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Synthesis of CdSe microspheres via solvothermal process in a mixed solution

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ABSTRACT

CdSe particles with wurtzite structure have been synthesized via solvothermal method using a mixed solution of triethylenetetramine (TETA) and de-ionized water (DIW). It was found that ball-like CdSe precursor with zinc-blende phase could be transformed to wurtzite structure after heat-treating at 580 °C in Ar atmosphere and the obtained microspheres were made up of many nanometer sized CdSe particles. The experimental results were compared with CdSe obtained via hydrothermal method using $N_2H_4{\cdot}H_2O$ as the reducing agent and it was found that CdSe nanorods with wurtzite structure were obtained. It was speculated that TETA in the mixed solution played the role of reducing agent and surfactant. Both the as-prepared products and the annealed powders were systematically characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared absorbance spectroscopy (FTIR) and thermogravimetric analysis (TGA).

1. Introduction

Cadmium selenide (CdSe) nanostructures are of great interest for both fundamental research and technical applications including electrical, optoelectronic devices and biological labeling [1,2]. CdSe has cubic and hexagonal structures and relatively wide direct band gap of 1.74 eV at room temperature [3,4]. It is reported that the properties, such as electrical and optical properties were mainly controlled by the particle size, size distribution and morphologies. Therefore, different methods, such as single molecule precursor [5], hydrothermal method [3], solvothermal synthesis [4], the microwave irradiation route [6] and the organometallic precursor route [7], have been employed to synthesize CdSe with controlled size and shape.

Among the numerous methods developed for the controllable synthesis of metal chalcogenide materials, solvothermal reaction in a homogeneous mixed solution has been proven to be a convenient way to fabricate semiconductor nanocrystals, especially to control the morphology and phase structure of the resulting products by adjusting the composition of the mixed solution [8,9]. Up to now, CdSe nanorods [4,10], nanoneedles [11], nanoflowers [12], microspheres [3] and hollow nanospheres [13] have all been successfully synthesized via a facial solvothermal approach. In our previous study, it was found that the phase and morphology of the as-prepared ZnSe could be controlled by changing the volume ratio of triethylenetetramine (TETA) and de-ionized water (DIW) in the mixed solution but the reaction mechanism had not been discussed [14].

In this paper, we synthesized CdSe microspheres by solvothermal method using $Cd(NO_3)_2$ and Se as raw materials in a mixed solution of TETA and DIW without further adding reducing agent. Results showed that CdSe microspheres with wurtzite structure could be obtained and the reaction mechanism, especially the role of TETA was also discussed.

2. Experimental

2.1. Sample preparation

Analytical-grade reagents, including cadmium nitrate ($Cd(NO_3)_2$), selenium (Se), were purchased from Shanghai Chemical Reagent Corporation and triethylenetetramine, was purchased from Sigma–Aldrich and used as received.

2.5 mmol $Cd(NO_3)_2$ and 1.25 mmol Se were added to a mixed solution (15 ml) of TETA and DIW with volume ratio ($V_{TETA}:V_{DIW}$) of 1:2. The mixed solution was stirred for 30 min and then transferred into a 25 ml stainless steel Teflon-lined autoclave. The autoclave was sealed, kept at 180 °C for 12 h, and then naturally cooled to room temperature. After the reaction, the solution was centrifuged and washed with distilled water and acetone three times each, and the product was dried in a vacuum at 60 °C for 4 h. To obtain pure CdSe, the as-prepared precursor was calcined in a tube furnace at 580 °C under Ar atmosphere for 4 h.

2.2. Characterization

The crystal structure and phase identity of the synthesized products were characterized by a Rigaku D/max 2500 powder X-ray diffractometer (XRD) with Cu Kα radiation ($\lambda = 1.5406$ Å). The morphology and microstructures were observed by a XL-30ESEM scanning electron microscope (SEM). High-resolution transmission electron microscopy (HRTEM) was conducted on a JEOL 2011 transmission electron microscope (TEM) at an accelerating voltage of 200 kV. Thermogravimetric analysis (TGA) of the precursor was conducted on a NETZSCH STA 449C thermogravimete.

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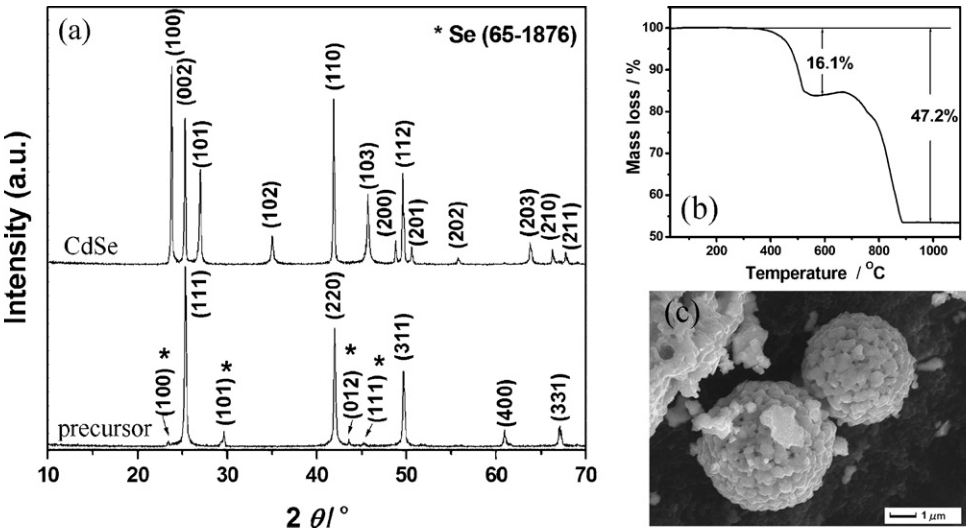

Fig. 1. (a) XRD patterns of obtained precursor and CdSe in TETA and DIW solution. (b) TG curve of precursor. (c) SEM image of precursor.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the obtained precursor and CdSe, and it can be seen that there are two structures existed in the XRD pattern of the precursor, one is zinc-blende CdSe (JCPDS card number 19-0191) and another can be indexed as un-reacted Se (JCPDS card number 65-1876). According to the XRD result, it can be concluded that during the reaction, Se is reduced to Se^{2-} and then reacted with Cd^{2+} to form CdSe, but the reducibility provided is not powerful enough. To remove the organic agent and the small quantity of Se, the obtained precursor must be heat-treated and the process is monitored by the TG experiment. Fig. 1(b) shows the TG curve of the precursor conducted in N_2 atmosphere. There are two regions of mass loss, one is from 330 to 550 °C with the mass loss about 16.1% and the other is in the temperature range of 640 to 880 °C with the mass loss about 31.1%. The first mass loss is mostly due to desorption of organic TETA and evaporation of elementary Se. The second mass loss might due to the melting and decomposition of the obtained CdSe [15]. According to the decomposition formula of CdSe, the theoretical mass loss is 41.4% when decomposed Se evaporated, which is similar to our experimental result (37.1%) considering the deduction of elementary Se and TETA in the original precursor. According to the TG result, pure CdSe could be got by heat-treating the precursor in the temperature range of 550 to 640 °C. In our experiment, we calcined the precursor at 580 °C in Ar atmosphere and the structure of the obtained product was investigated by XRD. As shown in Fig. 1(a), the Se and Zinc-blende peaks are not observed, but rather the wurtzite structure (JCPDS card number 08-0459) becomes prominent after the heat-treatment.

Fig. 1(c) is the SEM image of the obtained precursor and it can be seen that the particles are nearly spherical which are constructed

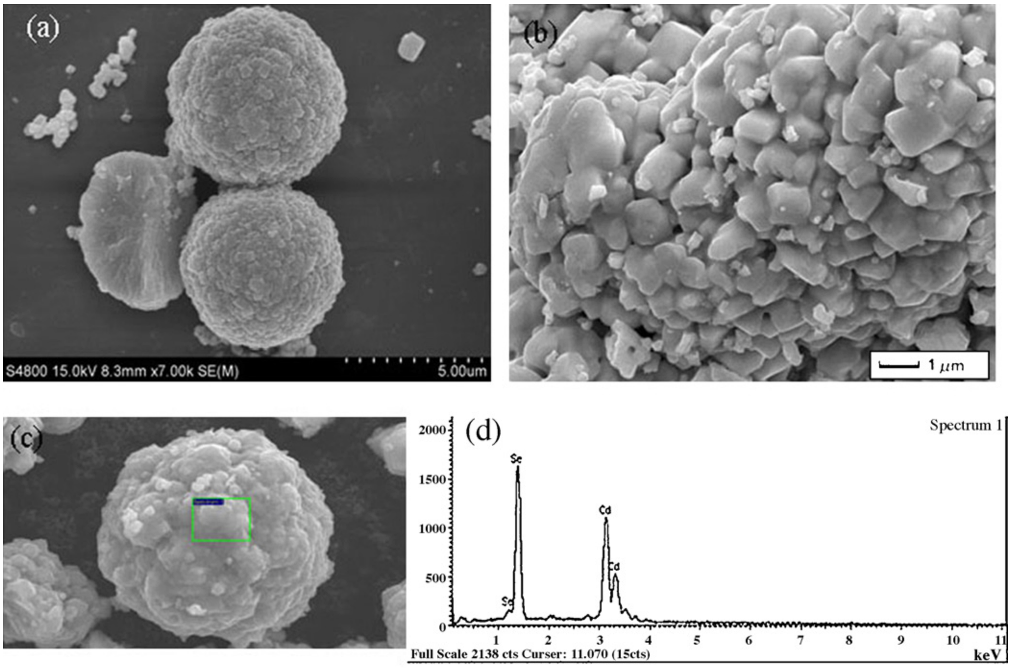

Fig. 2. (a–c) SEM images of CdSe. (d) EDS spectrum of the selected point in (c).

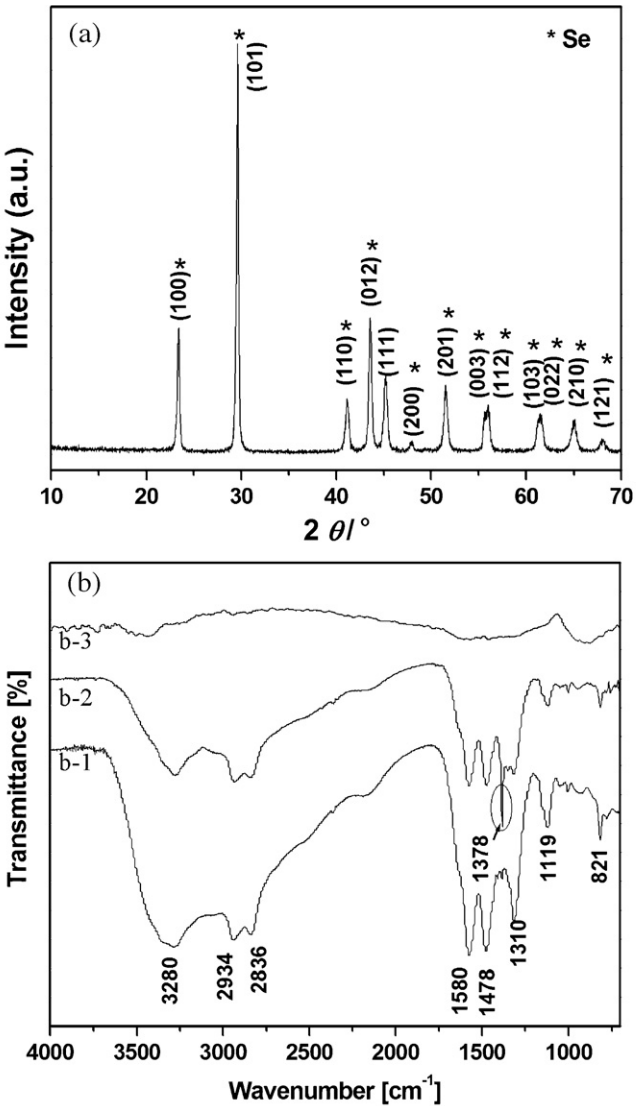

Fig. 3. (a) XRD pattern of product obtained without TETA. (b) FTIR spectra of (b-1): mixed solution before solvothermal reaction. (b-2): mixed solution after solvothermal reaction. (b-3) CdSe obtained after heat-treatment.

by small particles. This ball-like morphology is maintained after the heat-treating as shown in Fig. 2. In Fig. 2(a), one can see that the obtained solid ball-like particles have the average diameter of 5 μm and also are made up of small particles with the average diameter of 700 nm as shown in the magnified image (Fig. 2(b)). To get the average chemical composition of the particles, EDS analysis was carried out and the results are shown in Fig. 2(c) and (d). In the EDS spectrum of the selected point in CdSe particle shown in Fig. 2(c), there are two elements, Cd and Se with an average atom ratio (Cd/Se) of 0.48/0.52, which is near to the stoichiometric proportion of CdSe (1/1). Together with XRD analysis, it can be concluded that pure wurtzite structure CdSe has been prepared in our experiment.

In the experimental process, Cd^{2+} and elementary Se were used as raw materials of CdSe. To form CdSe, Se must be reduced to Se^{2-}. Usually, reducing agent, such as hydrazine hydrate [3], sodium borohydride [16], will be added in the reaction solution. But, in our experiment, the reaction was conducted in the mixed solution of TETA and DIW, without further adding reducing agent. We speculated that TETA might play the role of reducing agent and this could be confirmed by the following experiment. We changed the mixed solution to DIW and kept the same reaction condition, the obtained black powders were examined by XRD. In Fig. 3(a), it can be found that no reaction has been taken place, only elementary Se is obtained.

FTIR measurement of the as-synthesized CdSe and mixed solution before and after the solvothermal reaction was performed to further identify the role of the TETA in the solvothermal synthesis and the results are listed in Fig. 3(b). Bands above 3000 cm^{-1} are assigned to the stretching vibrations of N–H, and bands at about 2934 and 2836 cm^{-1} can be assigned to the C–H vibration. The band at about 1580 cm^{-1} is the scissors vibration of N–H, and the band at 1310 cm^{-1} can be assigned to C–N. Those bands around 1119 and 1478 cm^{-1} are caused by the vibration of CH_2. Band at about 821 cm^{-1} can be assigned to the flexural vibration of N–H. Compared with the solution before reaction, a new band at about 1378 cm^{-1} exists in the FTIR spectrum of solution after reaction, which can be assigned to the stretching vibration of $-NO_2$. Although we cannot make the reaction mechanism clear at the present stage, it can be concluded that a chemical reaction about TETA had taken place and TETA might be partly oxidized. In the redox process, TETA might be oxidized and Se be reduced. The organic species can be removed by heat-treating as shown in Fig. 3(b).

In our previous study, we found that TETA would also behave as surfactant and spherical ZnSe particles would be obtained by solvothermal process. To examine the role of TETA, we also car-

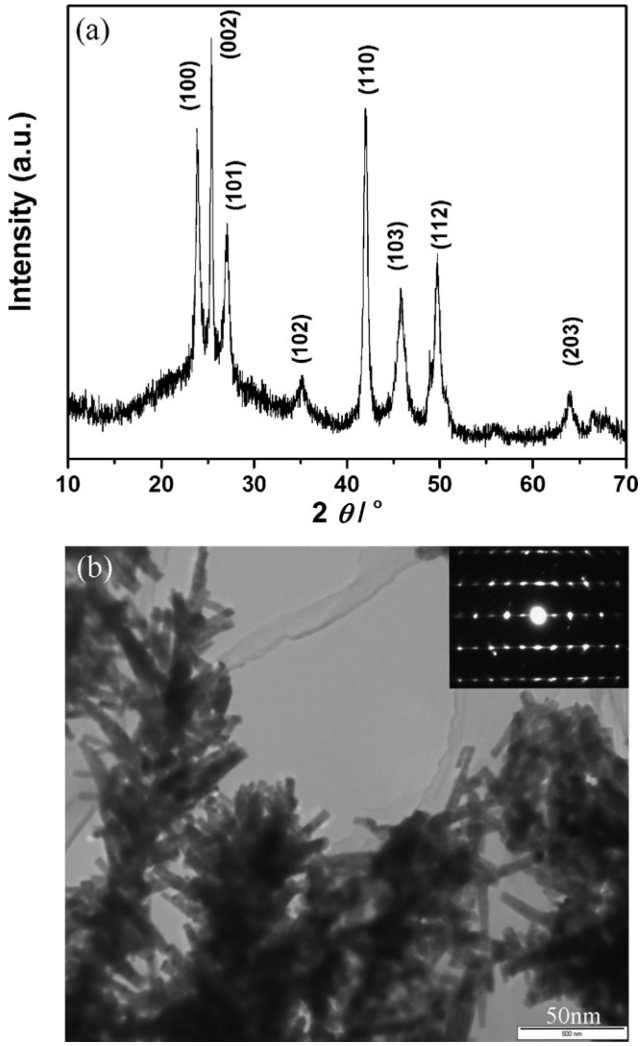

Fig. 4. (a) XRD pattern and (b) TEM image of the CdSe powders reacted without TETA but with hydrazine hydrate (inset is the SAED pattern).

ried out another experiment without TETA but with hydrazine hydrate. The powders collected after the hydrothermal reaction showed wurtzite structure with relatively low crystallinity because of the low reaction temperature (180 °C) as shown in Fig. 4(a). The different ratio of the relative intensity of peaks (1 0 0) and (0 0 2) (I_{100}/I_{002}) as shown in Fig. 1(a) and Fig. 4(a) indicating the different crystal orientation of the obtained particles and this can be confirmed by the morphology analysis. Fig. 4(b) is the TEM image of the obtained CdSe and it can be seen that CdSe nanorods gather together to form pinetree-like aggregates. The inset selected area electron diffraction (SAED) pattern reveals the single crystal nature. According to the literature, wurtzite structure is highly anisotropic [17], so anisotropic CdSe nanorods were obtained without surfactant. But in the solvothermal process, crystal growth will be limited at some faces because of the ligand effect between alkylamine molecules and metal ions. So different morphologies are obtained in different solutions.

4. Conclusion

CdSe microspheres with wurtzite structure have been prepared via solvothermal process in the mixed solution of TETA and DIW followed by heat-treating in Ar atmosphere. Experimental results indicated that TETA played the role of reducing agent and surfactant. A redox reaction took place during the solvothermal process. Because of the existence of TETA, the morphology of CdSe crystals was changed and solid microspheres composed with small particles were obtained. This solvothermal process can be popularized to the preparation of other metal chalcogenide microspheres.

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