2. Experimental

ZnSe nanowires were prepared according to the method described in our previous work [21]. An induction furnace was used for the synthesis of ZnSe nanowires. Graphite powders and fibers were put into a graphite crucible, above which the other crucible containing zinc selenide powders was arranged. All the components were enclosed in a graphite susceptor, and the susceptor was put in the center of the furnace with a flowing N_2 atmosphere (1.5 l/min). The temperature of the susceptor was controlled to ensure that graphite powders were heated to 1600 °C, while the zinc selenide powders were heated to 1250 °C. The N_2/H_2O stream (obtained from bubbling N_2 through distilled water) was managed to pass through and react with the graphite powders at 1600 °C for the generation of CO and H_2 gases. Next, the N_2 stream, together with the CO and H_2 gases, passed through zinc selenide powders. After the process was conducted for 2 h, the furnace was cooled down. A yellow product was obtained after the synthesis. After the product was dispersed into ethanol, it was transferred onto a copper mesh. The specimen was then characterized using a JEM-3000F (JEOL) field emission high-resolution transmission electron microscope (HRTEM) operated at 300 kV, which was attached with an energy dispersive X-ray spectrometer (EDS). PL measures were taken at room temperature using a He–Cd laser line of 325 nm as the excitation source.

3. Results and discussion

The TEM analysis shows that as-prepared nanowires have a uniform morphology with a mean diameter of 40 nm and a length of 1 μm, as shown in Fig. 1. Fig. 2 shows the HRTEM image and electron diffraction (ED) pattern of a ZnSe nanowire. The ED pattern can be indexed as a hexagonal phase with lattice constants of $a = 0.40$ nm and $c = 0.65$ nm, recorded from [1 −1 0] zone axis. The measuring *d*-spacings of (1 1 0) and (0 0 2) planes are 0.20 and 0.33 nm, respectively, which are consistent with the ideal values of wurtzite ZnSe (JCPDS Card: 80-0008). The axis direction of the as-prepared ZnSe nanowires is generally along [0 0 1], as confirmed by the ED pattern and

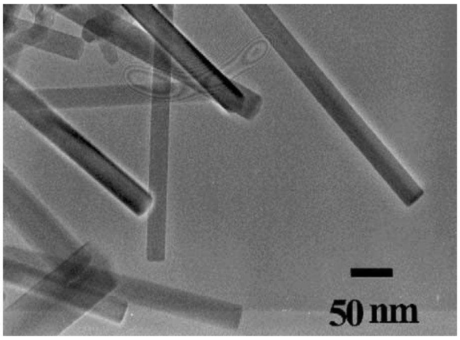

Fig. 1. TEM morphology of ZnSe nanowires.

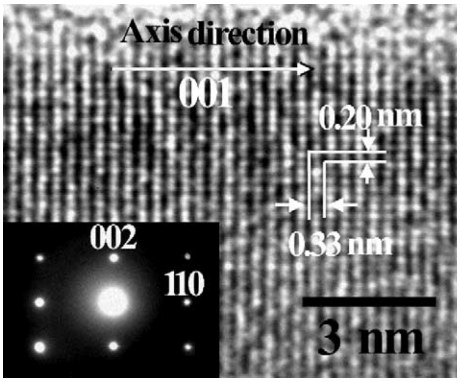

Fig. 2. HRTEM images of ZnSe nanowires. The inset is the corresponding ED pattern with [1 −1 0] incidence. The *d*-spacings of 0.33 and 0.20 nm correspond to the (0 0 2) and (1 1 0) planes.

HRTEM image. The perfect diffraction pattern and lattice fringes indicate that the nanowire is a single crystal.

A VLS mechanism is proposed for the formation of ZnSe nanowires, as confirmed by the evidence shown in Fig. 3. Fig. 3a shows the HRETM image of ZnSe nanowires in the intermediate growth stage. The columns of the nanowires are crystal ZnSe, which are composed of Zn and Se with a ratio of 1:1, as confirmed by the EDS in Fig. 3b. The tops of the nanowires have hemisphere morphology. The hemisphere is an amorphous phase and is mainly composed of Zn, as confirmed by the EDS in the inset of Fig. 3b. The EDS is performed with a nanobeam of 0.6 nm. The formation process of the ZnSe nanowires is a self-catalyzed process, without additional catalysts such as gold metal etc., as reported in many cases [20,21]. The overall process of the formation of ZnSe nanowires may involve the following reactions

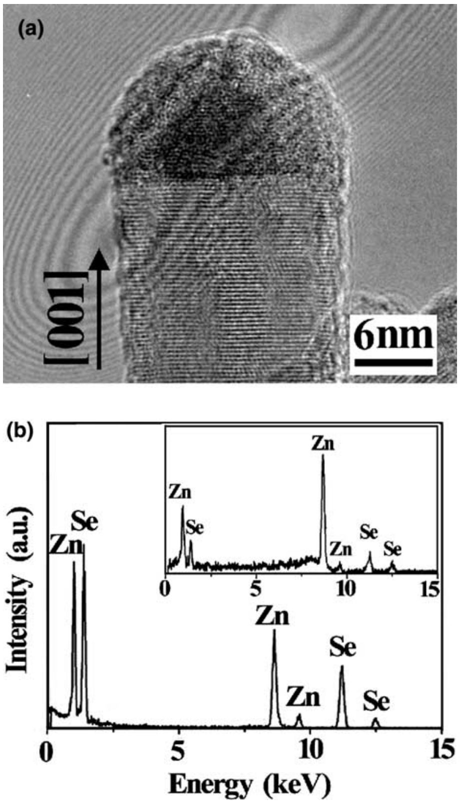

Fig. 3. (a) HRTEM images and (b) EDS of ZnSe nanowires in the intermediate growth stage. The column of the nanowires is single-crystal ZnSe, the top is Zn-rich amorphous phase which is in liquid state during the growth stage of ZnSe nanowires.

$$\mathrm{ZnSe}_{(s)} \leftrightarrow \mathrm{ZnSe}_{(g)} \tag{1}$$

$$\mathrm{ZnSe}_{(g)} \leftrightarrow \mathrm{Zn}_{g} + \mathrm{Se}_{(g)} \tag{2}$$

$$\mathrm{ZnSe}_{(g,s)} + \mathrm{H}_2 \leftrightarrow \mathrm{Zn}_{(g)} + \mathrm{H}_2\mathrm{Se} \tag{3}$$

$$\mathrm{Zn}_{(g)} \rightarrow \mathrm{Zn}_{(s)} \tag{4}$$

The ZnSe powders evaporated into vapors, which may be further decomposed into Zn, Se, and other clusters during the heating process. Zn vapors were solidified to form liquid Zn-rich nano-droplets in the low temperature regions due to the low melting point of Zn (ca. 410 °C) as shown in Fig. 3a. The Zn-rich droplets act as a catalyst for the formation of ZnSe nanowires. The Zn, Se and other gaseous clusters were dissolved into the nano-droplets forming eutectic composites. When ZnSe was supersaturated in the droplet, a ZnSe nanowire grew out of the droplet. The growth axis of ZnSe nanowires is along the [0 0 1] direction, which is consistent with its crystallographic characteristics. The hexagonal ZnSe crystal can be regarded as a stacking of $\{\mathrm{ZnSe}_4\}$ tetrahedra by sharing their common corners. In the [0 0 1] direction of the hexagonal ZnSe crystal, each tetrahedron has a corner that favors a rapid growth due to its stronger bond force comparing with the atoms at other positions [22,23]. The atmosphere is an important factor for the formation of sulfides and selenides nanostructures [24–26], because nanoscaled sulfides and selenides are easily oxidized. In this work, the atmosphere was controlled by mixing N_2 with reductive agents CO and H_2 produced in situ.

The as-prepared ZnSe nanowires show strong emission at room temperature, as shown in Fig. 4. The PL spectrum of ZnSe nanowires presents two emission bands around 447 and 617 nm when excited at 325 nm. The emission at 447 nm is very weak comparing with that at 617 nm. The weak emission band around 447 nm is usually attributed to the edge emission of ZnSe [27]. The strong orange emission at about 617 nm is associated with

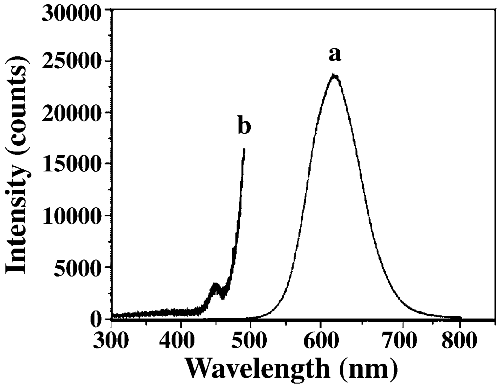

Fig. 4. Photoluminescence spectrum of ZnSe nanowires with an excitation wavelength at 325 nm. Curve (b) is the enlargement of a portion of curve (a).

the vacancies of Zn in ZnSe [30]. This emission band is often observed in bulk ZnSe, which is interpreted as well known 'self-activated' luminescence in II–VI compounds due to recombination of shallow donor–deep acceptor pairs [27–29,31]. ZnSe nanowires may have potential application as phosphors due to their strong emission.

4. Conclusion

In summary, single-crystal ZnSe nanowires were synthesized via a simple thermochemical process using ZnSe powders as a precursor in a N_2 atmosphere with CO and H_2. The as-prepared ZnSe nanowires have a hexagonal wurtzite structure and grow along the [0 0 1] direction. The formation mechanism of these nanowires is a self-catalyzed VLS process through the evaporation and decomposition of a precursor followed by the condensation, nucleation and growth. The PL of the nanobelts shows a weak emission band at 447 nm and a strong emission band around 617 nm.

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