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A hydrothermal method to prepare the spherical ZnS and flower-like CdS microcrystallites

Licheng Wang, Luyang Chen, Tao Luo, Yitai Qian *

Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

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Abstract

The spherical ZnS and flower-like CdS microcrystallites are prepared by a convenient hydrothermal process through the reactions of Zn $(CH_3COO)_2{\cdot}2H_2O$ or Cd$(CH_3COO)_2{\cdot}2H_2O$ with S and $NaH_2PO_2{\cdot}H_2O$ in aqueous solution at 180 °C for 12 h. Powder X-ray diffraction (XRD) is used to confirm the cubic phases of the ZnS and CdS microcrystallites. Their chemical compositions are characterized by X-ray photoelectron spectroscopy (XPS). Scanning electron microscope (SEM) images show the morphologies of the as-synthesized ZnS and CdS. The photoluminescence spectra (PL) exhibit their optical properties.

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Keywords: Crystal morphology; X-ray diffraction; Semiconducting materials; Hydrothermal crystal growth

1. Introduction

II–IV binary compound semiconductors possess many interesting physical properties and have potential applications in electronic and optical devices [1,2]. Of the binary compounds, ZnS and CdS are the most typical inorganic semiconductor materials. They play important roles in both basic science and application fields. For instances, ultrafine ZnS particles are the phosphor in thin film electroluminescent devices [3]. CdS has extensive applications in photoelectric conversion in solar cells [4]. Both ZnS and CdS can be used as the component of the light-emitting diode (LED) [5,6].

Fabrication of nanometer to micrometer scale inorganic materials with special morphologies is of great interest to material chemists due to their important influence in both basic scientific researches and potential technological applications [2,7]. A variety of methods have been developed to prepare the sulfides of zinc and cadmium, including solid phase reaction [8], gas phase reaction with H_2S or sulfur vapor [9], sol–gel process [10], hydrothermal or solvothermal route [11–13], gamma-irradiation technique [14,15]. ZnS and CdS with particular structures like quantum dots [16,17], nanowires [18,19], nanoporous particles [20], hollow submicrospheres [21], and so on have been successfully synthesized.

Here, a convenient hydrothermal process is applied to synthesize the spherical ZnS and flower-like CdS microcrystallites through the reactions of $Zn(CH_3COO)_2{\cdot}2H_2O$ or Cd $(CH_3COO)_2{\cdot}2H_2O$ with S and $NaH_2PO_2{\cdot}H_2O$ in aqueous solution at 180 °C for 12 h.

2. Experimental

All the chemicals were analytical grade and purchased from Shanghai Chemical Reagents. In a typical procedure, 0.005 mol of zinc acetate $[Zn(CH_3COO)_2{\cdot}2H_2O]$ and 0.01 mol of sodium hypophosphite $(NaH_2PO_2{\cdot}H_2O)$ were dissolved in 40 ml of distilled water, then 0.005 mol of sulfur sublimed (S) were added into the solution. The mixture was stirred vigorously for 10 min and transferred into a Teflon-lined autoclave with 60 ml capacity. The autoclave was sealed, maintained at 180 °C for 12 h, and then cooled to

* Corresponding author.
E-mail address: ytqian@ustc.edu.cn (Y. Qian).

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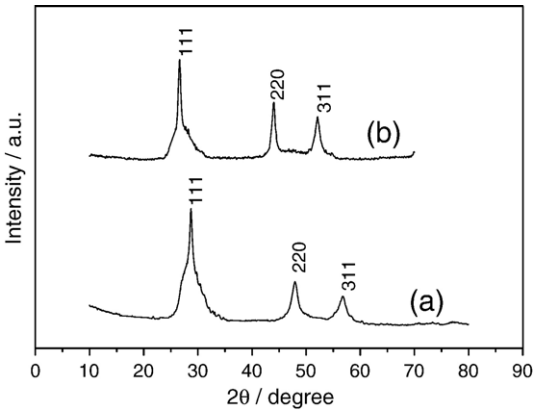

Fig. 1. XRD patterns of ZnS (a) and CdS (b).

room temperature naturally. At last, the white product was collected by filtration, washed with distilled water and ethanol, and then dried at 60 °C in vacuum. The CdS was prepared by the same method with ZnS. Differently, the reactant is $Cd(CH_3COO)_2{\cdot}2H_2O$ and the colour of the product is yellow.

Powder X-ray diffraction (XRD) was performed on a Rigaku D/max-γA X-ray diffractometer equipped with graphite-monochromatized CuKα radiation (λ=1.54178 Å) employing a scanning rate of 8.0000° min^{-1} in the 2θ range from 10° to 80°. The X-ray photoelectron spectra (XPS) were recorded on a VGESCALAB MKII X-ray photoelectron spectrometer, using a non-monochromatized MgKα (1253.6 eV) X-ray as the excitation source in high vacuum (5×10^{-9} Pa). The binding energy values were calibrated from that of C1s (284.6 eV). The morphology was observed by JEOL-KSM-6700F field emission scanning electron microscopy (SEM). The room temperature photoluminescent (PL) emission spectra were measured with a Hitachi-850 fluorescence spectrophotometer.

$$S + H_2PO_2^- + H_2O \xrightarrow[12h]{180^\circ C} S^{2-} + HPO_3^{2-} + 3H^+ \quad (a)$$

$$S^{2-} + Zn^{2+} \longrightarrow ZnS \quad (b)$$

$$S^{2-} + Cd^{2+} \longrightarrow CdS \quad (c)$$

Scheme 1. Chemical reactions in the experiment.

3. Results and discussion

The phase of ZnS is confirmed by its XRD pattern in Fig. 1a. The product has the face-centered cubic crystal lattice and the lattice constants are $a=b=c$=5.375 Å, which are in good agreement with the reported values ($a=b=c$=5.345 Å, JCPDS 80-0020). The broadening of all diffraction peaks indicates that the spherical ZnS is composed of many relatively small nanoparticles, of which the diameters are ca. 19 nm according to Scherrer formula. CdS has the similar XRD pattern to ZnS. Fig. 1b shows that all the diffraction peaks of CdS can also be indexed as the face-centered cubic phase and the lattice constants are calculated as $a=b=c$=5.798 Å, being close to the reported values ($a=b=c$=5.811 Å, JCPDS 75-2023). The particle size of the as-synthesized CdS is ca. 37 nm according to Scherrer formula. No other characteristic peaks for impurities are detected.

The chemical compositions of the as-synthesized ZnS and CdS are determined by the XPS. The binding energies of Zn2p3 and S2p for ZnS are located at 1021.95 and 161.55 eV, and that of Cd3d5 and S2p for CdS are at 405.25 and 161.48 eV respectively, which are in good agreement with the reported values [22–24]. The molar ratio of Zn to S is calculated as 0.93 and that of Cd to S is about 0.92, being close to 1. All the results confirm the formations of ZnS and CdS.

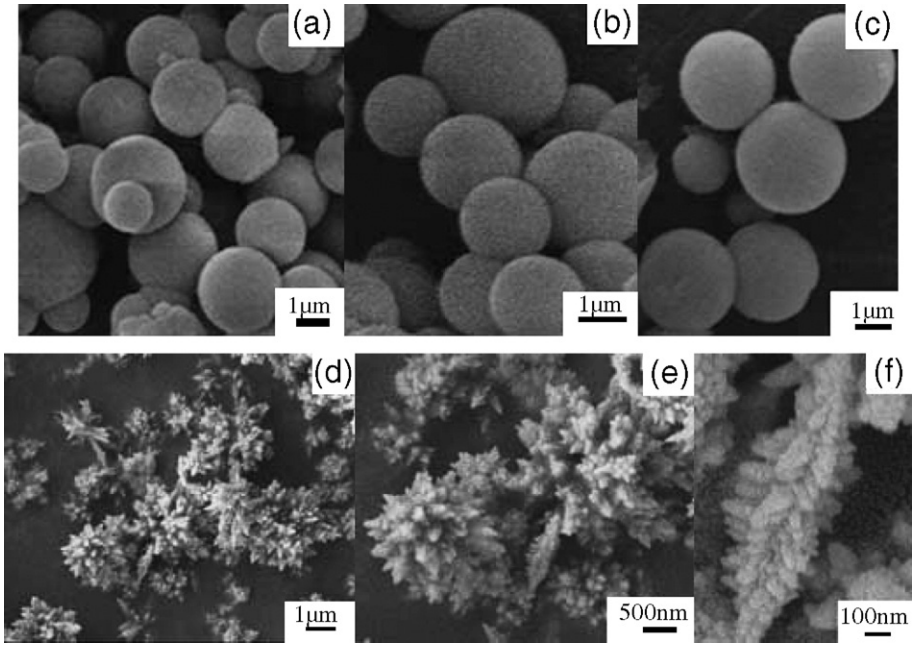

Fig. 2. SEM images of ZnS (a, b, c) and CdS (d, e, f) with different magnifications.