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Synthesis and characterization of ZnSe rose-like nanoflowers and microspheres by the hydrothermal method

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Abstract

ZnSe rose-like nanoflowers and microspheres were successfully grown on Zn foils by the hydrothermal method at 220 °C for 36 h. Scanning electron microscope (SEM), X-ray diffraction (XRD), energy dispersive spectrometer (EDS), ultraviolet–visible (UV–vis) absorption spectroscopy and photoluminescence (PL) spectroscopy were used to observe the morphologies, structures, chemical compositions and optical properties of the as-synthesized ZnSe samples. The XRD patterns revealed that as-synthesized ZnSe nanoflowers and microspheres have cubic zinc blende structure. The SEM observations showed that low concentration of EDTA was beneficial to obtain the ZnSe rose-like nanoflowers. With increase of EDTA concentration, the morphology of the as-synthesized samples transformed into microspheres. It was proved that EDTA played a significant role during the synthesis of ZnSe rose-like nanoflowers and microspheres. Room temperature photoluminescence (PL) spectroscopy of the samples showed that the spectra were wide band from blue light to orange light. Furthermore, a possible formation mechanism of ZnSe nanoflowers and microspheres was proposed and discussed.

Keywords: C. Optical properties; ZnSe; Nanoflowers; Microspheres

1. Introduction

Inorganic semiconductor nanocrystals have attracted significant attention over the past decade due to their promising characteristics in electronics, optics and photonics [1]. Their small size effect, surface effect, quantum size effect, quantum tunneling effect and confinement effect depend sensitively on size, shape and structure [2–4]. In particular, zinc selenide (ZnSe) is one of the most important direct band gap II–VI semiconductor materials, exhibits a direct band gap of 2.67 eV (1 eV=1.609 × 10^{-19} J) and a large exciton binding energy of 21 meV at room temperature. ZnSe semiconductor nanocrystals have been widely used in photodetectors [5–7], laser diodes [8,9], solar cells [10], photocatalysis [11], sensor [12] and so on.

Over the past decade, ZnSe nano/micro-structures with different morphologies have been obtained by several preparation approaches including the sol–gel method, evaporation method, wet chemical synthesis, hydrothermal and solvothermal synthesis [13–17]. ZnSe microspheres are easy to be obtained by using these methods. In order to control the morphology of ZnSe nanocrystals, organic additives such as ethylene diamine tetraacetic acid (EDTA), triethylenetetramine (TETA), polyvinyl pyrrolidone (PVP), hydrazine hydrate and ethylenediamine are commonly introduced into the reaction system to manipulate the nucleation and growth in hydrothermal and solvothermal reactions. However, ZnSe nanoflowers have rarely been reported in the literature. Yang et al. [18] have prepared ZnSe nanoflowers composed of nanowires

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Table 1
The experimental conditions of all the samples.

Sample	Chelating agent (EDTA), M	T, °C	t, h
1	0	220	36
2	0.15	220	36
3	0.30	220	36
4	0.35	220	36
5	0.35	220	48

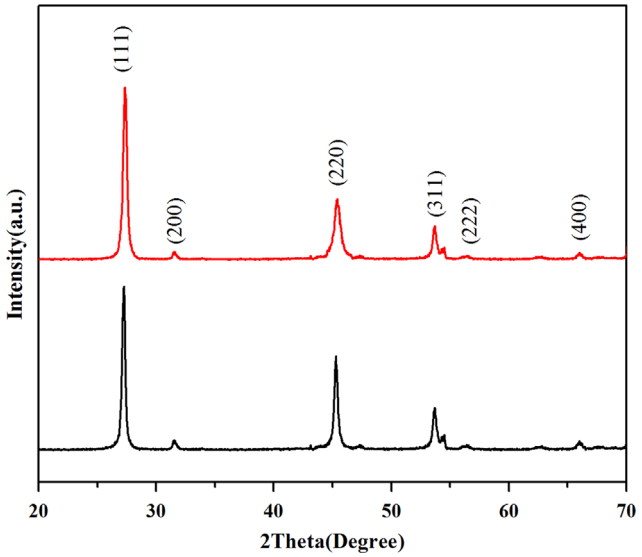

Fig. 1. XRD Patterns of ZnSe nanoflowers (a) and microspheres (b).

and spheres composed of nanoparticles by the solvothermal method. Cao et al. [19] reported that novel 3D wurtzite ZnSe hierarchical nanostructures have been synthesized by addition of EDTA. Dai et al. [20] reported that monodisperse ZnSe nanocrystals with both particle and flower shapes have been synthesized via green chemistry.

In the present work, ZnSe rose-like nanoflowers and microspheres formed by gathering ZnSe nanoparticles were prepared by the hydrothermal method. EDTA was used as a complexing agent and stabilizer to control the morphology of the samples. The reaction mechanism of as-synthesized ZnSe nanoflowers and microspheres has also been proposed. We also investigated the effects of ZnSe nanoflowers and microspheres on optical properties.

2. Experimental

2.1. Chemicals

All chemicals were of analytical grade and used as received without further purification. Zinc acetate ($Zn(CH3COO)_2 \cdot 2H_2O$) ($\geq 99.0\%$), ethylene diamine tetraacetic acid (EDTA) ($\geq 99.0\%$), sodium hydroxide (NaOH) ($\geq 97.0\%$), znic foils (Zn) ($\geq 99.0\%$) and Se powers(Se) ($\geq 99.7\%$) were purchased from Sinopharm Chemical Reagent Co., Ltd. All aqueous solutions were prepared using deionized water.

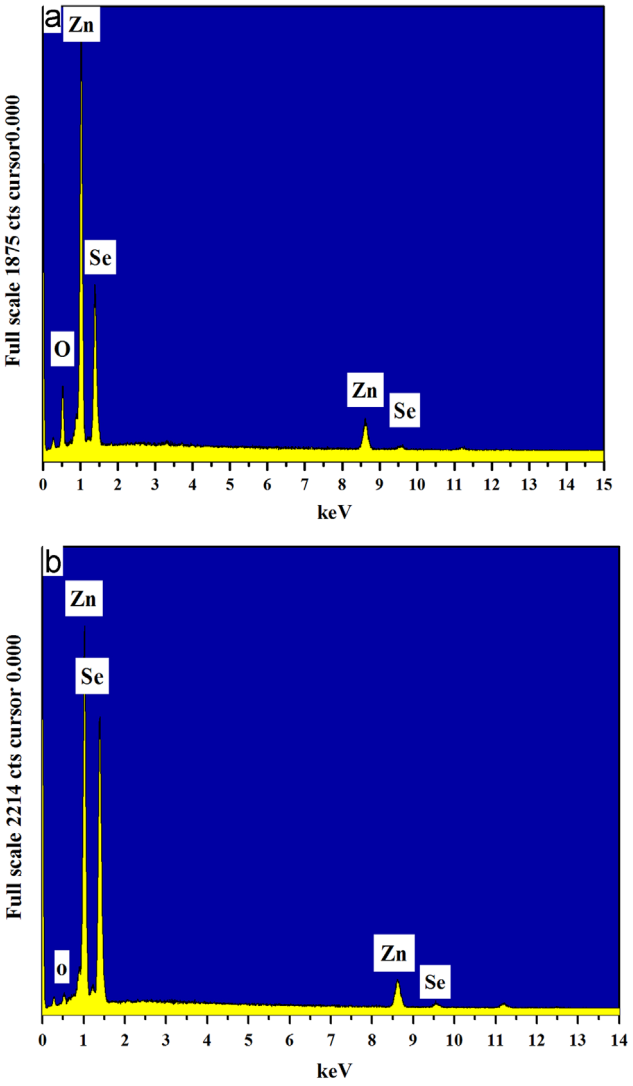

Fig. 2. EDS spectra of ZnSe nanflowers (a) and microspheres (b).

2.2. Preparation of the mixture solution

The hydrothermal synthesis process was carried out as follows. First of all, 0.5 g Se powder and 3.2 g NaOH were dissolved in 20 mL of deionized water. This solution was stirred with a magnetic stirrer for 50 min. At the same time, 0.4 g $Zn(CH_3COO)_2 \cdot 2HO$, 0.2 g Zn foil with dimension of 1 cm × 1 cm and 3.2 g NaOH were added into 20 mL of deionized water and the resulting solution was stirred thoroughly. Next, the two solutions mentioned above were mixed, and then different concentrations of EDTA (0 M, 0.15 M, 0.30 M and 0.35 M) were added to the mixture solution. The experimental conditions are shown in Table 1.

2.3. Preparation of samples

The final solution was transferred to a Teflon-lined autoclave with 0.75 filling factor and sealed, hydrothermally treated at 220 °C for 36 h. After the solution was cooled down