Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 24(2014) 2588−2597
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Characterization of ZnSe microspheres synthesized under different hydrothermal conditions

Yu-lu DUAN[1], Sheng-lian YAO[1], Cheng DAI[1], Xiao-he LIU[2], Guo-fu XU[1,3]

1. School of Materials Science and Engineering, Central South University, Changsha 410083, China;
2. School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China;
3. Key Laboratory of Nonferrous Materials Science and Engineering of Ministry of Education, Central South University, Changsha 410083, China

Received 29 July 2013; accepted 16 January 2014

Abstract: ZnSe microspheres were synthesized via a facile hydrothermal method under mild conditions using aqueous zinc nitrate and sodium selenite as raw materials. The effects of hydrothermal temperature, reaction time, concentration of NaOH and amount of hydrazine hydrate on the phase structure, morphology and size of final products were carefully investigated. The phase structures, morphologies and optical properties of the final products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and photoluminescence (PL) spectroscopy. ZnSe microspheres assembled by average size (about 20 nm) nanocrystals were prepared using 20 mL of 1 mol/L NaOH solution and 10 mL of hydrazine hydrate at 180 °C for 4 h. The results show that the products obtained at low hydrothermal temperature and short reaction time have poor crystallinity and contain impurity phases. The appropriate NaOH concentration and amount of hydrazine hydrate ensure to obtain pure ZnSe with spherical morphology and better luminescence property.
Key words: ZnSe microsphere; nanocrystal; hydrothermal method; luminescence property

1 Introduction

During the past decades, wide band gap semiconductor materials have attracted considerable attention due to their size-dependent properties and important technological applications [1,2]. Of the various II−VI semiconductors, zinc selenide (ZnSe) with a direct band gap of 2.70 eV (460 nm) is especially interesting because it is widely used for various applications [3], such as nonlinear optical devices [4], displays [5], sensors [6] and infrared windows [7]. Nanostructure of the photocatalytic materials can be considered a primarily promising strategy to gain factorial enhancements in photocatalyst due to both higher surface-to-volume ratios and higher redox potentials with an increase in band gap energy as a result of the so-called quantum size effect [8,9]. ZnSe has long been a material of choice of blue diode lasers and photovoltaic solar cells [10,11]. Efforts in the preparation of ZnSe usually focused on the synthesis of ZnSe nanocrystals with luminescent properties from single-molecular precursors [12,13]. Recently, many efforts have been devoted to the synthesis of spherical ZnSe semiconductors. XIONG et al [14] synthesized ZnSe nanobelts with high photocatalytic activity in the degradation of fuchsine and solution under UV light irradiation through a solvothermal approach. But the most important challenges in materials is to control the structure of materials on specific nanomorphologies [15,16].

Many new methods have been investigated to prepare ZnSe, including a variety of colloids and composite particles [17]. CAO et al [18] presented a simple hydrothermal route for the synthesis of wurtzite 3D flowerlike ZnSe nanostructures in high yield by a complex hydrothermal treatment using ethylenediamine-tetraacetic acid (EDTA). But most of the synthesis general involved intricate processing. To the best of our knowledge, no further studies have been reported on the synthesis of ZnSe nanostructures without any other organic additives (like ethylenediaminetetraacetic acid) although they are strongly desired. And the effects of the experiment parameters, such as concentration of NaOH, amount of hydrazine hydrate, reaction time, and

Foundation item: Project (13JJ1005) supported by the Natural Science Foundation for Distinguished Young Scholars of Hunan Province, China
Corresponding author: Guo-fu XU; Tel: +86-731-88877217; E-mail: csuxgf66@csu.edu.cn
DOI: 10.1016/S1003-6326(14)63387-2

temperature, on the evolution of ZnSe microspheres morphology and structure have not been reported detailedly. Therefore, the development of simple template-free and facile methods for the preparation of ZnSe microspheres with intrinsic optical properties still maintains a highly challenge. Here, ZnSe microspheres have been successfully synthesized via a facile hydrothermal method under mild conditions using aqueous zinc nitrate and sodium selenite as zinc and selenium source, sodium hydroxide as precipitating reagent and hydrazine hydrate as both alkaline and complexing reagent. The effects of hydrothermal temperature, reaction time, concentration of NaOH and amount of hydrazine hydrate on the phase structure, morphology and size of final products have been carefully investigated. The phase structures, morphologies and optical properties of the final products were characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and photoluminescence (PL) spectroscopy.

2 Experimental

All chemical solvents and reagents used in this work, such as aqueous zinc nitrate ($Zn(NO_3)_2·6H_2O$), sodium selenite (Na_2SeO_3), sodium hydroxide (NaOH) and hydrazine hydrat ($N_2H_4·H_2O$), were of analytical grade and used without any further purification. Deionized water was used in all preparations.

In a typical procedure, 0.298 g of $Zn(NO_3)_2·6H_2O$ and 0.173 g of Na_2SeO_3 were added into a Teflon-lined stainless steel autoclave of 50 mL capacity and dissolved in 20 mL of 1 mol/L NaOH solution through supersonic vibration. Then 10 mL of hydrazine hydrate (80% v/v) solution was added dropwise during vigorous stirring. Next, 10 mL of deionized water was added into the autoclave that was filled up to 80% of the total volume. After 10 min stirring, the autoclave was sealed and maintained at 180 °C for 4 h. Subsequently, the system was allowed to cool to the room temperature naturally. The resulting precipitate was collected by centrifugal sedimentation, washed with absolute ethanol and distilled water in sequence several times. The final product was dried at 60 °C for 8 h.

The obtained products were characterized by a Rigaku D/MAX2500 X-ray diffractometer (XRD) with Cu K_α radiation (λ=0.154051 nm). The operation voltage and current were kept at 40 kV and 40 mA, respectively. The size and morphology of the as-synthesized products were determined at 10 kV by a Sirion 200 field emission scanning electron microscope (SEM) and at 200 kV by a Tecnai G^2 20ST transmission electron microscope (TEM) and a JEOL JEM−2100F high-resolution transmission electron microscope (HRTEM). Energy-dispersive X-ray spectroscopy (EDS) was taken on the SEM. The room-temperature photoluminescence (PL) measurement was carried out on an F−4500 spectrophotometer using the 329 nm excitation line of Xe light.

3 Results and discussion

3.1 Morphology and structure

The crystal structure of the ZnSe microspheres prepared using 20 mL of 1 mol/L NaOH solution and 10 mL of hydrazine hydrate at 180 °C for 4 h were investigated by XRD. Figure 1 shows a typical XRD pattern of ZnSe precursors, in which all the diffraction peaks can be well indexed to cubic ZnSe with lattice constant a=0.567 nm, which is in good agreement with the standard PDF data (37−1463).

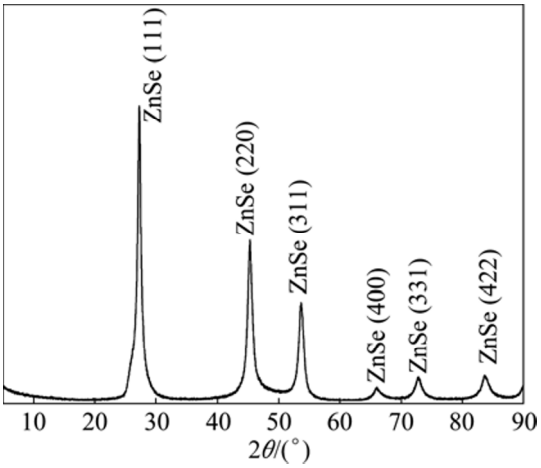

Fig. 1 XRD pattern of as-prepared ZnSe products using 20 mL of 1 mol/L NaOH solution and 10 mL of hydrazine hydrate at 180 °C for 4 h

Figure 2 shows the morphology, phase structure, and size of ZnSe microspheres prepared using 20 mL of 1 mol/L NaOH solution and 10 mL of hydrazine hydrate at 180 °C for 4 h. As shown in Fig. 2(a), the diameter of ZnSe spheres is in the range of 1−3 μm. Figure 2(b) shows an individual broken ZnSe microsphere assembled by uniform nanocrystals with the size of about 20 nm from inside to outside. SAED pattern of as-prepared ZnSe microspheres could be indexed to pure cubic ZnSe (Fig. 2(c)), which suggests that those microspheres are polycrystalline. Further investigations of the ZnSe nanocrystals come from the HRTEM analyses (Fig. 2(d)). The legible spacing was calculated to be about 0.328 nm, which is in good agreement with the (111) plane of face-centered cubic ZnSe.