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Ceramics International 40 (2014) 699–702

CERAMICS INTERNATIONAL

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Preparation and optic properties of 3D ZnSe hierarchical nanostructure

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Received 21 May 2013; received in revised form 9 June 2013; accepted 17 June 2013
Available online 21 June 2013

Abstract

ZnSe hierarchical nanostructures with high crystallinity were prepared via a solvothermal reaction at the water–oil interface without the help of templates or surfactants. X-ray diffraction, transmission electron microscope, absorption spectrum and photoluminescence spectrum were used to characterize the products. Meanwhile, a possible mechanism for the formation of the ZnSe hierarchical nanostructures is discussed. The experimental results indicate that the ZnSe hierarchical nanostructures adopt spherical flower-like morphology assembled from nanosheets and possess high crystallinity. The oil–water interface plays an important role in the formation of hierarchical nanostructures. Moreover, the ZnSe hierarchical nanostructures exhibit a narrow emission with full width at half maximum (FWHM) of approximate 13 nm.

Keywords: A. Powders: chemical preparation; B. Hierarchical nanostructure; C. Optical properties

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1. Introduction

Recently, II–VI semiconductor nanomaterials are of great interest because of their great potential for both fundamental research and technical development in the fields of light emitting diodes [1], sensors [2], photoluminescence [3], biomedical labeling [4], photovoltaic devices [5], photocatalysis [6] and so on. Therein, most of the studies are focused on cadmium chalcogenide, such as CdS, CdSe and CdTe. However, the intrinsic toxicity of cadmium makes their future become doubtful. As a result, it is meaningful to develop cadmium-free substitutes.

ZnSe is a semiconductor with a wide direct band gap (2.7 eV) at room temperature [7], and possesses large exciton binding energy (21 meV), low absorptivity at infrared wavelength, visible transmission, giant photosensitivity as well as excellent photoluminescence property [8,9], which makes it an ideal alternative of cadmium chalcogenide. Therefore, ZnSe nanomaterials with various morphologies, such as nanoparticles [10], nanowires [11], hollow nanospheres [12], array of nanorods [13], hierarchically solid/hollow spheres [14] *etc*., have been prepared. Meanwhile, a variety of synthetic methods were developed, such as ultrasonic-assisted aerosol spray pyrolysis [15], the solvothermal process [16], the reverse microemulsion method [17], the vapor transport technique [18], thermolysis [19], the hot-injection method [9] and so on. However, in general, these synthetic routes often involve the use of toxic and expensive initial reactants including surfactants. Moreover, the color purity of emission of ZnSe nanomaterials obtained previously is unsatisfactory, which is unfavorable to their applications in the fields of light emitting diodes, laser and full-color displays. Therefore, it is worthwhile to find a simple surfactant-free method for the preparation of ZnSe nanomaterials with narrow emission.

In our previous work, the SnO_2 nanoparticles [20] have been successfully synthesized via the reaction at the water–oil interface in the solvothermal process. This route is simple and does not involve any expensive surfactants. Moreover, the results show that the products obtained possess high crystallinity. In the present work, the simple solvothermal route was used to prepare the 3D ZnSe hierarchical nanostructure with high crystallinity. Meanwhile, the optic properties of the products were also investigated. At last, a possible mechanism for the formation of the 3D ZnSe hierarchical nanostructure was discussed.

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http://dx.doi.org/10.1016/j.ceramint.2013.06.057

2. Experimental

In a typical procedure, (1) $Zn(CH_3COO)\cdot 2H_2O$ (0.3 mmol) was dissolved in distilled water (15 mL). After addition of hydrazine hydrate (2 mL, 1.2%) under stirring, the pH value of the solution was adjusted to 14 using NaOH aqueous solution. Then, the solution was poured into the Teflon liner of a 50 mL stainless steel autoclave and deaerated using nitrogen for 20 min. (2) Dimethyl diselenide (0.3 mmol) was dissolved in cyclohexane (15 mL). The solution of dimethyl diselenide was added into the autoclave containing the aqueous solution of (1). After deaerated using nitrogen for another 20 min, the autoclave was sealed and heated at 180 °C for 48 h. (3) The resulting solid was collected by centrifugation. (4) After washed with distilled water and ethanol for several times, the product was dried in a vacuum desiccator at room temperature.

The powder X-ray diffraction (XRD) analysis was made on a PANalytical Xpert Pro MRD X-ray diffractometer (Netherlands). High resolution transmission electron microscope (HRTEM) images were recorded using a JEOL JEM-2100 transmission electron microscope (Japan). The scanning electron microscope (SEM) images were recorded with a Hitachi S-4800 field emission scanning electron microscopy (Japan). The energy-dispersion X-ray analysis (EDX) was taken with a JEOL JSM-6360LV electron microscopy (Japan). The UV–vis spectrum of the solid sample was measured with a Varian Cary 100 spectrophotometer with an attachment of integrating sphere (USA). The photoluminescence (PL) spectrum was measured with a Varian Cary Eclipse spectrophotometer (USA).

3. Results and discussion

Fig. 1 shows the XRD pattern of 3D ZnSe hierarchical nanostructure. It can be observed from Fig. 1 that there exist five peaks at 27.3°, 45.4°, 53.8°, 66.1° and 72.9°, corresponding to the (111), (220), (311), (400) and (331) planes of cubic zinc blende ZnSe, respectively (JCPDS file no. 37-1463) [8,21]. The lattice parameter a is calculated to be 0.565 nm, which is close to the reported data (a=0.567 nm) [22]. Meanwhile, these diffraction peaks are fairly strong and sharp. No evidence of crystalline impurities is found in the pattern. EDX analysis (not shown here) shows that the sample is composed of the elements of Zn and Se. Therefore, it can be deduced that the cubic zinc blende ZnSe with high phase-purity and high crystallinity can be obtained in the process reported.

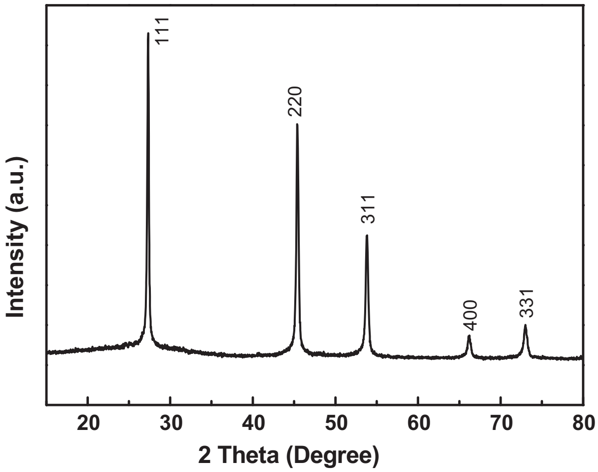

Fig. 1. XRD pattern of 3D ZnSe hierarchical nanostructure.

The morphology of the sample was measured with SEM, as shown in Fig. 2A and B. As can be seen from these SEM images, the sample consists of spherical flowerlike hierarchical nanostructures with diameters of approximate 9 μm, which are made from nanosheets with a rough surface and mean thickness of approximate 30 nm. In order to further affirm that the as-prepared 3D ZnSe hierarchical nanostructure is constructed with nanosheets, the samples were sonicated, and then their TEM images were taken (Fig. 2C). From Fig. 2C, we can clearly observe some nanosheets with rough surface, implying that the spherical flowerlike hierarchical nanostructures disassemble as nanosheets under ultrasonic treatment. These results indicate that the spherical flowerlike hierarchical nanostructure originates from the assembly of nanosheets.

Fig. 2D shows a typical HRTEM image of a nanosheet. In Fig. 2D, some lattice fringes are clearly recorded, suggesting that the as-prepared ZnSe flowerlike hierarchical nanostructure has a good crystallinity [17]. Furthermore, the spacing between two conjoint planes is about 0.326 nm, corresponding to the (111) plane of cubic zinc blende ZnSe, which coincides with the XRD result. The crystallite size is approximately 8 nm, implying that the nanosheet is composed of nanoparticles (the inset of Fig. 2D). Based on the experimental results above, the mechanism for the formation of the hierarchical nanostructures is suggested as follows. Firstly, dimethyl diselenide decomposes. Zn^{2+} ions react with the decomposed products from dimethyl diselenide at the water–oil interface. ZnSe nanoparticles are formed in this stage. Here, hydrazine is used in order to avoid the oxidization of decomposed products from dimethyl diselenide. Then, the nanoparticles coalesce and grow into nanosheets due to the induction of the water–oil interface. The drive force in the formation of ZnSe nanosheets may originate from the difference in surface tensions between cyclohexane and water. At last, the nanosheets aggregate to form the ZnSe hierarchical nanostructures.

Fig. 3 shows the UV–vis spectrum of the ZnSe flowerlike hierarchical nanostructure. As can be seen from Fig. 3, the ZnSe flowerlike hierarchical nanostructure gives a strong absorption band with an edge at approximately 346 nm (3.58 eV) for the ultraviolet light with the wavelength less than 354 nm, which should be ascribed to the first exciton absorption caused by $1S^e$-$1S^h_{2/3}$ transition [9]. Compared with the band gap of the bulk ZnSe (2.69 eV) [12], the absorption edge of the ZnSe flowerlike hierarchical nanostructure obviously shifts to shorter wavelength. Since the diameter of Bohr exciton of bulk ZnSe is approximately 9 nm [23,24], this blue-shift is mainly caused by spin–orbit coupling and quantum confinement [19]. Meanwhile, we also found an adsorption peak at 430 nm. Liu et al. reported ZnSe hollow nanospheres with two spectral features which resemble ours [12]. In their paper, this phenomenon was attributed to

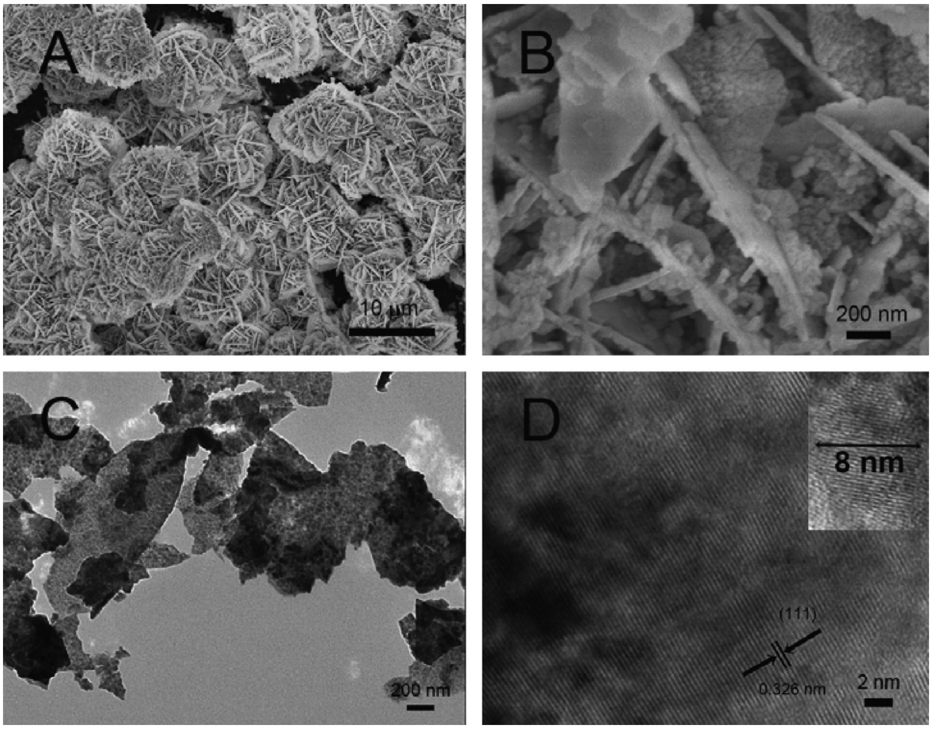

Fig. 2. (A and B) SEM images of 3D ZnSe hierarchical nanostructure and (C and D) HRTEM images taken on the nanosheet of 3D ZnSe hierarchical nanostructure, the inset is the HTTEM image of ZnSe nanoparticle in the nanosheet.

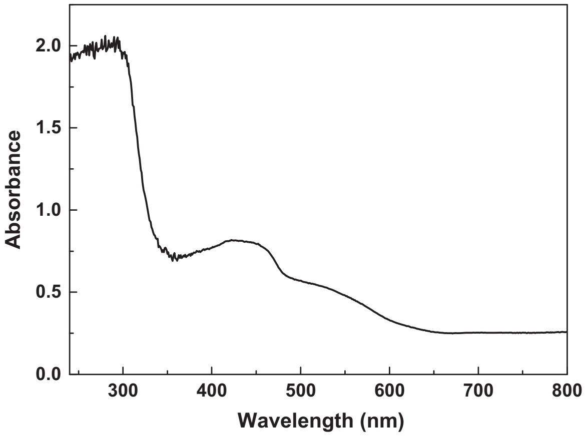

Fig. 3. UV–vis spectrum of 3D ZnSe hierarchical nanostructure.

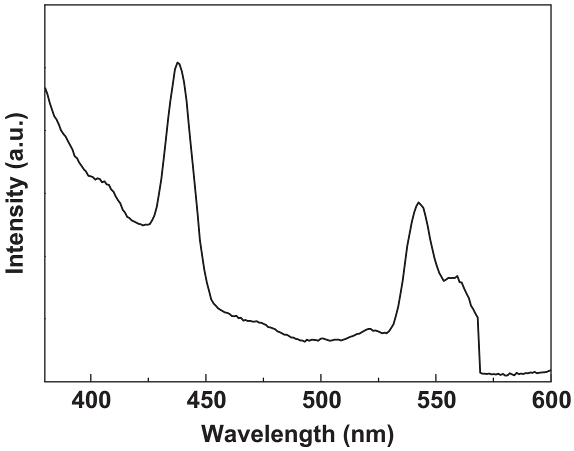

Fig. 4. PL spectrum of 3D ZnSe hierarchical nanostructure obtained under excitation of 320 nm.

the small dimension of the primary ZnSe nanoparticles or hollow-spherical structure. Therefore, we conjecture that the absorption peak at 430 nm is probably due to the ZnSe flowerlike hierarchical nanostructure. Moreover, the edge at 346 nm is very steep, implying that the ZnSe flowerlike hierarchical nanostructure possesses high crystallinity [20]. From this, we can expect that the as-prepared ZnSe flowerlike hierarchical nanostructure may offer exciting opportunities in the field of blue emitters as a potential alternative of CdSe nanocrystals.

The photoluminescence (PL) spectrum of the ZnSe flowerlike hierarchical nanostructure is shown in Fig. 4. From Fig. 4, it can be found that the ZnSe flowerlike hierarchical nanostructure exhibits a narrow blue emission at 437 nm, which may be ascribed to the near-band-edge emission of ZnSe [13]. The emission linewidth is approximately 13 nm (full width at half maximum). And the side of luminescence is sharp, which may be due to the fringe effect [25]. Moreover, we can also observe from Fig. 4 that there exist a relatively sharp emission peak at 542 nm and a broad emission peak at 558 nm. These PL peaks are defect-related emissions and may be ascribed to three causes: (1) the self-activated vacancies of Zn in ZnSe, (2) interstitial states associated with dislocations, stacking faults, and nonstoichiometric defects, (3) impurities [13,19,26]. The results above indicate that the ZnSe flowerlike hierarchical nanostructure may be used as a high color purity emitter, which is very encouraging for potential application of ZnSe in the fields of light emitting diodes, laser and full-color displays.

4. Conclusions

In conclusion, the ZnSe flowerlike hierarchical nanostructure with high crystallinity has been successfully prepared via the reaction at the water–oil interface in the solvothermal process. This route offers a simple, template-free approach for the fabrication of highly crystalline hierarchical nanostructures. In addition, the ZnSe flowerlike hierarchical nanostructure shows a narrow emission, implying that it is a promising alternative of CdSe nanocrystal. Further efforts are currently being undertaken.

Acknowledgments

This work was financially supported by the Key Project of the National Natural Science Foundation of China (No. 20933007).

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