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Synthesis of ZnSe nanodonuts via a surfactant-assisted process

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ABSTRACT

ZnSe nanodonuts with outer diameters ranging from 0.5 to 1.5 μm and the wall thickness in the range of 100–300 nm were synthesized by a simple and convenient surfactant-assisted process. XRD and TEM results show the as-prepared sample is single crystalline zinc blende ZnSe. The formation mechanism of the ZnSe nanodonuts has been discussed. Polyethylene glycol (PEG) and hydrazine hydrate play key roles in the forming the donut-like shape of ZnSe. This method may be extended to fabrication of donut-like nanostructure of other chalcogenides.

1. Introduction

Wide-bandgap II–VI nanostructured semiconductors have attracted much attention over the past decade due to their excellent electronic and optical properties and potential applications in various nanodevices such as light–emitting diode, solar cells, sensors and optical recording media [1–5]. Among the II–VI semiconductors, ZnSe, as a direct band gap material, is considered as a good candidate for short-wavelength lasers and other photoelectronic devices such as blue-green laser diodes and turnable mid-IR laser sources [6,7]. On the other hand, size and dimensionality are known to play important roles in determining the physical and chemical properties of nanostructured materials. In this regard, one-dimensional nanostructures of ZnSe have been fabricated using various methods including laser assisted catalytic growth, thermal chemical evaporation, metal organic chemical vapor deposition [8–10] etc. More recently, specific shapes of nanostructures, together with the size effect, are also expected to induce novel physical properties [11–13].

Recently, solvothermal process is found to be effective and convenient in synthesizing different nanostructures such as nanorwires nanorods and nanotubes at low temperatures [14,15]. Solution phase synthesis with surfactants as soft templates has been proved to be effective and convenient to control the shape of nanomaterials [16,17]. It is found that micelles with diverse shapes such as rods, tubes, and disks can be formed from surfactants by adjusting experimental parameters [18]. The micelles with specific shape can act as a template in controlling the growth of nanostructures. Polyethylene glycol (PEG), a nonionic surfactant, is widely used as templating material to prepare desired nanostructures including nanowires, nanorods and nanotubes [19,20]. However, little studies have been reported to prepare donut-like nanostructures with PEG as a template. Here we report a solvothermal approach to prepare ZnSe donut-like particles on a large scale by using PEG as a soft template, which control the growth of ZnSe donut-like structure.

2. Experimental section

All reagents are analytical grade and used without further purification. In a typical procedure, 10 ml ethanol and 1.5 g NaOH were firstly added with stirring for 2 min after 0.02 g polyethylene glycol (PEG, Mw 20 000) was dissolved in 6 ml distilled water. 0.09 g $Zn(CH_3CO_2)_2 \cdot 2H_2O$, together with 2 ml hydrazine hydrate and 0.16 g Se powder were then added to the above solution. The mixture was stirred for 5 min. before being transferred into a 20 ml stainless steel teflon-lined autoclave. The autoclave was sealed and the temperature was maintained at 180 °C for 10 h. before being cooled down to room temperature. A yellowish product was then collected and washed with absolute ethanol and distilled water several times and finally dried in vacuum at 40 °C for 4 h.

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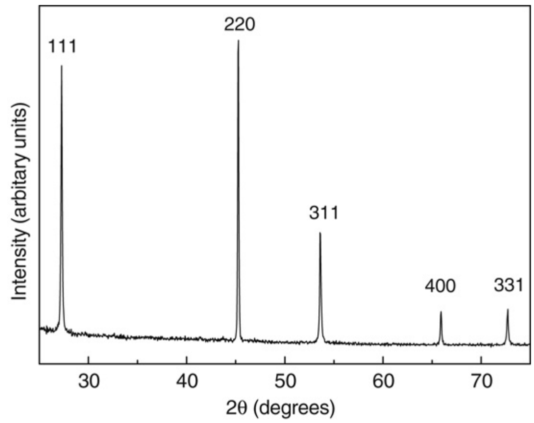

Fig. 1. XRD pattern of the ZnSe nanodonuts sample.

The overall crystallinity of the product is examined by X-ray diffraction (XRD, Rigakau RU-300 with Cu Kα radiation). The general morphology of the products was characterized using scanning electron microscopy (SEM LEO 1450VP). Detailed microstructure analysis was carried using transmission electron microscopy (TEM, PhilipsCM120). The chemical composition analysis was obtained by energy dispersive X-ray spectrometry (EDX) using an EDX spectrometer attached to the same microscope. Room-temperature Raman spectra were measured using a micro-laser Raman spectrometer (Renishaw) in a backscattering configuration, employing the 514.5 nm line of Ar laser as the excitation source.

3. Results and discussion

A typical XRD pattern of the as-prepared sample is shown in Fig. 1, all the diffraction peaks can be indexed to those of zinc blende ZnSe. No evidence of other crystalline phase can be found in the XRD pattern. The lattice constant obtained from the XRD data is $a = 5.67$ Å, which is consistent with that of the bulk cubic ZnSe ($a = 5.668$ Å, JCPDS, No.37-1463).

The SEM image in Fig. 2(a) shows the general morphology of the as-prepared products, which consist of a large quantity of donut-like particles. A magnified SEM image in the inset of Fig. 2(a) clearly illustrates the donut-like shape. The typical outer diameter of the nanodonut is in the range of 0.5–1.5 μm and the wall thickness in the range of about 100–300 nm.

TEM study of the sample further confirms the donut-like structure. Fig. 3(a) shows a low magnification TEM image taken from a single nanodonut with wall thickness of about 200 nm. The EDX spectrum (Fig. 3(b)) taken from the sample shows intense peaks of Zn and Se, suggesting the composition as Zn and Se only. A corresponding selected-area electron diffraction (SAED) pattern in Fig. 3(c) is taken from the cubic ZnSe [011] zone axis, revealing the single crystallinity of the nanodonut, despite its rough surface. A typical HRTEM image shown in Fig. 3(d) indicates that the nanodonuts are free from line and plane defects such as dislocations and stacking faults. The measured *d*-spacing from the HRTEM image is ∼3.27 Å, which is consistent with the *d*-spacing of the cubic ZnSe (111) planes.

The high quality of single crystalline ZnSe is further confirmed by Raman spectrum taken from the nanodonuts. The Raman peaks (Fig. 5) at 206 and 251 cm^{-1} can be attributed to the transverse optic (TO), and longitudinal optic (LO) phonon modes of ZnSe, respectively. Vibration modes induced by impurities are not found. The sharp and symmetrical Raman peaks suggest that the ZnSe nanostructures are of high crystalline quality and phase purity, which is in good accordance with the above TEM observation. It has been reported that LO phonon frequency of single-crystal ZnSe

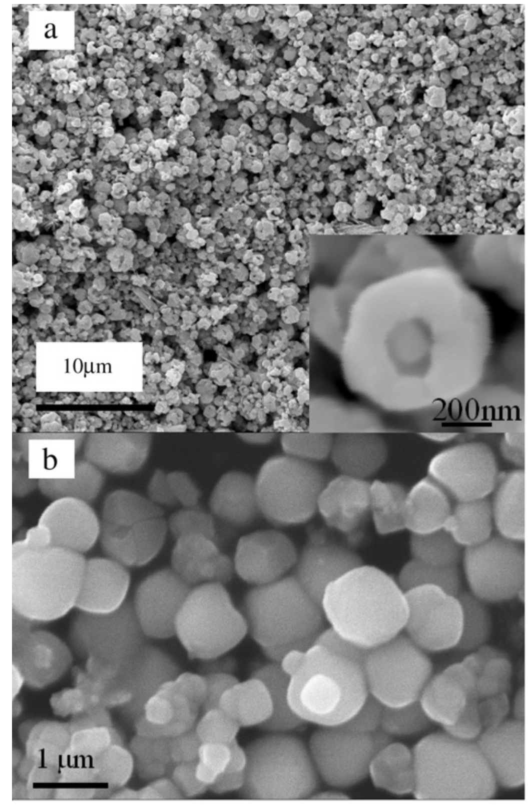

Fig. 2. (a) SEM image of the ZnSe nanodonuts sample. Inset: a magnified SEM image of a ZnSe nanodonut. (b) SEM image of the ZnSe sample prepared without the use of PEG.

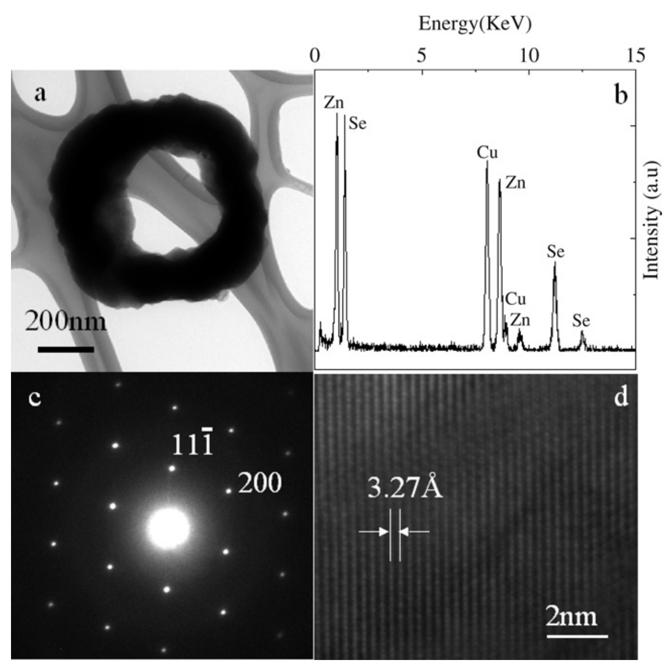

Fig. 3. (a) TEM image of a ZnSe nanodonut, (b) the corresponding EDX spectrum taken from sample shown in Fig. 3 (a), (c) Selected area electron diffraction pattern of a ZnSe nanodonut, revealing the single crystallinity of the ZnSe nanodonut (d) High-resolution TEM image of a ZnSe nanodonut, indicating that the ZnSe nanodonuts are free defects.

is 255 cm^{-1} at room temperature. As for the nanocrystalline ZnSe, the TO and LO phonon peaks are 210 and 255 cm^{-1}, respectively [21,22]. Based on these reports, the TO and LO phonon peaks of

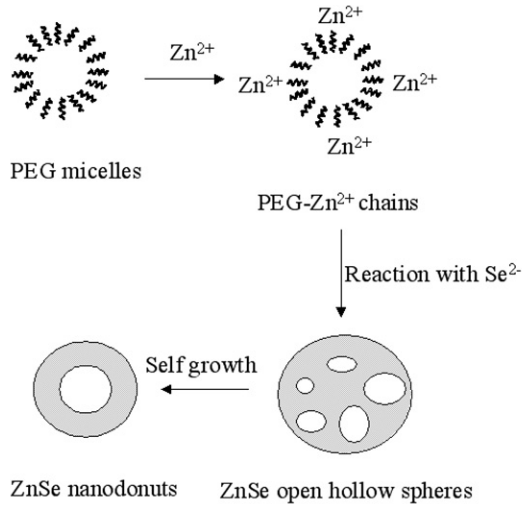

Fig. 4. Schematic illustration for the formation process of the ZnSe nanodonuts.

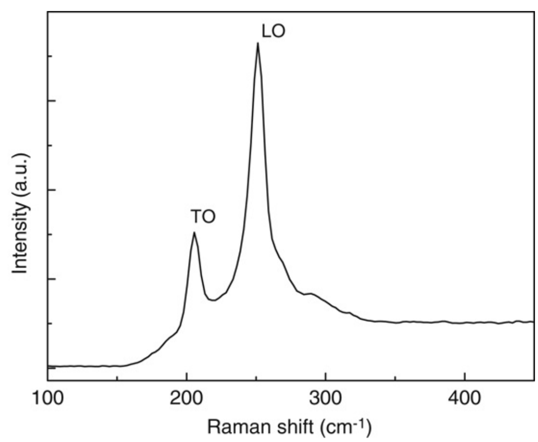

Fig. 5. Room temperature Raman spectrum of the ZnSe sample, showing peaks at 206 and 251 cm^{-1}.

the as-prepared ZnSe nanodonuts are found to shift both toward lower frequency, this may originate from the effects of small size and donut nanostructure of the ZnSe sample.

Two factors are identified as critical to the formation of the ZnSe nanodonuts. In terms of chemical reaction, hydrazine is found to be necessary in helping the selenium dissolution process. In addition, hydrazine behaves as a strong reducing agent in solution with PH > 7, based on Eqs. (1) and (2), resulting in Se being reduced to Se^{2-}.

$$N_2 + 4H_2O + 4e \rightarrow N_2H_4 + 4OH^- \quad E^o = -1.15 \text{ V} \tag{1}$$

$$Se + 2e \rightarrow Se^{2-} \quad E^o = -0.92. \tag{2}$$

This is important for the production of ZnSe. Control experiment performed at similar conditions but in the absence of hydrazine leads to little dissolving of the Se powder and thus little ZnSe in the final product.

PEG is found to play a key role in the formation process of the donut morphology. Without PEG added while keeping other conditions unchanged, only large ZnSe particles with irregular shapes are obtained, as shown in Fig. 2(b). The experimental results suggest that the PEG acts as not only a stabilizing agent preventing aggregation of the ZnSe nanoparticles but also a shape controller for the growth of ZnSe donuts.

The formation process of the ZnSe nanodonuts is proposed schematically in Fig. 4. PEG is firstly dissolved in the limited amount of water and exists as rugged chains' structure [23]. As a nonionic surfactant, PEG has polar hydrophilic heads and hydrophobic hydrocarbon tails, leading to a stable morphology of spherical micelles in the water. When Zn^{2+} ions are added to the solution, reaction between the PEG and the Zn^{2+} ions are expected due to existence of activated O in the PEG molecular chains. This leads to the formation of the PEG-Zn^{2+} complex. In the alkaline solution, hydrazine reduces Se to Se^{2-}, which diffuses to the PEG-Zn^{2+} complex chain and reacts with the Zn^{2+}. With the micelles as template, ZnSe hollow spheres are produced by such reaction. At the same time, nitrogen is generated as one of the products in the reduction reaction (Eq. (1)), leading to simultaneously N_2 void formation in the ZnSe hollow sphere. When heating up, the nitrogen bubbles expand and escape the ZnSe, leading to collapse of the ZnSe walls and eventually donut morphology, as determined by the minimum surface energy. This also explains the rough surface morphology of the nanodonuts.

In summary, we report a solvothermal process to synthesize single crystalline ZnSe nanodonuts. The PEG and hydrazine are found to be critical in the formation of ZnSe nanodonut shape. Such method can be generally applied to other chalcogenide material systems for the growth of donut morphology.

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