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Synthesis, field emission and optical properties of ZnSe nanobelts, nanorods and nanocones by hydrothermal method

Q.Z. Zeng, S.L. Xue*, S.X. Wu, K.X. Gan, L. Xu, J.W. Han, W.K. Zhou, Y.T. Shi, R.J. Zou

College of Science, Donghua University, Shanghai 201620, China

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ABSTRACT

ZnSe nanostructures, such as nanobelts, nanorods and nanocones, were successfully synthesized on Zn foils via a hydrothermal method using EDTA as soft template at low temperature. EDTA played a significant role on the morphology of ZnSe nanomaterials. X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM) and energy dispersive spectrometer (EDS) were carried out to characterize the microstructures and chemical compositions of the as-synthesized ZnSe samples. XRD patterns indicated that the as-synthesized ZnSe samples belonged to a cubic zinc blende structure. SEM observation obviously showed that the nanocones had very sharp tips compared to nanorods and nanobelts. The field emission (FE) measurement showed that the as-synthesized ZnSe nanocones had a lower turn-on field of $\sim 1.6\ \mathrm{V\ \mu m^{-1}}$ at the current density of $10\ \mathrm{\mu A\ cm^{-2}}$. A high field enhancement factor of ~4514 was achieved for the ZnSe nanocones. The superior field emission properties were probably attributed to the sharp tips of the ZnSe nanocones. Room temperature photoluminescence (PL) spectroscopy of the ZnSe nanostructures showed a wide band emission from blue light to orange light. The as-prepared ZnSe nanomaterials have promising applications in optoelectronic devices. A possible formation mechanism of ZnSe nanobelts, nanorods and nanocones was also proposed and discussed.

1. Introduction

One-dimensional (1D) semiconductor nanostructures such as nanotubes, nanowires, nanobelts, and nanorods have received considerable interest due to their novel electrical and optical properties, superior to their bulk counterparts for applications [1–4]. For example, Zhen et al. [5] reported that the optical and field emission (FE) properties of layer-structure GaN nanowires by using chemical vapor deposition (CVD). Yang et al. [6] studied that the needle-shaped MoO_3 nanobelts are stable enough for various field emission applications. Ranjusha [7] also studied the electrical and optical properties of ZnO nanotubes. All these one-dimensional semiconductor nanomaterials are perfect materials as field emission cathode because of their small tip radius, high aspect ratios, small radii of curvature and high electrical conductivities [8–10]. Among various applications of these nanostructures, field emission is of great scientific and commercial interest due to its potential applications in flat-panel displays, X-ray sources, microwave power amplifiers, traveling wave tubes, and other vacuum microelectronic devices [11–16].

As an important wide-band gap semiconductor material, ZnSe exhibits a direct band gap of 2.67 eV ($1\ \mathrm{eV} = 1.609 \times 10^{-19}$ J) with a large exciton binding energy of 21 meV at room

* Correspondence to: 2999, North Renming Road, Songjiang District, Shanghai 201620, China. Tel.: +86 21 66792089 561.

E-mail address: slxue@dhu.edu.cn (S.L. Xue).

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temperature [17]. One-dimensional ZnSe nanostructures have been extensively investigated by many researchers due to their unique properties, which have wide applications in photodetectors [18,19], blue light-emitting diodes (LEDs) [20,21], laser diodes (LDs) [22], sensors [23], solar cells [24], and field emitters [25], and so on. ZnSe nanorods/wires have been synthesized by a variety of preparation methods, including thermal evaporation [23,26], chemical vapor deposition [27], laser ablation [28], and solvothermal reaction [29,30]. However, to the best of our knowledge, a few reports are available which investigated the field-emission behavior of ZnSe nanostructures. For example, Su et al. [31] reported that ZnSe nanoarrays had good FE properties with a low turn-on field of 4.05 V μm^{-1}. Zhao et al. [25] synthesized ZnSe nanoribbons with a high field enhancement factor of 1382.

In the present work, novel ZnSe nanostructures were synthesized by a hydrothermal method. Different morphologies of ZnSe were obtained by changing the amount of EDTA. The as-prepared samples were characterized by XRD, EDS, SEM and TEM. The as-prepared ZnSe nanomaterials were of cubic zinc blende structure. The experimental results showed that the as-prepared ZnSe nanostructures, such as nanobelts, nanorods and nanocones, all exhibited high field emission performance and good optical characteristics. Such ZnSe nanostructures have the potential for optoelectronic applications.

2. Experimental details

2.1. Synthesis of ZnSe nanostructures

All chemicals were of analytical grade and used as received without further purification. Zinc acetate dihydrate ($Zn(CH_3COO)_2\cdot 2H_2O$) ($\geq$99.0%), ethylene diamine tetraacetic acid (EDTA) ($\geq$99.0%), sodium hydroxide (NaOH) ($\geq$97.0%), zinc foils (Zn) ($\geq$99.0%) and selenium powder (Se) ($\geq$99.7%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All aqueous solutions were prepared using deionized water.

The hydrothermal synthesis process was carried out as follows. First of all, Se (0.005 mol, 0.39 g), Zn $(CH_3COO)_2\cdot 2H_2O$ (0.005 mol, 1.10 g) and NaOH (0.16 mol, 6.4 g) were dissolved in 40 ml of deionized water. This solution was stirred with a magnetic stirrer for 70 min. Subsequently, Zn foils (0.003 mol, 0.20 g) with a dimension of (1 cm $\times$ 1 cm) and different amounts of EDTA were added into the mixing solution. At last, the final solution was transferred to a Teflon-lined autoclave with 0.75 filling factor and sealed, hydrothermally treated at 190 °C for 36 h. After the solution was cooled down to room temperature, the Zn foils were taken from the yellow precipitate. The Zn foils were washed several times with distilled water and ethanol. The final samples were dried in a vacuum at 60 °C for 2 h. All measurements were directly performed on the Zn foils to characterize the as-synthesized samples at room temperature. The exact conditions during the synthesis were given in Table 1.

2.2. Characterization

The crystal structure and phase composition of the as-synthesized samples were identified using an X-ray diffraction (XRD; Rigaku D/Max 2550) with Cu Kα radiation operated at 40 kV and 200 mA in a 2θ range of 20–70°. The surface morphology and composition of the as-synthesized samples were investigated by a scanning electron microscope (SEM; JEOL JSM-5600LV), equipped with X-ray energy dispersive spectroscope (EDS; Oxford IE 300 X). Detailed microstructure was investigated by transmission electron microscopy (TEM; Hitachi H-600) and high-resolution transmission electron microscopy (HRTEM; JEOL JEM-2100). Field emission properties of the as-synthesized samples were measured in a vacuum chamber under the pressure of $\sim 5\times10^{-4}$ Pa (FE; CS-180 field emission performance testing instrument). The room temperature photoluminescence (PL) spectrum was recorded by a luminescence spectrometer (PL; Edinburgh FLS920).

Table 1
Samples were prepared at different amounts of EDTA.

Morphology	EDTA (mol)	Reaction temperature (°C)
Nanobelts	0.010	190
Nanorods	0.015	190
Nanocones	0.020	190

3. Results and discussion

3.1. XRD and EDS analysis

The XRD patterns of the as-synthesized ZnSe nanostructures with three different morphologies on the Zn foils are presented in Fig. 1(a). All the diffraction peaks in the pattern can be indexed to (111), (200), (220), (311) and (222), which are consistent with the standard values in JCPDS File no.37-1463. Hence, the as-synthesized ZnSe samples are in accordance with cubic zinc blende (ZB) structure ZnSe with the lattice constant of a=5.669 Å. Very narrow and sharp diffraction peaks indicate the as-synthesized ZnSe samples with good crystallinity. The average grain size of the samples can be evaluated according to most prominent XRD peak using Scherrer's formula as follows:

$$D = k\lambda/\beta \cos\theta$$

where D is grain size in nm, k is the Scherrer constant of 0.89, λ is wavelength of X-ray radiation (1.5406 Å) used, θ is Bragg diffraction angle and β is FWHM. The average grain sizes of the ZnSe nanostructures with three different morphologies are listed in Table 2. The increase of average crystallite size may be due to different amounts of EDTA.

Fig. 1(b), (c) and (d) shows the element composition of the as-synthesized ZnSe nanobelts, nanorods and nanocones respectively, by energy dispersive spectrometer (EDS). The EDS spectra show that all the as-synthesized samples are principally composed of Zn and Se, and the atomic ratio of Zn to Se is 0.98:1 in nanobelts, 0.94:1 in nanorods and 0.97:1 in nanocones, respectively. Because the atomic ratio of Zn to Se is slightly less than 1 there may be some Zn vacancies in the as-prepared ZnSe samples. The EDS results corresponded to the XRD results demonstrate that the as-synthesized samples are of cubic zinc blende ZnSe.