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Synthesis and characterization of CdS:Zn nanoparticles by microwave irradiation method

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Abstract

Nanoparticles of $Cd_{1-x}Zn_xS$ (x = 0-0.3) were prepared in ethylene glycol using microwave irradiation. Zinc acetate, cadmium acetate and thioacetamide were used as the sources of zinc, cadmium and sulfur respectively. Diffraction peaks in powder X-ray diffraction (XRD) patterns of the nanoparticles showed a gradual shift to higher angles with increase in zinc content. Diffuse reflectance spectroscopy (DRS) of the specimens revealed that the absorption edges for $Cd_{1-x}Zn_xS$ nanoparticles blue-shifted upon increasing x value. Energy dispersive X-ray analysis (EDX) data proved the ability of microwave in producing a desired compound. FTIR studies of the specimens revealed the presence of Zn in the produced compounds.

Keywords: $Cd_{1-x}Zn_xS$ nanoparticles; microwave irradiation; X-ray diffraction (XRD); diffuse reflectance spectroscopy (DRS)

1. Introduction

II-VI nanoparticle semiconductors, especially $Cd_{1-x}Zn_xS$ ternary system has received considerable attention because of its potential applications in solar cells and flat panel displays fabrication [1-3]. $Cd_{1-x}Zn_xS$ nanoparticles have been synthesized by various techniques such as hydrothermal method [4], solvothermal synthesis [5], microwave irradiation [6], vapor transport chemical conversion [7], reverse micelle's technique [8] etc. Compared to the above mentioned techniques, the use of microwave irradiation has several advantages as it is less sophisticated, a faster process and at room temperature technique. Microwave is an electromagnetic radiation with the frequency range 0.3–300 GHz. It provides a uniform environment for chemical reaction to occur. Variety of nanosized materials have been synthesized by this technique [9-11]. In microwave processing, microwave radiation is absorbed and converted to thermal energy which is the activation energy for initiation the chemical reaction of the starting materials [12,13]. Wang et al synthesized $Cd_{1-x}Zn_xS$ solid solution using $Zn(CH_3COOH)_2$, $Cd(CH_3COOH)_2$ and thioacetamide (TAA) as starting materials and sodium dodecyl sulfate (SDS) as surfactant and water as solvent at 80 °C for 5 h [14]. Sreejith et al synthesized hexagonal $Cd_{1-x}Zn_xS$ (x=0–0.75) by solution phase method using $CdCl_2$, $Zn(CH_3COO)_2 \cdot 2H_2O$ and thiourea, NH_2CSNH_2 in ethylene glycol as solvent at 160 °C

[1]. Chen et al, have synthesized $Zn_{1-x}Cd_xS$ nanomaterials in presence of polyamidoamine (PAMAM) at 300°C for 120 min [15]. $Cd_{1-x}Zn_xS$ nanoparticles were also prepared by a one-pot solvothermal process from $Zn(CH_3COO)_2$, $Cd(CH_3COO)_2$ and $NaS_2CNEt_2 \cdot 3H_2O$ (sodium diethyldithiocarbamate, DDTC) [16].

In the present work, $Cd_{1-x}Zn_xS$ nanoparticles (with x=0-0.3) were synthesized by microwave irradiation method. The produced powders were studied by powder X-ray diffraction (XRD), energy dispersive X-ray analysis (EDX), Fourier transform infrared spectroscopy (FT-IR) and UV–Vis diffuse reflectance spectroscopy (DRS).

2. Experimental

Zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$ extra pure), cadmium acetate ($Cd(CH_3COO)_2 \cdot 2H_2O$ extra pure), thioacetamide (TAA, CH_3CSNH_2 GR for analysis), ethylen glycol and absolute ethanol were obtained from Merck, and used without further purification. Double distilled water was used for the experiments. In a typical synthesis procedure for preparation of $Cd_{0.8}Zn_{0.2}S$ nanoparticles, cadmium acetate dehydrate (1.066g) and zinc acetate dehydrate (0.219g) were dissolved in 15ml of ethylene glycol under stirring at room temperature. Also, 0.375g of TAA was dissolved in 15ml of ethylene glycol. Then, the TAA solution was slowly added to the above mentioned solution under magnetic stirring. The solution was irradiated in air for 10 cycles. Each cycle was 100s long, and composed of 30s and 70s

for the on and off periods, respectively. The formed suspension was centrifuged to get the precipitate out and washed three times with double distilled water and ethanol to remove the unreacted reagents and dried at 80 $^\circ$C for 24h and further analyzed.

3. Results and discussion

3.1. Crystalline structure

Figure1 shows the powder XRD patterns for $Cd_{1-x}Zn_xS$ nanoparticles as a function of composition (x).
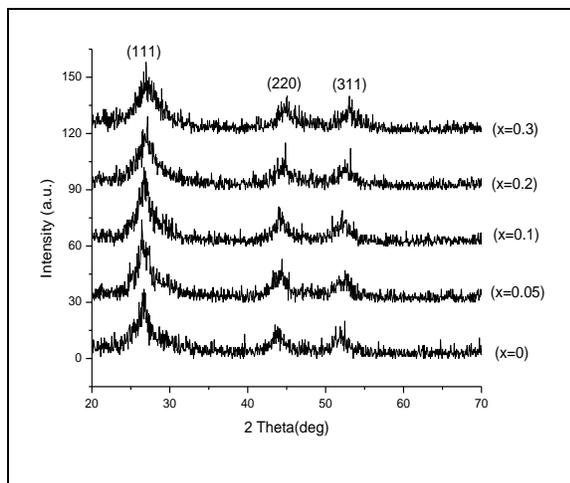
Figure 1. XRD patterns of $Cd_{1-x}Zn_xS$ nanoparticles (x = 0–0.3).

As can be seen, the diffraction peaks corresponding to (1 1 1), (2 2 0) and (3 1 1) planes of cubic crystal gradually shift to larger diffraction angles as the Zn content increased. This can be attributed to the formation of $Cd_{1-x}Zn_xS$ nanoparticles. Li et al reported the same observation and argued that Zn^{2+} is incorporated in the CdS lattice or enters its interstitial sites [10].

The peak broadening in the patterns indicates that the $Cd_{1-x}Zn_xS$ nanoparticles are very small in size. The XRD data were used to estimate the average size of constituent crystallites by Scherrer's equation [17]. The average particle size, D, was determined as follows:

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

where λ is the wavelength of X-ray radiation (0.15406nm), K the Scherrer constant (K=0.9), θ the characteristic X-ray radiation and β the full-width-at-half-maximum of the (111) plane (in radians). In Table 1, mean particle size for the nanoparticles of $Cd_{1-x}Zn_xS$ with different Zn contents calculated by Eq. (1) is tabulated.

3.2. Optical properties

$Cd_{1-x}Zn_xS$ nanoparticles (with x=0-0.3) have been studied by diffuse reflectance spectroscopy (DRS) technique using Avantes Avaspec-2048-TEC. The DRS of the samples are demonstrated in Fig. 2. CdS has an absorption edge located at about 518 nm. It is observed from the figure that the increment in the Zn content of the $Cd_{1-x}Zn_xS$ system led to a blue-shift in the diagram which is well in agreement with the XRD pattern shown in Fig 1.
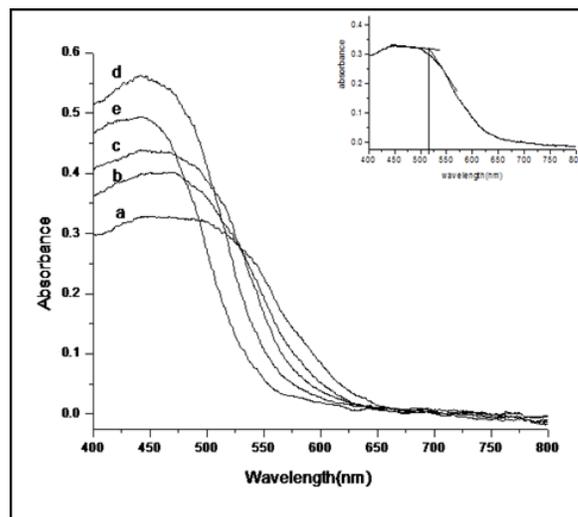
Figure 2. The diffuse reflectance spectra (DRS) for the $Cd_{1-x}Zn_xS$ nanoparticles with different x values: (a) 0, (b) 0.05, (c) 0.1, (d) 0.2 and (e) 0.3. Top right corner shows the way to calculate the band gap for (a).

Table 1. Mean particle size (D), wavelength of absorption edge and band gap calculated from onset of the absorption .edge for the Cd1−xZnxS nanoparticles (x = 0–0.3)

Nanoparticles	D (nm)	$2\theta_m$(°)	Wavelength (nm)	Bandgap (eV)
CdS	4.16	26.558	518	2.39
$Cd_{0.95}Zn_{0.05}S$	4.21	26.705	505	2.45
$Cd_{0.90}Zn_{0.10}S$	4.45	26.749	500	2.48
$Cd_{0.80}Zn_{0.20}S$	3.45	26.965	475	2.61
$Cd_{0.70}Zn_{0.30}S$	3.13	27.099	469	2.64

The formation of homogeneous solid solution is worth noting. Furthermore, absorption edge of the prepared $Cd_{1-x}Zn_xS$ nanoparticles shows a continuous shift which enables one to control the band gap of the $Cd_{1-x}Zn_xS$ nanoparticles. Band gaps for the nanoparticles are estimated from the onset of the absorption edges. According to the manner proposed by Zhao et al [18] for calculating band gap, which is typically shown for CdS sample on the top right side of Fig. 2, the band gap of the samples were calculated and the results are given in Table 1. It is found from the figure that the absorbance of all the specimens is high in visible region, compared to other regions, which suggest that the material can act as an absorptive one in this region.

3.3. Compositional studies

The actual composition of as-synthesized $Cd_{1-x}Zn_xS$ nanoparticles was found by EDX. Figure 3 shows representative EDX spectrum of $Cd_{0.8}Zn_{0.2}S$ nanoparticles.

No appreciable impurity is observed in the spectrum. The actual compositions of $Cd_{1-x}Zn_xS$ nanoparticles with x value varying from zero to 0.3 are given in Table 2. It is observed from Table 2 that a deviation in sulfur contents from stoichiometry value, due to its high vapor pressure, has happened. It is also seen in the Table that the actual amount of Zn concentration in the samples is nearly in accordance with the desired x value of the specimens. This is an indication of the microwave ability in producing the desired compound.

The FT-IR spectra of Cd1-xZnxS nanocrystals are presented in Fig. 4. The band at 3417.63 cm-1 is due to O–H stretching vibrations of water molecules. Bending vibrations of water molecules appeared at 1627.81 cm-1 [19]. The vibrations of C=O and C–O are typically at 1558.38 cm-1 and 1404.37 cm_1, the appearance of these vibrations is due to the presence of the zinc acetate and cadmium acetate [18]. The vibrational absorption peaks of the Cd–S bond at 407 cm−1 and 669 cm-1 are also observed. The band at 694.07 cm-1 is assigned to Zn-S stretching vibration mode [20-22].

Table 2. Actual composition of $Cd_{1-x}Zn_xS$ nanoparticles

Sample	Cd^{2+}(mol) ($\times 10^{-3}$)	Zn^{2+}(mol) ($\times 10^{-4}$)	S^{2-} (mol) ($\times 10^{-3}$)	actual composition
CdS	5.00	0.00	5.00	$Cd_{0.57}S_{0.43}$
$Cd_{0.95}Zn_{0.05}S$	4.75	0.25	5.00	$Cd_{0.55}Zn_{0.03}S_{0.42}$
$Cd_{0.90}Zn_{0.10}S$	5.50	0.50	5.00	$Cd_{0.51}Zn_{0.06}S_{0.43}$
$Cd_{0.80}Zn_{0.20}S$	4.00	1.00	5.00	$Cd_{0.45}Zn_{0.11}S_{0.44}$
$Cd_{0.70}Zn_{0.30}S$	3.50	1.50	5.00	$Cd_{0.41}Zn_{0.16}S_{0.43}$
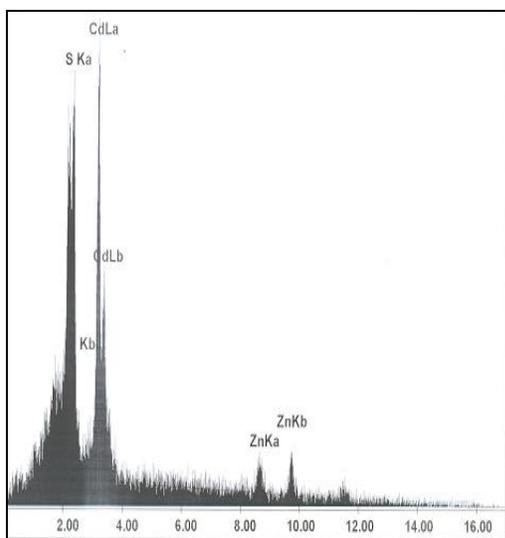
Figure 3. Representative EDX spectrum of $Cd_{0.8}Zn_{0.2}S$ nano-crystals.
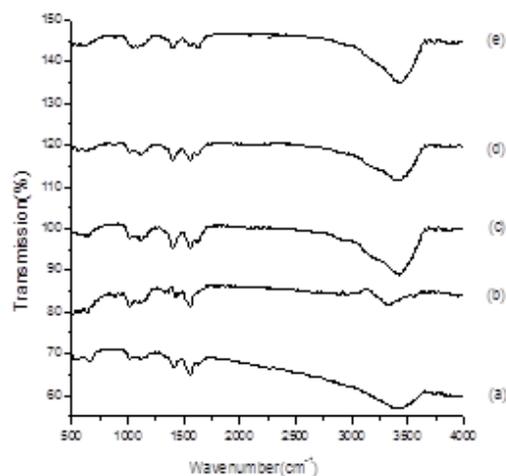
Figure 4. FT-IR spectra of Cd1−xZnxS nanocrystals with different x values: (a) 0, (b) 0.05, (c) 0.1, (d) 0.2 and (e) 0.3.

4. Conclusions

$Cd_{1-x}Zn_xS$ nanoparticles were prepared by microwave irradiation. The proposed method is known as a fast, simple and cheap way to prepare nanomaterials. The grain size calculated from Debye–Scherer formula showed a decrease in the grain size with increase in Zn^{2+} concentration. UV–Vis DRS showed increment in band gap of the nanoparticles upon substituting Cd^{2+} by Zn^{2+}. With increasing Zn content from 0 to 0.3, the absorption edge experienced a blue shift in the diagram. EDX results revealed a good agreement in $Cd_{1-x}Zn_xS$ ions content concentrations with the expected values. FTIR results showed the presence of Zn functional groups indicating the formation of $Cd_{1-x}Zn_xS$ system.

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سنتز و مشخصه یابی نانوذرات CdS:Zn توسط روش تابش دهی مایکروویو

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چکیده:

نانوذرات($x = 0$-0.3) $Cd_{1-x}Zn_xS$ با استفاده از تابش دهی مایکروویو در اتیلن گلیکول تهیه گردید. روی استات، کادمیم استات و تیو استامید به ترتیب به عنوان منابع روی، کادمیم و گوگرد مورد استفاده قرار گرفتند. قله‌های تفرق الگوهای تفرق اشعه ایکس (XRD) نانوذرات یک جابجایی به زوایای بزرگتر در اثر افزایش میزان روی موجود نشان داد. طیف نگاری بازتابی نفوذ (DRS) نمـونه‌ها آشکار نمود که لبه‌های جذب نانو ذرات $Cd_{1-x}Zn_xS$ در اثر افزایش اندازه x، به سمت آبی جابجا گردیدند. داده‌های حاصل از تجزیه و تحلیل متفرق کننده انرژی اشعه ایکس (EDX)، قابلیت امواج مایکروویو را برای تولید یک ترکیب مورد نظر اثبات نمود. مطالعات FTIR نمونه ها، حضور روی را در ترکیبات تولید شده آشکار نمود.

کلمات کلیدی: نانوذرات $Cd_{1-x}Zn_xS$، تابش دهی مایکروویو، تفرق اشعه ایکس (XRD)، طیف نگاری بازتابی نفوذ (DRS)

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