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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

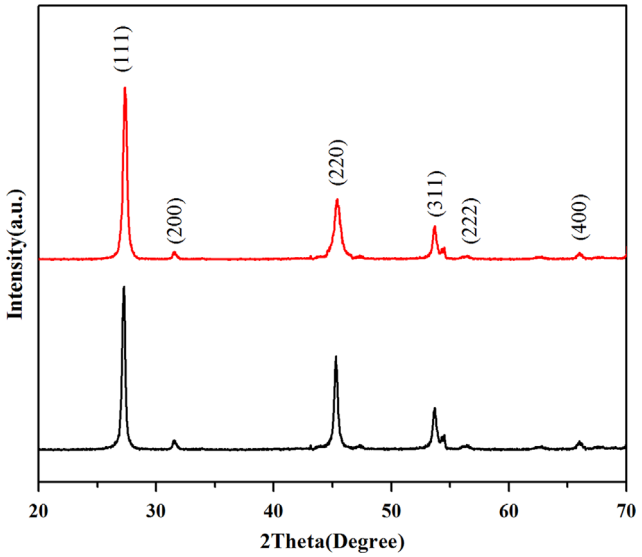

Fig. 1. XRD Patterns of ZnSe nanoflowers (a) and microspheres (b).

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.

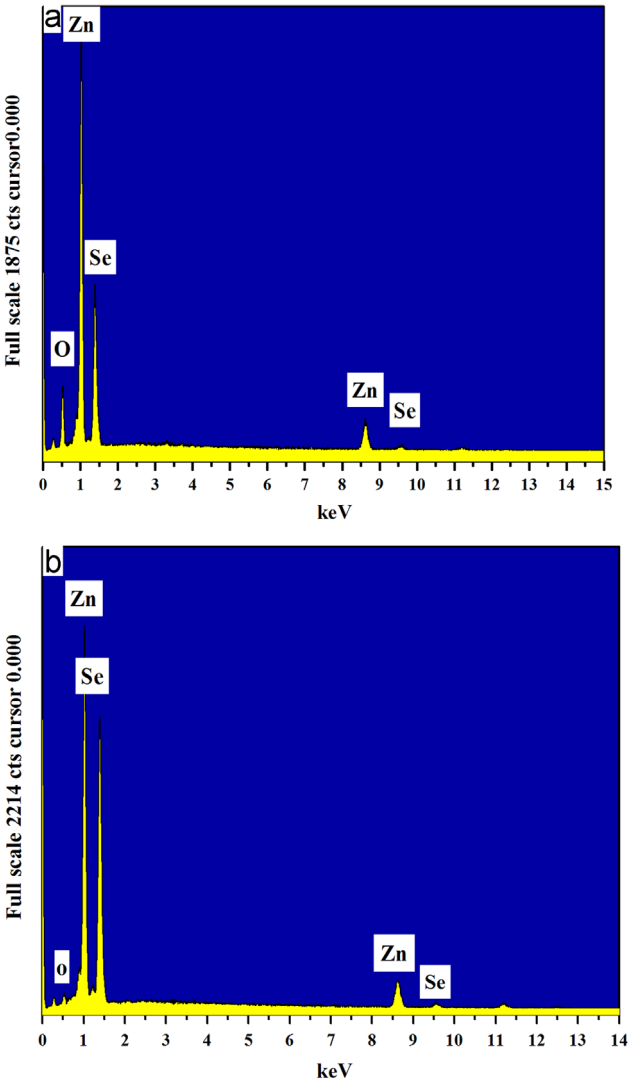

Fig. 2. EDS spectra of ZnSe nanflowers (a) and microspheres (b).

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

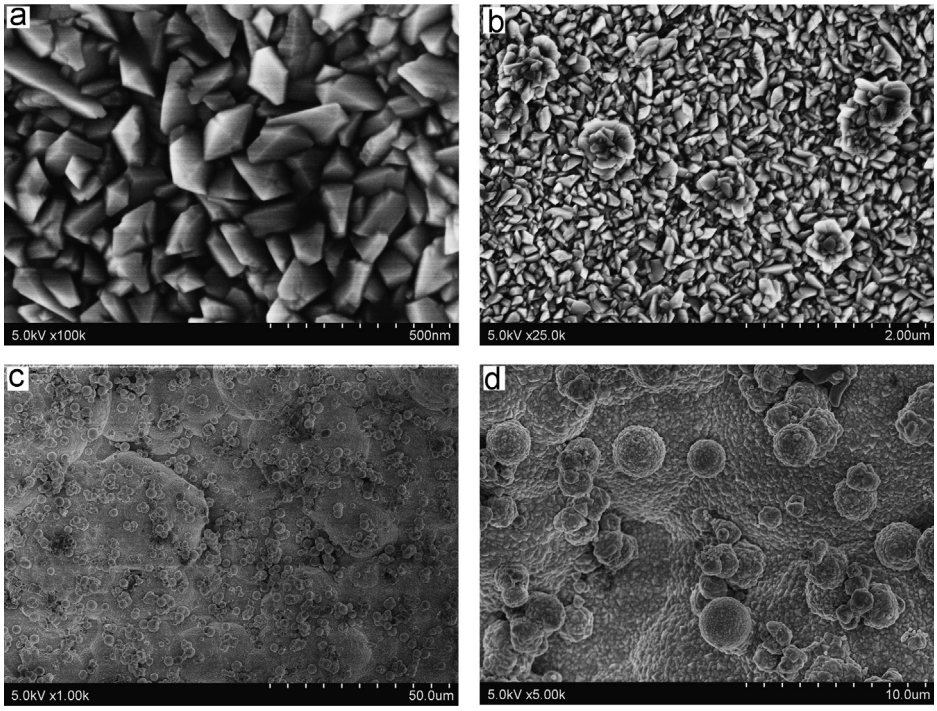

Fig. 3. SEM images of ZnSe prepared with different EDTA concentrations in solution (a) without EDTA, (b) 0.15 M, (c) 0.25 M and (d) 0.35 M.

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 at room temperature.

2.4. Characterizations

The crystal structure and phase composition of the samples were identified using an X-ray diffraction (XRD; Rigaku D/Max 2550, Japan) 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 samples were investigated by a scanning electron microscope (SEM; JEOL JSM-5600LV), equipped with X-ray energy dispersive spectroscope (EDS; Oxford IE 300 X). The optical absorbance was measured by ultraviolet–visible (UV–vis; PerkinElmer Lambda 35). The room temperature photoluminescence (PL) spectra were recorded by a luminescence spectrometer (PL, Edinburgh FLS920).

3. Results and discussion

3.1. XRD analysis

Fig. 1(a) and (b) shows the XRD pattern of as-synthesized ZnSe nanoflowers and microspheres on the Zn foils, respectively. Most of the diffraction peaks can be indexed as cubic zinc blende ZnSe with the lattice constants $a=5.669$ Å for samples, which is in good agreement with the reported data for ZnSe of JCPDS File no.80-2346. Very narrow and sharp diffraction peaks indicates the good crystallinity of the as-prepared samples.

3.2. Component analysis

Fig. 2(a) and (b) shows the element composition of as-synthesized ZnSe nanoflowers and microspheres, respectively. Fig. 2(a) and (b) shows that samples are principally composed of Zn and Se, and their molar ratio is approximately 1.8:1 in ZnSe nanoflowers and 0.98:1 in ZnSe microspheres, respectively. Because the X-ray probe may penetrate the thin ZnSe nanoflowers into Zn substrates, therefore the molar ratio is larger than 1:1 in ZnSe nanoflowers. In both spectra, besides the seldom O signals come from oxygen absorbtion of samples, only Zn and Se are detected. The EDS results corresponded to the XRD results demonstrate that samples are cubic zinc blende ZnSe.

3.3. Morphological analysis

Fig. 3 shows SEM images of ZnSe nano/micro-structures grown on Zn foils at different EDTA concentrations (0 M, 0.15 M, 0.25 M and 0.35 M). Fig. 3(a) shows that the samples are composed of nanoparticles without addition of EDTA. These nanoparticles are lack of regular arrangement. With increase of EDTA concentration from 0 up to 0.15 M, rose-like structures with the average size of ~0.35 μm can be clearly observed in Fig. 3(b). As increasing EDTA concentration further up to 0.25 M and 0.35 M, microspheres can be observed in Fig. 3(c) and (d), respectively. The average diameter of microspheres is ~2.5 μm, which is of the same

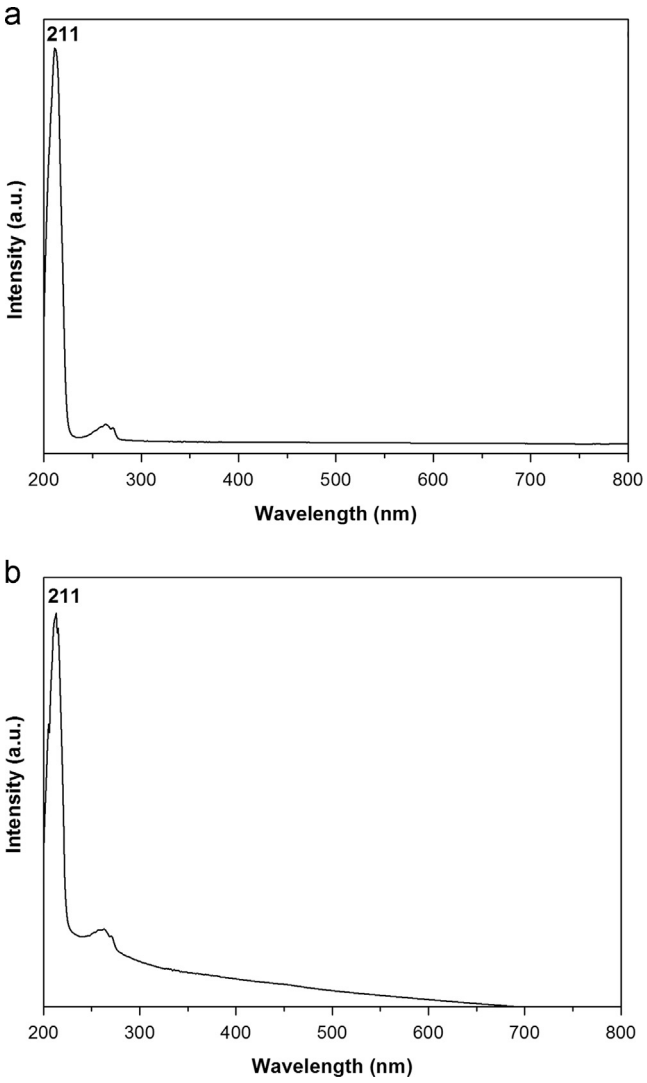

Fig. 4. UV–visible absorption spectra of the ZnSe nanflowers (a) and microspheres (b).

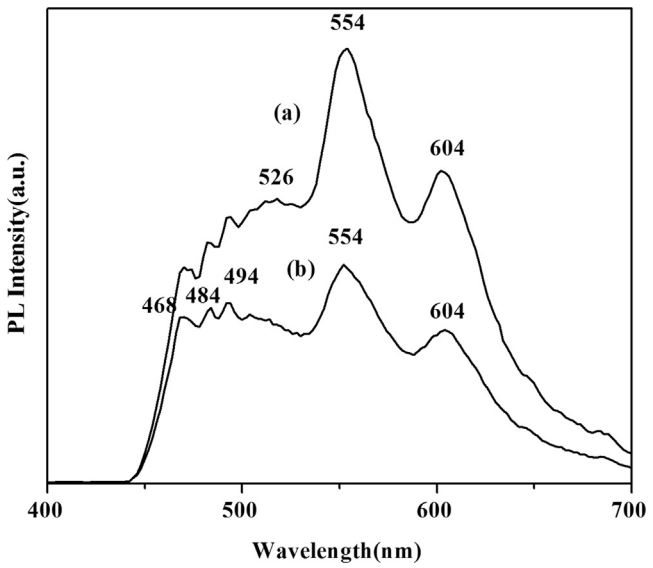

Fig. 5. Room temperature PL spectra of the ZnSe nanflowers (a) and microspheres (b).

shape and size. This shape transition mechanism of samples is discussed later in the paper.

3.4. Optical properties

The UV–vis spectra of the as-synthesized ZnSe nanoflowers and microspheres are presented in Fig. 4(a) and (b), respectively. One strong absorption peak was observed at 211 nm for the as-synthesized ZnSe nanoflowers and microspheres.

The as-prepared ZnSe nanoflowers and microspheres show strong light emission at room temperature when samples were excited at 211 nm, as shown in Fig. 5(a) and (b), respectively. Fig. 5(a) shows that there are three light emission peaks centered at about 526 nm (2.36 eV), 554 nm (2.24 eV), and 604 nm (2.05 eV). Fig. 5(b) shows that there are five light emission peaks centered at about 468 nm (2.65 eV), 484 nm (2.56 eV), 494 nm (2.51 eV), 554 nm (2.24 eV), and 604 nm (2.05 eV). The emission peak at 468 nm (2.65 eV) corresponds to the bulk band emission of ZnSe [17]. The emission peaks at 484 nm, 494 nm, 526 nm and 554 nm are usually assigned to self-activated luminescence, probably as a result of some donor-acceptor pairs that are related to Zn vacancy and interstitial states, or associated with surface emission [21–24]. The strong orange emission peak at about 604 nm is probably because of the existence of non-stoichiometric defects, dislocations, and stacking faults [25]. Besides, the emission bands gap energy may be attributed to the differences of shapes or sizes of ZnSe crystal. These results suggest that the optical properties of ZnSe are quite sensitive to the detailed reaction conditions. Obviously, synthetic conditions, crystal size, and shape strongly influence the optical quality of ZnSe semiconductor nanocrystals [26].

3.5. Mechanism

The mainly reactions in the process are shown as follows:

$$3Se + 6OH^- \rightarrow 2Se^{2-} + SeO_3^{2-} + 3H_2O \quad (1)$$

$$Zn + 2H_2O + 2OH^- \rightarrow [Zn(OH)_4]^{2-} + H_2\uparrow \quad (2)$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2\downarrow \quad (3)$$

$$Zn(OH)_2 + 2OH^- \rightarrow [Zn(OH)_2]^{2-} \quad (4)$$

$$[Zn(OH)_2]^{2-} + Se^{2-} \rightarrow ZnSe\downarrow + 4OH^- Zn^{2+}(EDTA) + Se^{2-} \rightarrow ZnSe\downarrow \quad (5)$$

An excess of standardized NaOH provides a good alkaline environment, adjusting the pH value of the reaction solution. OH^- not only ensures that the Se^{2-} is not oxidized into Se element, but also does not produce Zn $(OH)_2$ precipitate according to reaction (1–4). Fig. 3(a) shows the scattered arrangement of ZnSe nanoparticles without addition of EDTA. Fig. 3(a–d) illustrates that EDTA plays a significant role in the formation of the ZnSe micro/nano-structures. EDTA in water can be expressed as $[(OOCCH_2)_2NHCH_2CH_2NH(CH_2COO)_2]^{4-}$, and act as a

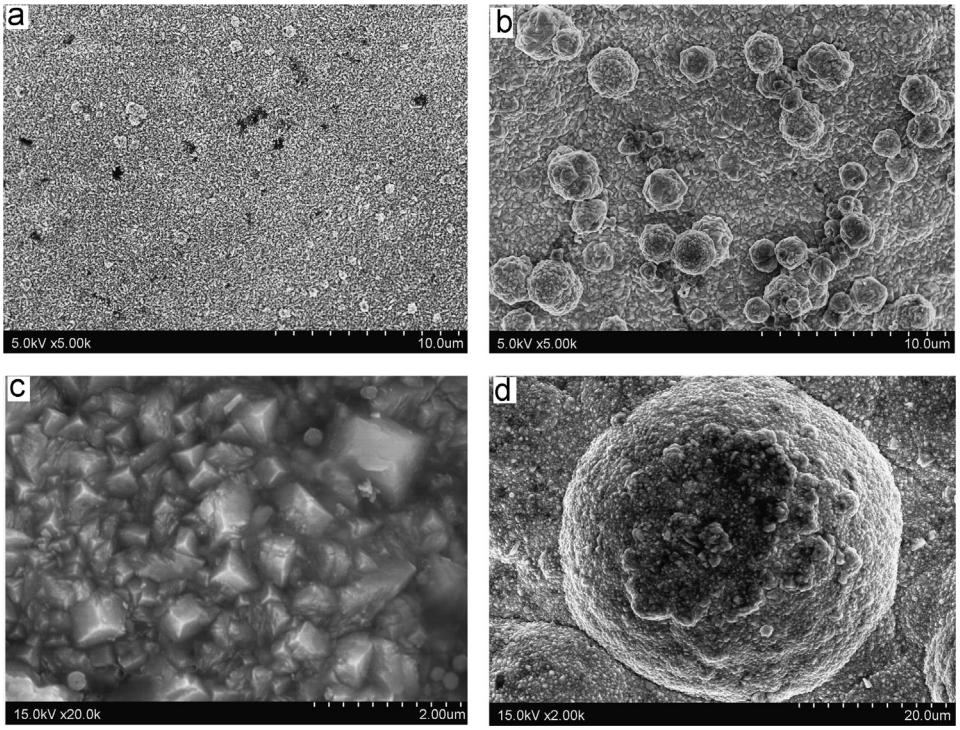

Fig. 6. SEM images of ZnSe nanflowers and microspheres.

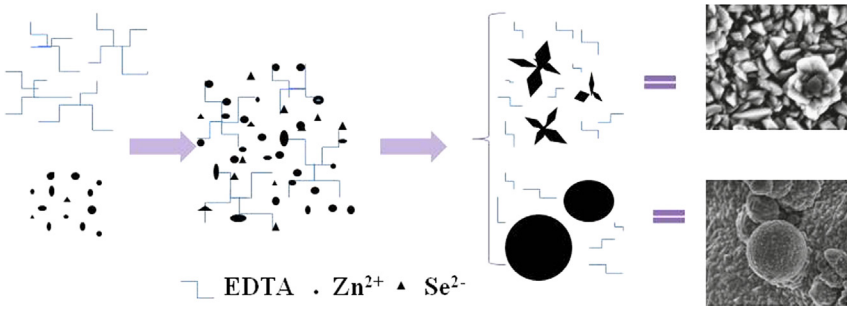

Fig. 7. The formation process of ZnSe nanflowers (a) and microspheres (b).

bridge-like complexing agent, which can combine with Zn ions to form polynuclear complexes by using both ends of the hydrophilic carboxyl group. Then, the chemical reaction between Se ions and Zn^{2+} (EDTA) complexes happens, and gradually grows into the primary ZnSe nanoparticles. With the continuous separation of EDTA and the primary ZnSe nanoparticles, flower-like structures have been synthesized, as shown in Fig. 6(a). Although further investigation is necessary to accurately explain the mechanism of the growth of ZnSe flower-like structure, we believe that EDTA is also the main driving force during the course of flower-like ZnSe structure formation.

Higher amount of EDTA is vital to the formation of ZnSe microspheres. As increasing concentration further, the primary ZnSe nanoparticles have higher surface free energy. Their high surface energy provides the driving force for the aggregation of the primary nanoparticles to form the ZnSe microspheres [27], as shown in Fig. 6(b) (sample 4). When the reaction time is prolonged to 48 h on the basis of the sample 4, it is clear that the diameter of the ZnSe microspheres increases up to ~40 μm, as shown in Fig. 6(d) (sample 5). The high-magnification image of the sample 5 shows that the large-scale ZnSe microspheres are composed of the ZnSe nanoparticles, as shown in Fig. 6(c). This result is consistent with our growth mechanism proposed. A schematic presentation of the nanoflowers and microspheres is shown in Fig. 7.

4. Conclusions

In conclusion, ZnSe rose-like nanoflowers and microspheres have been successfully synthesized by hydrothermal method. The as-synthesized ZnSe nanoflowers and microspheres were highly dispersed and uniform in size, the average size of ZnSe nanoflowers was ~0.35 μm and the diameter of ZnSe microspheres was ~2.5 μm. The large-scale ZnSe microspheres with a diameter of ~40 μm have been achieved by adding the reaction time. In the hydrothermal environment,

the morphology of the final samples strongly depended on the concentrations of chelator EDTA. Room temperature photoluminescence (PL) spectroscopy showed that the broad multi-bands emission which was ascribed to deep level emission and structure defects. As-synthesized ZnSe nanoflowers and microspheres had good luminescence properties and can be used in various optical fields.

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