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Mixed-solvothermal synthesis of CdS micro/nanostructures with optical and ferromagnetic properties

Zhufeng Zhang[b], Yinshuan Ren[a,b,c,*], Lu Han[b], Guoya Xie[b], Bo Zhong[b]

[a] School of Physics and Electronics, Qian Nan Normal College for Nationalities, Guizhou Duyun 558000, PR China
[b] College of Mobile Telecommunications Chongqing University of Posts and Telecom, Chongqing, Hechuan 401520, PR China
[c] Optoelectronic Information Laboratory of School of Physics and Electronics, Qian Nan Normal College for Nationalities, Guizhou Duyun 558000, PR China

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ABSTRACT

Several special CdS micro/nanostructures, including microspheres, microrods, nanorods, nanosheets and nanoparticles were successfully synthesized by a simple solvothermal method using ethylenediamine (EN), ethanolamine (EA) and ethylene glycol (EG) as pure and mixed solvents with different S and Cd sources. X-ray diffraction (XRD) measurements showed that micro/nanostructures CdS had a hexagonal wurtzite structure. Scanning electron microscopy (SEM) images showed that the morphologies of CdS consisted of microrods, microsphere and nanosheets at different preparation conditions. Transmission electron microscopy (TEM) images revealed the CdS consisted of nanoparticles and nanorods at different preparation conditions. The optical properties of the CdS were measured by optical absorption spectroscopy. A vibrating sample magnetometer (VSM) measured that the CdS nanoparticles exhibited room temperature ferromagnetism. The saturation magnetization of the CdS nanoparticles was 9.109 (10^{-3} emu/g). The origin of the CdS nanoparticles with ferromagnetic properties is attributed to structural defects.

1. Introduction

Synthesis of inorganic crystals with special morphologies have attracted much interest owing to their importance in basic scientific research and potential technological applications in a lot of fields, such as solar cells, lithium batteries, photo-detectors, light waveguides, gas sensing and photo catalysis [1–4].

Cadmium sulfide (CdS) is regarded as one of the most effective visible-ligth photocatalysts because of its narrow band gap (2.4 eV for bulk material) and sufficient conduction band overpotential [5–9]. CdS can be deposited by several techniques including spin coating technique [10], sputtering [11], spray prolysis [12] and electrodeposition [13] that are used for preparing the mentioned material. S. Butt et al. [14] have prepared polycrystalline CdS by close spaced sublimation technique. They have obtained various thicknesses ranging from 250 to 940 nm. Y. Al-Douri et al. [15] have used the density function theory (DFT) for energy band calculations of CdS and CdTe to research the energetic transition and optical properties calculations as a function of quantum dot diameter. Also, they [16,17] have studied the effect of temperature on structural and optical properties of CdS nanostructures deposited on the glass substates. Y.Q. Zhu et al. [18] have presented novel, very simple and low-cost thin film position sensitive detectors (TFPSDs) which employ indium tin oxide (ITO)-cadmium sulfide (CdS)-Au structures. CdS is chosen as the photosensitive layer since its excellent photoconductive property, low cost and suitable for depositing on different type substrates with large areas. Y. Al-Douri et al. [19] have used the sol-gel spin coating technique to prepare CdS nanostructures include Polythylene glycol (PEG 200) with different thiourea concentrations 0.01, 0.05, 0.07 and 0.1 mol/L deposited on quartz substrate for photovoltaic applications. The CdS nanostructures were prepared with spin coating technique. The effect of annealing temperature on structural, morphological, optical, electrical and thermal properties of CdS nanostructures deposited on p-Si and quartz substrates was investigated [20,21]. M. Ameri et al. [22] have aimed to combine CdX compounds having different structural and electronic properties in order to obtain new material, $CdS_{1-x}Te_x$ ternary alloy. H.S. Al-Jumaili et al. [23] have studied nanoheterojunction solar cells $CdS/Cd_{2x}(CuIn)_{1-x}S_2$. While hydrothermal/solvothermal route have been proved to be a practical approach for the preparation of CdS nanoparticles in 3D complex structures. For example, spherical CdS nanostructures via a solvothermal process were reported by P.T. Zhao et al. [24]. F. Chen et al. [25] prepared 3D CdS superstructures of flowerlike structure by a simple hydrothermal method. A variety of specific three dimensional CdS micro/nanocrystals were prepared

* Corresponding author at: School of Physics and Electronics, Qian Nan Normal College for Nationalities, Guizhou Duyun 558000, PR China.
E-mail addresses: zzf221@126.com (Z. Zhang), renyinshuan318@163.com (Y. Ren).

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using a hydrothermal method [24]. The CdS nanoparticles and nanorods were successfully synthesized via a solvothermal method at 200°Cfor 24 h with ethylenediamine and water as pure and mixed solvents [26].

However, few reports have been intensively focused using a variety of Cd and S sources for the preparation of CdS micro/nanostructures in different mixed solutions [27]. Few authors have investigated the ferromagnetism of CdS nanoparticles.

In this work, several special CdS micro/nanostructures have been synthesized by a simple mixed-solvothermal method in the presence of oxalic acid. The effects of solvent composition, oxalic acid concentration, sulfur source and cadmium source on the synthesis were systematically investigated. The CdS nanoparticles exhibited room temperature ferromagnetism. The origin of the ferromagnetism in CdS nanoparticles is attributed to structural defects.

2. Experimental

The synthesis of CdS nanostructures has been carried out in a closed cylindrical teflon-lined stainless steel chamber, using solvothermal technique. All of the chemical reagents used in this experiment were of analytical grade and used without further any purification. In a typical procedure, 1 mmol of $CdCl_2$ and lmmol of oxalic acid were dissolved in mixed solvents of ethylenediamine (EN) and ethylene glycol (EG) with a 1:2 volume ratio (total volume of 30 ml). The mixture was put into a 40 ml Teflon vessel. Then the mixture was magnetically stirred for 10 min. After that, l mmol of S powder was added to the solution and 10 min stirring was continued. After being sealed, the autoclave was heated to 180 ℃ in 30 min and maintained at this temperature for 24 h, then natural cooled to room temperature. The yellow colored product was collected, washed with anhydrous ethanol and with distilled water several times, and then dried at 60 ℃ for 6 h in vacuum. The similar synthetic methods were used for the preparation of other samples. The prepared products were recorded as sample A-L, respectively (Tables 1 and 2).

The crystal structures of the samples were analyzed by X-ray diffraction (XRD) using a Japan Mac X-ray diffraction with Cu Kα radiation (λ=0.154 nm).

The morphologies and sizes of the products were measured by a field emission scanning electron microscopy (FE-SEM, Philips XL-30) and transmission electron microscopy (TEM, hitachi-8100 transmission electron microscopy, Japan). UV–Vis diffuse reflectance spectroscopy (UV–Vis) was performed with a Perkin lambda-20 spectrometer. The magnetic properties of samples were measured by vibrating sample magnetometer (VSM, Lakeshore 7400).

Table 1
The reaction conditions of the prepared products were summarized (All experiments were carried out at 180 ℃ for 24 h).

Sample	Composition of solvent	Sulfur, Cadmium Source	Concentration of oxalic acid (M)
A	30 ml EN	1 mmol S +1 mmol $CdCl_2$	0.025
B	5 ml EN+25 ml $N_2H_4{\cdot}H_2O$	1 mmol S +1 mmol $CdCl_2$	0.025
C	5 ml EN+25 ml EG	1 mmol S +1 mmol $CdCl_2$	0.025
D	10 ml EN+20 ml EG	1 mmol S +1 mmol $CdCl_2$	0.025
E	15 ml EN+15 ml EG	1 mmol S +1 mmol $CdCl_2$	0.025
F	20 ml EN+10 ml EG	1 mmol S +1 mmol $CdCl_2$	0.025

Table 2
The reaction conditions of the prepared products were summarized (All experiments were carried out at 180 ℃ for 24 h).

Sample	Composition of solvent	Sulfur, Cadmium Source	Concentration of oxalic acid (M)
G	10 ml EN+20 ml EA	5 mmol CH_4N_2S +5 mmol CdO	0
H	15 ml EN+15 ml EA	5 mmol CH_4N_2S +5 mmol CdO	0.012
I	20 ml EN+10 ml EA	5 mmol CH_4N_2S +5 mmol CdO	0.025
J	20 ml EN+10 ml EA	5 mmol CH_4N_2S +5 mmol CdO	0.040
K	20 ml EN+10 ml EA	5 mmol CH_4N_2S +5 mmol CdO	0.055
L	20 ml EN+10 ml EA	5 mmol CH_4N_2S +5 mmol CdO	0.070

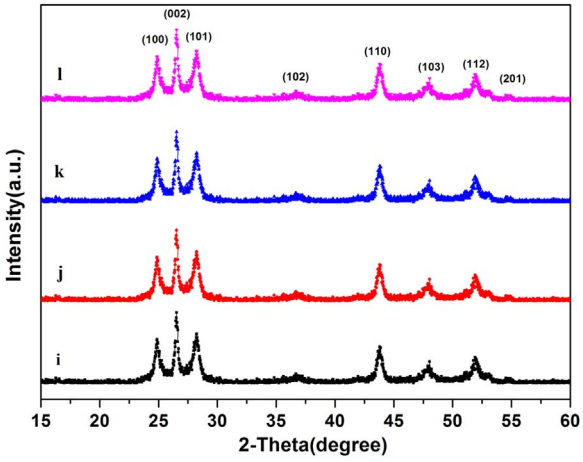

Fig. 1. Shows some of the powder XRD patterns of the as-obtained samples. (i) sample I; (j) sample J; (k) sample K; (l) sample L.

3. Results and discussion

The chemical composition and crystal structure of the products were analyzed by XRD method. Fig. 1 shows some of the powder XRD patterns of the as-obtained samples. (i) sample I; (j) sample J; (k) sample K; (l) sample L, which were synthesized with different concentration of oxalic acid at solution composition composed of 20 ml EN and 10 ml EA via thiourea as S source and CdO as Cd source with other conditions unchanged. The diffraction peaks positioned at 2 θ values of 24.9°, 26.4°, 28.5° 37.0°, 43.7°, 48.1°, 52.2° and 54.5° match well with the respective, (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2) and (2 0 1) reflections of hexagonal wurtzite CdS, which are in good agreement with the PDF reference data [PDF 41–1049 (ICCD, 2002), a =4.15 Å, c =6.750 Å]. On comparing the CdS diffraction peaks in Fig. 1, it is found that the preferential orientation of CdS nanostructures is along the (0 0 2) plane, as its intensity highest. No trace of any other secondary phase is observed in Fig. 1. At the same time, the narrow and sharp peaks indicate the good crystallinity of the prepared products. The average particle size of CdS nanoparticles has been calculated with the Scherrer's formula [28].

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

Where D is the grain size, k is a fixed constant taken as 0.94, λ is the wavelength of the X-ray used (λ=0.154 nm),β is the full width at half maximum and θ is the diffraction angle. The particle size of CdS nanoparticles are found to be within the range 35–70 nm. The lattice constants (a) and (c) were deduced via [21].