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Influence of different solvents on the structural, optical and morphological properties of CdS nanoparticles

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ABSTRACT

CdS is one of the most important II–VI semiconductors, with applications in solar cells, optoelectronics and electronic devices. CdS nanoparticles were synthesized via microwave-assisted solvothermal technique. Structural and morphological characterization revealed the presence of crystalline structures presenting single phase with different morphologies such as "nanoflowers" and nanoplates depending on the solvent used. Optical characterization was made by diffuse reflectance and photoluminescence spectroscopy, revealing the influence of the different solvents on the optical properties due to structural defects generated during synthesis. It is proposed that these defects are related to sulfur vacancies, with higher concentration of defects for the sample synthesized in ethylene glycol in comparison with the one synthesized in ethylene diamine.

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1. Introduction

Development of morphology-controlled synthesis methodologies is of great interest in materials chemistry [1]. The synthesis of binary metal chalcogenides of group II–VI semiconductors has been the focus of recent scientific research due to their important non-linear optical properties, luminescent properties, quantum size effect and other important physical and chemical properties [2]. Among these materials, CdS, one of the most important II–VI group semiconductors, has potential applications for light-emitting diodes, solar cells, optoelectronics and photocatalysts [3]. It has a direct band gap of 2.5 eV for bulk hexagonal wurtzite structure [3], and a Bohr exciton diameter around 5.8 nm [4].

Several methods exist for the synthesis of CdS. Some examples are metal-organic precursors, sol–gel, sonochemical, microwave assisted synthesis and chemical bath deposition, etc. [5]. Zhu et al. [6] reported the preparation of CdS nanoribbons by the microwave irradiation of an ethylene diamine solution of 1-pyrrlidine dithio carboxylic acid ammonium salt (APDTC) and cadmium chloride under ambient air. Singh et al. [5] reported the synthesis of CdS by sonochemical and microwave-assisted hydrothermal method. Zhang and Gao [7] reported the synthesis of CdS nanorribons via hydrothermal microemulsions, and they observed that modifying some parameters in the synthesis route such as temperature and surfactant type it was possible to control the shape and size of the particles.

The microwave-assisted solvothermal method combines the advantages of both hydrothermal and microwave-irradiation techniques such as very short reaction time, production of small particles with a narrow size distribution and high purity which might be attributed to fast and homogeneous nucleation of the mixture [8]. The effect of heating is created by the interaction of the dipole moment of the molecules with the high frequency electromagnetic radiation (2.45 GHz) [9]. Recently, microwave-heating method has attracted researchers' attention, because of very short reaction time, production of small particles with narrow particle size distribution, and low energy consumption compared with conventional methods [10].

Although CdS nanoparticles had been synthesized before in different solvents [2], a study more focused on the influence of the synthesis condition on the structural and optical properties is necessary. This study involved the synthesis of CdS nanoparticles via a microwave-assisted solvothermal method. A study of the influences of the solvent on the particles morphology, structural and optical properties was carried. The samples were characterized by X-ray diffraction, diffuse reflectance and colorimetric coordinates, photoluminescence and FE-SEM techniques.

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2. Experimental

2.1. Preparation of CdS samples

CdS nanoparticles were synthesized using cadmium chloride monohydrated ($CdCl_2{\cdot}H_2O$ – *Vetec* 99%) and thiourea (NH_2CSNH_2 – *Vetec* 99%) as precursors. In a typical procedure, 0.01 mol of cadmium chloride and 0.03 mol of thiourea were, separately, dissolved in 50 mL of different solvents (ethylene glycol or ethylene diamine). Next, the cadmium solution and the thiourea solution were mixed together and loaded in a 110 mL Teflon autoclave reaching 90% its volume, which was sealed and placed in a homemade microwave-solvothermal system using 2.45 GHz microwave radiation with maximum power of 800 W. The reactional mixture was heated at 180 °C for 32 min at a heating rate of 20 °C min^{-1} and then air cooled at room temperature, and washed with absolute ethanol.

The yellow products were dried in N_2 atmosphere at 100 °C for 5 h. The sample synthesized in ethylene glycol is named Cd01EG and the one synthesized in ethylene diamine is named Cd01EN.

2.2. Characterization of CdS samples

The powders were structurally characterized using an automatic X-ray diffractometer (Rigaku, Rotaflex RU200B) with CuKα radiation (50 kV, 100 mA, λ = 1.5405 Å) and in a θ–2θ configuration using a graphite monochromator. The scanning range was between 20 and 70° (2θ), with a step size of 0.02°. Diffuse reflectance and colorimetric coordinates of the samples were measured in the 400 and 700 nm range, using a spectrophotometer (Minolta, CM2600d) equipped with standard type D65 (day light) light source, following the CIE-$L^*a^*b^*$ colorimetric method recommended by the CIE (Commission Internationale de l'Eclairage) [11]. The different morphologies of CdS were determined by field emission scanning electron microscopy using a (FE-SEM, Zeiss Supra™ 35) equipment. Infrared spectra were obtained by diffuse reflection infrared Fourier transform (DRIFT) with a Shimadzu spectrometer (IRPrestige 21) with a diffuse reflectance device. Aluminum mirror was used as reference. Photoluminescence spectra were collected at room temperature with a Thermal Jarrel-Ash Monospec 27 monochromator and a Hamamatsu R446 photomultiplier. The 350 nm exciting wavelength of a kripton ion laser (Coherent Innova) was used, with the nominal output power kept at 550 mW.

3. Results and discussion

3.1. Reaction mechanism

In general, it is believed that the reaction mechanism of cadmium salts and thiourea in the solution to produce nanocrystalline CdS has two possible routes. According to the literature, many metals in M^{n+} can complex with thiourea (Tu) to form M–Tu complexes. Therefore, one possible reaction mechanism is that the Cd–Tu complex decomposes at a given temperature under autogenous pressure produced by microwave to produce nanocrystalline CdS. The process can be expressed in the Eq. (1) [2]:

$$Cd^{2+} + 2Tu \rightarrow [Cd(Tu)_2]^{2+} \rightarrow CdS \quad (1)$$

In spite of this general mechanism, it was also proposed that the reaction mechanism in ethylene diamine (en) is different from that in the other solvents since the coordination ability of ethylene diamine is much stronger than those of other solvents and thiourea. Thus, the complex ion $[Cd(en)_2]^{2+}$ will form in the solution instead of $[Cd(Tu)_2]^{2+}$ [2], since $[Cd(en)_2]^{2+}$ has stability constant higher than $[Cd(Tu)_2]^{2+}$, pk = 5.47 and 1.58 respectively [12,13].

In this way, Cd^{2+} ions reacted with ethylene diamine, a strongly bidentate ligand, to form $[Cd(en)_2]^{2+}$ complex. Simultaneously, the strong nucleophilic nitrogen of ethylenediamine ($NH_2CH_2CH_2NH_2$) molecules formed bonds with the carbon of thiourea (NH_2CSNH_2) molecules. Thus the C=S double bonds of thiourea were weakened, decomposed by the temperature that the solvothermal reactions undergo, and S^{2-} ions are slowly developed. Finally, the $[Cd(en)_2]^{2+}$ complex combines with S^{2-} to produce CdS, as described in Eq. (2) [14]:

$$[Cd(en)_2]^{2+} + S^{2-} \rightarrow CdS(en)_2 \rightarrow CdS + 2(en) \quad (2)$$

The formation of uniform nanosized particles demands a uniform growth environment, and microwave heating afforded this.

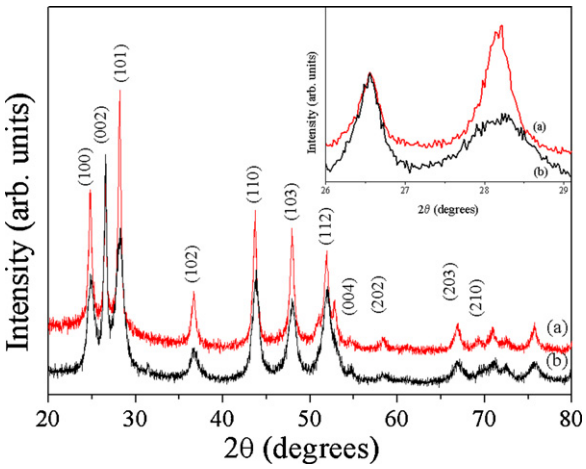

Fig. 1. X-ray diffraction pattern of (a) Cd01EG and (b) Cd01EN. *Inset*: magnification of the (0 0 2) and (1 0 1) peaks.

With microwave irradiation of reactants in polar solvents, temperature and concentration gradients can be avoided, providing a uniform environment for the nucleation. During the process, microwave not only provided the energy for the decomposition of the complexes, but also greatly enhanced the nucleophilic attack by ethylene diamine, which accelerated the nucleation [6].

3.2. XRD analysis

Fig. 1 presents the X-ray diffraction (XRD) patterns of the CdS samples. Comparison with the standard (JCPDS No 41-4019) clearly revealed the formation of single phase CdS with a hexagonal crystal structure.

The inset in Fig. 1 shows that the (0 0 2) and (1 0 1) peaks have different intensities depending on the solvent used. For the one synthesized with ethylene glycol the (1 0 1) peak is the most intense while for the one synthesized with ethylene diamine the most intense peak is the (0 0 2). Murugan et al. [2] observed that varying the solvent during synthesis the CdS crystals presented preferential growth in different crystalline directions. In the same manner, we believe that a less pronounced preferential growth occurred in our samples.

3.3. FE-SEM analysis

It is well known that defect types and concentrations, as well as nanostructure morphology, are determined by fabrication conditions (pressure, temperature, flow rate, etc.) [15]. Fig. 2 presents FE-SEM images of the CdS samples. It is found that the solvent has a significant effect on the morphology. Sample Cd01EG is constituted of flowerlike nanostructures with approximately 200 nm in width and 25 nm in thickness, while sample Cd01EN is formed by nanoplates with approximately 200 nm in width and 40 nm in thickness. Many authors [3,12,14] reported the synthesis of CdS nanorods and nanoparticles via hydrothermal and solvothermal methods without microwave heating. It was observed that CdS nanostructures were formed after extensive periods of time (12–72 h) whereas the samples prepared here were synthesized in 32 min. Hence, microwave-assisted solvothermal method is an efficient approach for fast synthesis of CdS nanostructures.

3.4. Optical properties

Qualitative and quantitative information about the color of the samples were obtained using spectral methods. Fig. 3 presents the

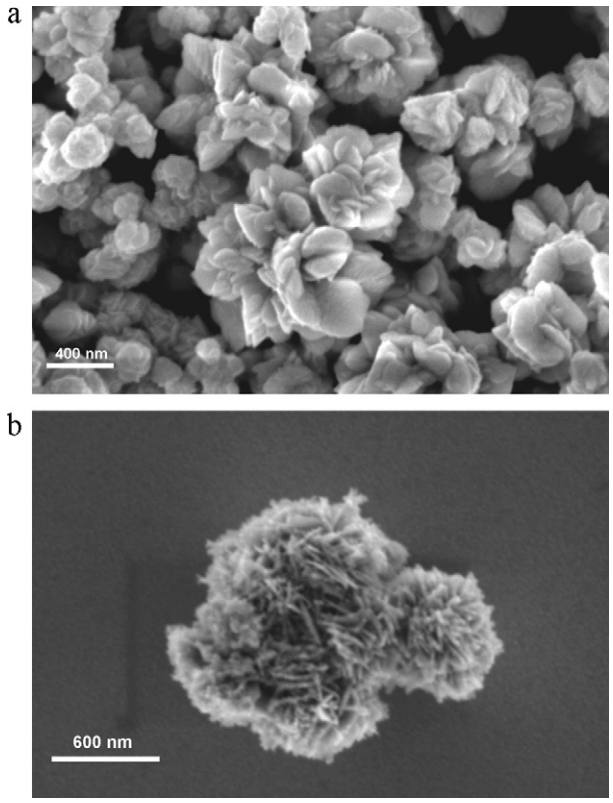

Fig. 2. FE-SEM of samples (a) Cd01EG and (b) Cd01EN.

diffuse reflectance spectra for the CdS nanoparticles. CdS is characterized by direct transitions between the valence and conduction bands [16]. Cd01EG sample showed an absorption edge around 400–440 nm (yellow). On the other hand, the absorption edge of Cd01EN sample presented a shift to higher wavelengths, around 400–470 nm, resulting in an orange color.

Structural defects, such as impurities inserted in the matrix or vacancies created, could be responsible for the differences observed in the diffuse reflectance spectra. These defects can facilitate the electronic transition in semiconductors, since they can create holes that diminish the energy for the transition to occur (red-shift); however, if these defects are excessive, an opposite effect could be obtained resulting in larger band-gap (blue-shift) [17].

Table 1
Colorimetric coordinates of CdS nanoparticles.

Sample	Light source	a^*	b^*	L^*
Cd01EG	D65-10^0	9.85	97.13	83.39
Cd01EN	D65-10^0	20.70	98.38	79.96

We believe that our samples present defects related to sulfur vacancies, with higher concentration of defects for sample Cd01EG in comparison with sample Cd01EN.

Table 1 presents the colorimetric coordinates (L^*, a^*, b^*) of CdS nanoparticles, using type D65-10° (day light) light source, according to the CIE-$L^*a^*b^*$ standard colorimetric method. These colorimetric coordinates must be analyzed simultaneously to determine the final color of pigments, especially the a^* and b^* coordinates.

An increase in the a^* coordinate is observed for sample Cd01EN in comparison with sample Cd01EG, resulting in an orange color for the one synthesized in ethylene diamine and an yellow color for the one synthesized in ethylene glycol.

Fig. 4 shows the normalized DRIFT spectra for the CdS samples. The Cd–S stretching frequency is normally observed below 700 cm^{-1} [18]. The peak around 665 cm^{-1} for sample Cd01EG indicates the presence of the Cd-S bond. This peak is shifted to 635 cm^{-1} for sample Cd01EN indicating a structural change due to the different solvents used during synthesis. The bands around 1440, 2870 and 2941 cm^{-1} present in sample Cd01EG is related to residual ethylene glycol adsorbed on the surface of the nanoparticles. Sample Cd01EN display four bands around 1369, 1450, 2864 and 2930 cm^{-1} related to residual ethylene diamine adsorbed on the surface of the nanoparticles. The remaining bands present in both samples are related to C–O stretching (950–1200 cm^{-1}) [18], water (1500–1750 cm^{-1}, 1990–2155 cm^{-1}) and CO_2 (2290–2400 cm^{-1}) which could have been adsorbed during preparation or from the atmosphere.

Fig. 5 shows the normalized photoluminescence spectra for the CdS samples. One explanation for the luminescent emission of CdS is that either free electrons and holes or excitons recombine in the pure lattice so that this emission is “lattice” emission. Also, CdS luminescence can be related with specific lattice defects [19].

The Cd01EG spectrum display a broad band emission centered around 692 nm and a shoulder at 808 nm, while sample Cd01EN also presented a shoulder at 482 nm and a broad emission band centered around 541 nm.

The shoulder at 482 nm is related to a band edge emission while the band centered around 541 nm is attributed to a broad trap state

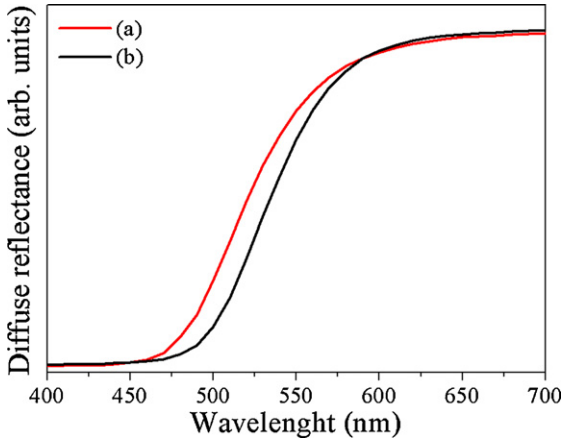

Fig. 3. Diffuse reflectance spectra of (a) Cd01EG and (b) Cd01EN nanoparticles.

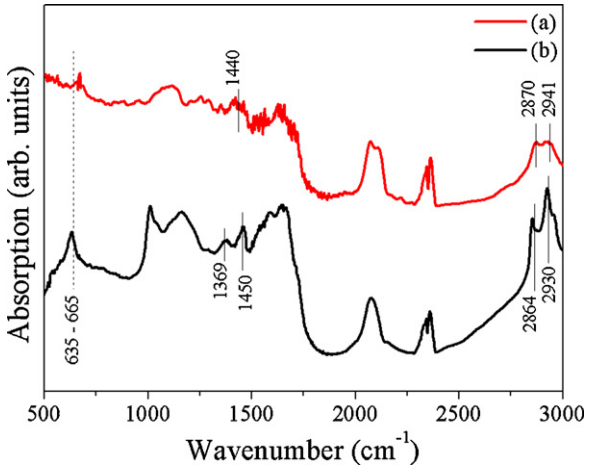

Fig. 4. Normalized DRIFT spectrum of (a) Cd01EG and (b) Cd01EN.

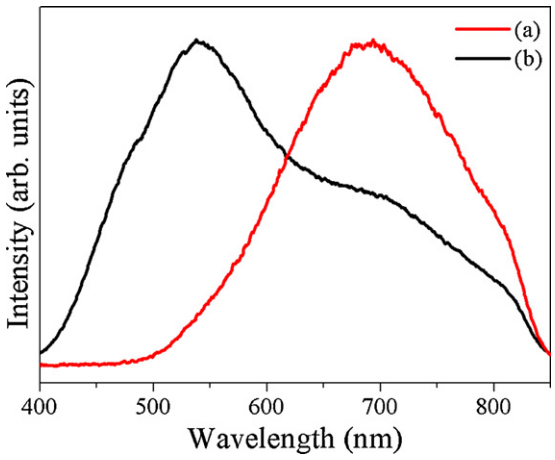

Fig. 5. Normalized photoluminescence spectrum of (a) Cd01EG and (b) Cd01EN.

emission [20]. According to the literature [21–24] peaks around 600 nm may be attributed to recombination of an electron trapped in a sulfur vacancy with a hole in the valence band of CdS.

These results are in accordance with our assumption that samples synthesized in ethylene glycol show a higher concentration of defects than the samples synthesized in ethylene diamine. According to Murugan et al. [2] Cd–Thiourea complex decomposes at a given temperature under autogenous pressure produced by microwave to produce nanocrystalline CdS. During our synthesis the pressure measured for sample Cd01EG was about 2 bar and for sample Cd01EN 6 bar. We believe that the smaller pressure obtained for sample Cd01EG induced the formation of sulfur vacancies resulting in a more pronounced defect related band (around 600 nm) for sample Cd01EG.

4. Conclusions

Nanocrystalline CdS particles with different morphologies were synthesized by a microwave-assisted solvothermal method. The samples showed colors ranging from yellow to orange. X-ray diffraction measurements detected the presence of hexagonal CdS for the synthesized samples. Secondary phases were not observed. FE-SEM images showed that solvent plays a key role in controlling the morphology, resulting in flowerlike nanostructures for the ones synthesized in ethylene glycol and nanoplates for the ones synthesized in ethylene diamine. Optical properties of the products are influenced by the different solvents due to structural defects generated during synthesis. We believe that these defects are related to sulfur vacancies, with higher concentration of defects for sample Cd01EG in comparison with sample Cd01EN.

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