

Rapid synthesis and visible photoluminescence of ZnS nanobelts†

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Received (in Cambridge, UK) 9th August 2004, Accepted 27th September 2004

First published as an Advance Article on the web 29th November 2004

DOI: 10.1039/b412289e

Belt-like ZnS with visible photoluminescence was synthesized rapidly with Zn and S in the vapor phase.

ZnS, a II–VI semiconductor with a band-gap energy of 3.7 eV at room temperature, has received much attention due to its prominent application in many fields.¹ As a well-known luminescence material, ZnS shows various luminescence properties such as photoluminescence,² electroluminescence³ and mechanoluminescence,⁴ which enables it to be widely applicable in the fields of displays, sensors and lasers. Transition-metal-element or rare-earth-element doped ZnS has been used as an effective phosphor material for a long time.⁵ Core-shell structured CdS/ZnS nanocrystals have recently been found to exhibit a laser effect.⁶ However, controlling the size and the dimensionality of ZnS crystals may lead to further novel properties due to the quantum confinement effect, which may extend their application area.⁷ Much attention has been focused on the synthesis of the zero-dimensional, one-dimensional or films of ZnS *via* several approaches, for example, ZnS nanoparticle synthesis with reversed micelles,⁸ ZnS nanowire preparation with a liquid crystal template and a micelle template.⁹ Since the discovery of oxide semiconductor nanobelts, the preparation and characterization of different kinds of nanobelts have attracted much attention.¹⁰ ZnS nanobelts have been synthesized through a thermal evaporation process by using zinc sulfide powder as the starting material. Lee and collaborators have prepared large scale ZnS nanobelts by the assistance of a reductive gas.¹¹ Li, Zhu and collaborators have prepared ZnS nanobelts by using gold as the catalyst.¹² Zhu and collaborators have recently found that only when the temperature is lower than 1180 °C can ZnS nanobelts be prepared by an evaporation method.¹³ Jiang and collaborators have prepared modulated ZnS nanobelts by a laser ablation method.¹⁴ A vacuum, relatively high temperature, use of a special gas and occasionally the use of a catalyst are crucial in the preparation of ZnS belts; besides which, a very long time (more than 1 hour) is needed to collect a sufficient amount of nanobelts during the evaporation process. In our present work, a convenient method is reported to synthesise ZnS nanobelts rapidly; the product shows belt-like morphology and visible photoluminescence.

The synthesis of ZnS nanobelts was carried out in a quartz tube mounted horizontally inside a tube furnace with Zn and S used as the source materials. Zn (0.25 g) was enclosed by a network and placed in the center of the quartz tube, while S (0.3 g) was placed about 15 centimeters away. A pure N₂ flow was used as the protection and carrier gas which blew from the S side to the center

of the tube. The temperature was kept constant during the whole process. After reacting for 5 minutes, a white fluffy product can be obtained inside the network. The product was characterized as the following which showed a belt-like morphology. Nanobelts can be obtained at a temperature range of 700 to 1000 °C with an iron, copper or asbestos network; without the network, only particles can be found. At low temperatures, a small amount of nanobelts was found with a large quantity of particles. At high temperatures, excessively grown nanobelts reached bulk ZnS. The most suitable temperature for the synthesis is 900 °C. Excessive S is employed in the synthesis which can be easily sublimed over 700 °C. As a result, no unreacted Zn or S was found in the product. The samples used in the following are prepared within an iron network.

Scanning electron microscopy (SEM) was employed in the morphology characterization and elemental analysis (Fig. 1). The typical length of the ZnS nanobelts is in the range of several tens to several hundreds of micrometers and width of several hundreds of nanometers to several micrometers. The thickness of most of the belts is estimated to be about 20 to 30 nanometers through high magnification. As synthesized through previous methods, most of the ZnS nanobelts are uniform in morphology. Energy dispersion spectroscopy (EDS) showed that the atomic content of Zn and S is almost the same in the samples. The SEM and EDS results reveal the formation of the ZnS nanobelts, which is consistent with XRD results.

The structure and morphologies of the ZnS nanobelts were further characterized by transmission electron microscopy (TEM). They are transparent to the electron beam which suggests that the thickness of these nanobelts is small. Dark lines due to bending contours can be typically observed by TEM in slightly bent nanobelts. Almost all of the nanobelts showed large width to thickness ratio and uniformity in width. Selected-area electron diffraction (SAED) presented a perfect single crystal property. The corresponding high-resolution TEM studies showed a wurtzite structure with a [100] zone axis (Fig. 2). The measured spacing of

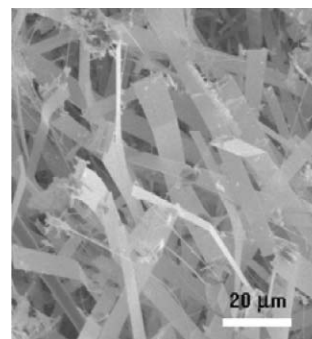


Fig. 1 SEM image of ZnS nanobelts.

† Electronic supplementary information (ESI) available: XRD and PL microscopic images of ZnS nanobelts. See <http://www.rsc.org/suppdata/cc/b4/b412289e/>

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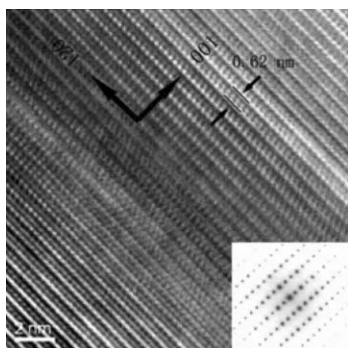


Fig. 2 High resolution TEM image of the ZnS nanobelt.

the crystallographic plane is 0.62 nm which corresponds to the {001} lattice planes of hexagonal ZnS. Electron diffraction shows that the length of the nanobelt is parallel to a [120] direction while the width is parallel to a [001] direction.

A small amount of ZnS nanocombs was observed in the TEM studies. This kind of morphology has been observed recently in ZnO nanostructures which is reported to be applicable to short wavelength nanolaser arrays.¹⁵ For ZnO nanostructures, comb-like structures are grown from the (001)-Zn surface, which is suggested to be a self-catalyzed process due to the enrichment of Zn at the growth front.¹⁶ The nanobelt is regarded as the growth base for cantilevers of either ZnO or ZnS nanocombs. It is estimated that similar things happened in the growth of ZnS combs; the cantilevers grew from the (001)-Zn surface of ZnS nanobelts through the self-catalyzed process due to the enrichment of Zn at the growth front.¹⁷

As an important fluorescence material, ZnS will emit luminescence under excitation. Fig. 3 shows a PL microscopic image of ZnS nanobelts excited by 380 nm ultraviolet light. Visible blue-green fluorescence was observed under the PL microscope. The belt-like shape of the ZnS nanobelts is easily distinguishable in the PL microscopic images. For a single nanobelt, enhancement of the fluorescence can be found at the ends due to the waveguide effect of the nanobelt. The strong fluorescence of the ZnS nanobelts indicates their potential application in photoluminescence devices. Further detail of the PL spectra of the ZnS nanobelts was studied by a spectrometer with a He-Cd laser as the excitation. Under the stimulation of the 325 nm laser, the PL spectrum of the ZnS nanobelts was collected and is presented in Fig. 4. Although pure Zn and S were used as the starting materials,



Fig. 3 PL microscopic image of ZnS nanobelts excited by light with a wavelength of 380 nm.

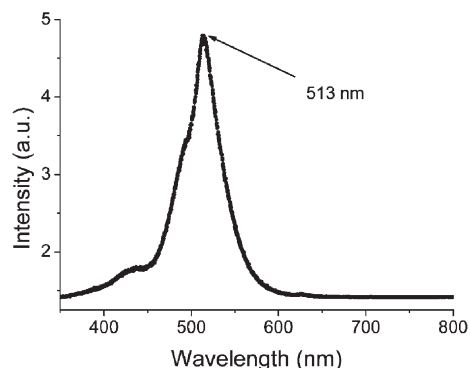


Fig. 4 PL spectrum of ZnS nanobelts under the excitation of a He-Cd laser with a wavelength of 325 nm.

little impurity should be contained in the ZnS nanobelts. The PL spectrum with the center at about 513 nm, which is similar to the previous result in the PL study of ZnS nanobelts,¹¹ reveals the impurity property as mentioned in ref. 18. The PL spectrum is almost the same even after 2 months, which reveals the stability of the ZnS nanobelts.

Recently, the study of nanobelts has become a very exciting topic. In previous works, a vacuum was necessary in the preparation of ZnS nanobelts. ZnS powder is used as the source material which is sublimated at high temperatures and forms nanobelts over a relatively lower temperature area. In some experiments, gold as a catalyst is also needed. Because the ZnS sublimates at a very low rate, a period longer than one hour should be used to ensure the collection of enough ZnS nanobelts. In the present work, since the easily sublimated Zn and S are used as the starting materials, ZnS nanobelts can be prepared at relatively lower temperatures. Because the reaction of the Zn and S is very fast in the vapor phase, ZnS nanobelts can be rapidly prepared.

In summary, ZnS nanobelts have been rapidly synthesized using Zn and S as the starting materials. Most of the ZnS nanobelts are single crystals with a uniform morphology and hexagonal wurtzite structure. The PL spectrum of the belts shows an emission band with the central wavelength at 513 nm. The strong blue-green fluorescence suggests possible applications of the ZnS nanobelts in PL devices. Compared with previous works, the method mentioned here has many advantages. This method has also been successfully applied in the preparation of other II-VI semiconductor nanostructures, such as CdS, ZnSe and CdSe.

The work was supported by JNSNF (No.BK2001404) and NSFC (No.60390072).

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