

SYNTHESIS AND CHARACTERIZATION OF CADMIUM SULFIDE OBTAINED AT ROOM TEMPERATURE

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Cadmium sulfide uniform fine particles have been synthesized in soft conditions, at room temperature, using cadmium complex compounds and thioacetamide. The microstructure and morphology of cadmium sulfide were characterized by X - ray Diffraction, Transmission Electron Microscopy, High Resolution Transmission Electron Microscopy, and Selected Area Electron Diffraction. The optical properties of the samples were examined by UV – Visible spectroscopy.

(Received February 1, 2010; accepted February 23, 2010)

Keywords: Cadmium sulfide, X – ray Diffraction, Transmission Electron Microscopy, Electron Diffraction.

1. Introduction

The cadmium sulfide (CdS) is an important II–VI semiconductor ($E_g = 2.42$ eV (515 nm) at room temperature) with many excellent physical and chemical properties, which has promising applications in multiple technical fields including photochemical catalysis, gas sensor, detectors for laser and infrared, solar cells, nonlinear optical materials, various luminescence devices, optoelectronic devices and so on [1–7]; it is also most promising candidate among II-VI compounds for detecting visible radiation.[8] CdS can be obtained in thin film form, by various methods [9–11] or in powder form, by hydrothermal/solvothermal methods, thermal decomposition etc. [8, 12, 13]. In last decades, efforts have been devoted to the preparation of high - quality CdS nanoparticles and the investigation of optical properties.[14] The possibility of tuning the properties of particles by controlling their sizes and shapes implies search of new experimental methodologies that yield very low size- and shape-dispersion nanoparticles. For example, sea-urchin like cadmium sulfide nanoparticles with nanorod-based architecture were prepared by solvothermal method, with cadmium chloride and thiourea in ethylenediamine solution [15]; the CdS nanoparticles have been assembled into CdS nanorods and arrayed nanorod bundles by a thioglicolic acid [16]; cadmium sulfide nanorods were also synthesised in micro-emulsions formed by non-ionic surfactants [17]. There are many reports about cadmium sulfide nanoparticles, obtained by different methods and from different precursors.[18 - 23]

We continued our previous works in the field of II – VI semiconductors [13, 24 - 28] and obtained cadmium sulfide fine particles from complex compounds, by a hydrolytic method, using thioacetamide (TAA) as source for sulfide ions, at room temperature.

2. Experimental

2.1. Synthesis

All the reagents were purchased from commercial sources and used as received.

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Synthesis of CdS (1). Cd(CH₃COO)₂·2H₂O (5 mmoles, 1.33 g) and *o*-diaminobenzene, *o*-dab, (10 mmoles, 1.08 g) were dissolved in 50 mL water and stirred for two hours. In the resulted suspension was added thioacetamide (10 mmols, 0.75 g) and the mixture was stirred again for four hours. An orange precipitate was formed. It was isolated by vacuum filtration, washed with water and then with methanol and dried. Elemental analysis: Calc. for CdS: Cd, 77.78%; S, 22.22%. Found: Cd, 78.35%; S, 21.93%.

Synthesis of CdS (2). Cd(CH₃COO)₂·2H₂O (5 mmoles, 1.33 g) and *m*-diaminobenzene, *m*-dab, (10 mmoles, 1.08 g) were dissolved in 50 mL water and stirred for two hours. In the resulted suspension was added thioacetamide (10 mmols, 0.75 g) and the mixture was stirred again for four hours. An orange precipitate was formed. It was isolated by vacuum filtration, washed with water and then with methanol and dried. Elemental analysis: Calc. for CdS: Cd, 77.78%; S, 22.22%. Found: Cd, 78.68%; S, 22.43%.

2.2. Physical measurements

The X-ray diffraction (XRD) patterns for cadmium sulfide samples were recorded on a Shimadzu XRD 6000 X-ray powder diffractometer with Cu K α radiation (Cu K α : $\lambda = 1.5406 \text{ \AA}$) with 2θ ranging from 10° to 80° at the speed of 2°min^{-1} . The samples were deposited on the glass substrates. After the ethanol was volatilized, the samples were analyzed.

The Transmission Electron Microscopy (TEM), High Resolution Transmission Electron Microscopy (HRTEM), and Selected Area Electron Diffraction (SAED) investigations were performed on a Philips CM 120 ST transmission electron microscope operated at 100 kV, with 2 \AA resolution. The samples were pestled with an agate mortar. Specimen of TEM samples were prepared by ultrasonic dispersion of pestled sample in anhydrous ethylic alcohol and then placing drops of the suspension on a Cu microgrid with carbon film and immediately evaporating the solvent.

IR spectra (KBr pellets) were recorded on a BRUKER Vector 22 spectrometer in the 400 - 4000 cm^{-1} region. The optoelectronic properties were measured by ultraviolet - visible absorption spectra in the range 220 – 850 nm, on a Jasco V 550 spectrometer, using diffuse reflectance technique, with MgO as standard.

The elemental chemical analyses were performed by usual micro-methods.

3. Results and discussion

3.1. IR spectra

The elemental chemical analysis of the obtained powders showed that they are cadmium sulfide. These results were confirmed by IR spectra, which showed that there are no impurities, e. g. acetate, diaminobenzene, thioacetamide, or other impurities, which could be detected in the samples.

3.2. X - ray diffraction

The powder X - ray Diffraction (XRD) patterns of CdS samples **1** and **2** are shown in Fig. 1.

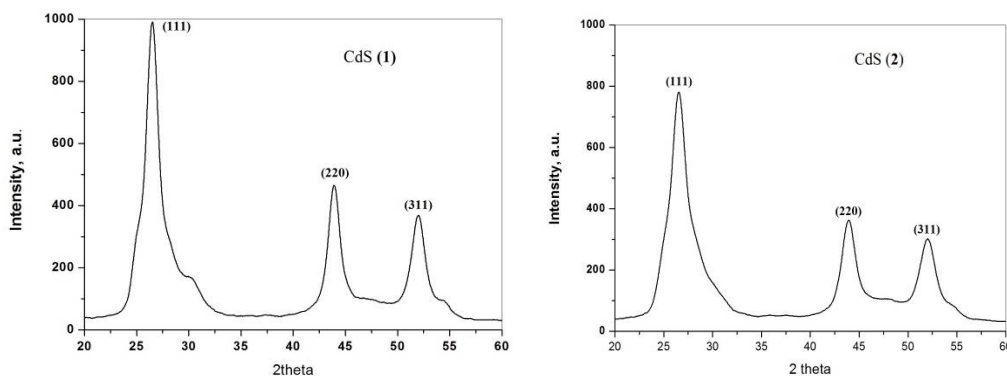


Fig. 1. XRD patterns of CdS samples.

The XRD patterns of the CdS samples **1** and **2** exhibit a single phase sphalerite crystal structure. The three peaks with 2θ values of 26.54, 43.88 and 51.98 for sample **1**, respective 26.54, 43.92 and 52 for sample **2** correspond to the (1 1 1), (2 2 0) and (3 1 1) planes of the cubic phase β - CdS (JCPDS 80-0019).

No other peaks, characteristic diffraction peaks arising from the possible impurity phases were observed, indicating the preparation of phase-pure cubic - CdS powders by the proposed molecular precursor decomposition route.

The crystallite size (D_{hkl}) of cadmium sulfide crystals were estimated from line broadening of the (1 1 1) diffraction peak, according to the Debye-Scherrer equation [29]:

$$D_{hkl} = K\lambda / (B \cos\theta)$$

where λ is the wavelength of Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), B is the full-width at half maximum intensity, θ is the diffraction angle (in radian) of the considered diffraction peak, and K is a Scherrer constant taken as 0.90 for the almost spherical particles.

Broadening of the peaks indicates the nanocrystalline nature of the material and the crystallite sizes are 5.34 and 3.85 nm for samples **1** and **2**, respectively.

3.3. Transmission electron microscopy and electron diffraction

The particles size and morphology of obtained cadmium sulfide were investigated by TEM.

Evaluation of mean diameter was performed using a semi-automated algorithm implemented in analysis software. Mean diameter was calculated as arithmetic mean of all diameters measured on particles at angles that varies with 15° steps. The final mean diameter was approximated assuming a lognormal distribution of resulted diameters. Experimental diameter measured from TEM micrograph was fitted with function given by:

$$y = y_0 + A e^{-\frac{\ln^2(x/x_c)}{2w^2}}$$

where A is an arbitrary constant related to particle number, x_c represents the distribution maximum and w is strong correlated with particle diameter dispersion.

Fig. 2.a. depicts the Bright Field TEM (BFTEM) micrographs of CdS (**1**). The figure indicates that CdS is formed by crystalline aggregates, resulted from fine and spherical nanoparticles. As shown in Fig. 2.b, the particles of CdS are uniform, and the diameters are in range of 3.55 - 10.70 nm with a mean diameter of 6.82 nm.

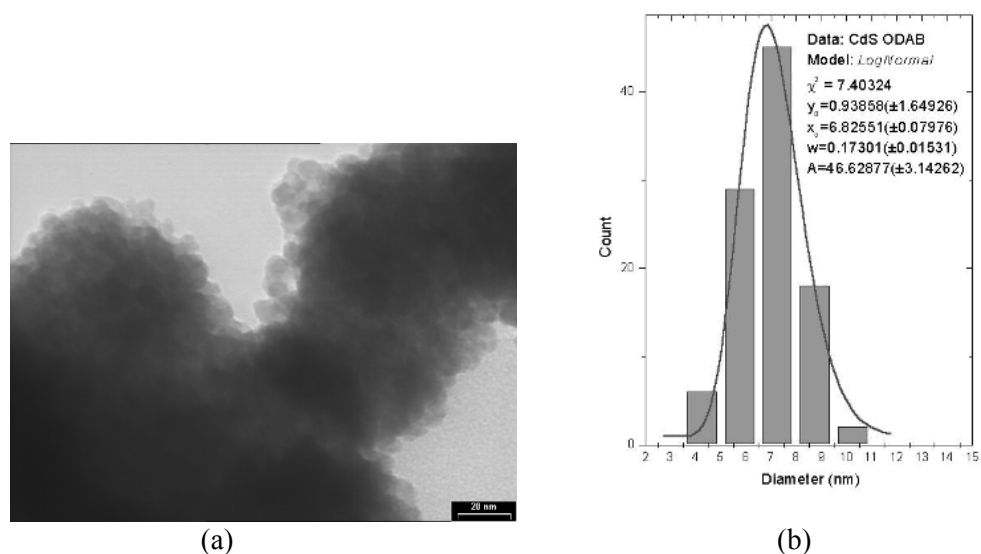


Fig. 2. BFTEM image of CdS (1) (a); Mean particle size and particle distribution for CdS (1) (b).

The BFTEM image and the fitted curve of evaluated diameters using function for lognormal distribution for CdS (2) are presented in the Fig. 3.

Fig. 3.a. shows a crystalline aggregates of CdS, which consists of uniform, fine and spherical particles.

Fig. 3.b. presents lognormal distribution curve for mean diameter of CdS (2) particles, having a narrow size distribution, with the diameters in the range of 4.11 – 10.05 nm and a mean diameter of 6.65 nm.

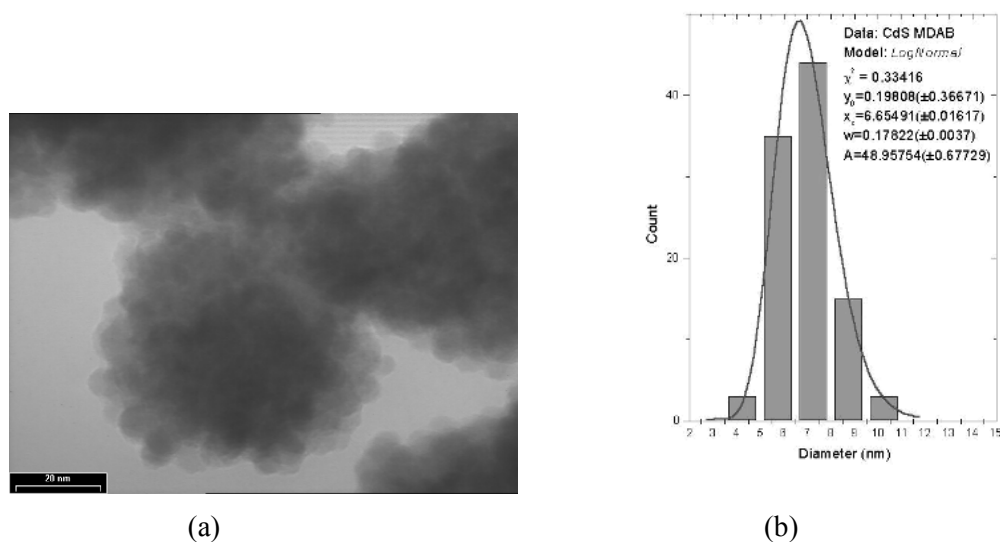


Fig. 3. BFTEM image of CdS (2) (a); Mean particle size and particle distribution for CdS (2) (b).

In one of our previous papers, we analysed the CdS nanoparticles obtained using $\text{Cd}(\text{CH}_3\text{COO})_2$ and thioacetamide.[30] In those conditions, the particles dimensions are in range of 9.01 – 25.21 nm, with mean diameter of 15.51 nm. The diamines (odab and mdab) used in this study can act as chelating ligands and, in the first step, were obtained complex compounds of cadmium.[31]

These data support the idea that specific cadmium complex formation modulates crystal growth. Both CdS samples obtained through complex compounds are composed of smaller and more uniform particles beside our previous results. The particles dimensions and medium

diameters for the two samples, CdS (**1**) and CdS (**2**), are approximately similar, probably because of the ligands and of the complexes, which display structural similarities.

The mechanism of CdS formation is expected to be similar with those proposed for ZnS synthesis [25, 32], the bidentate chelating ligands forming, in a first step, Cd(II) complexes. The thioacetamide is ready decomposed and acts as the sulfur source, generating S^{2-} .

These results illustrate the importance of intermediate metal-ligand complex formation to nanocrystal arrested precipitation growth kinetics, particle stabilization, and ultimately, their optical properties[33].

In the previous literature [34, 35] has been suggested that bidentate coordination agents were a prerequisite for the solvent in the solvothermal synthesis of CdS nanorods. Later, other researchers showed that [36] both bidentate and monodentate coordination agents used as the template in the hydrothermal process can form rod-like CdS crystallites and that the coordinating configuration, i.e. bidentate or monodentate coordination, is not a critical factor for the shape control of CdS nanocrystallites.

Our present research demonstrates that the use of a bidentate ligand as template is not a prerequisite for obtaining nanorods. Probably, the proposed mechanism [36] is not general valuable. Thus, in this mechanism, an essential condition for nanorods synthesis is the square planar geometry of complex intermediate, which can't be obtained in all complexes.

For the dimension of particles, the source of sulfide ion seems to be important, too. In the same reaction conditions, using thiourea as sulfur source, the mean diameter of CdS particles was about 14 nm (starting from complex with odab as precursor), respective 16 nm (starting from complex with mdab as precursor). The shape of nanoparticles was almost the same.[31]

The nature of the metal is another factor which affects the formation mechanism and the particle dimensions. Thus, for ZnS particles obtained in the same conditions, the diameters were smaller compared with those of CdS; they were also smaller in the case of using odab complex as precursor (2.90 nm), in comparison with those for ZnS from mdab complex (4.69 nm). The results may be explained having in view the stereochemical compatibility between the metallic ions dimensions and the position of ligands donor atoms.

HRTEM can provide structural information at better than 0.2 nm spatial resolution. In most crystalline inorganic materials, including semiconductors, the positions of individual atomic columns can be resolved, at least in low-index zones.[37]

Both samples have a cubic structure with lattice parameter $a = 0.58(2)$ for CdS (**1**) and $a = 0.58(4)$ for CdS (**2**), values close to 0.5811 nm from JCPDS 80-0019 for CdS cubic structure and space group F43m [38].

The HRTEM images and SAED patterns, with measured and indexed lines, are presented in Figure 4 for CdS (**1**), respective Figure 5 for CdS (**2**).

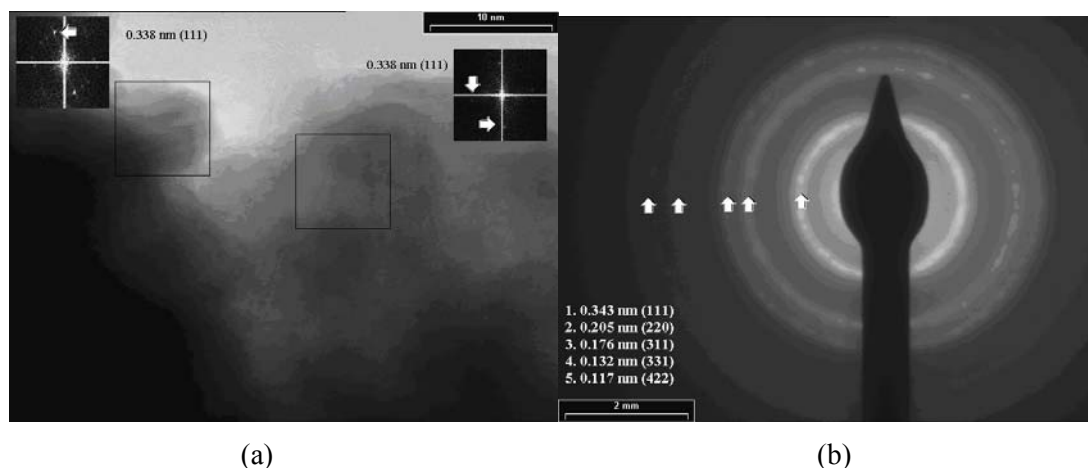


Fig. 4. HRTEM image of CdS (1) single crystal (a); SAED pattern for CdS (1) (b).

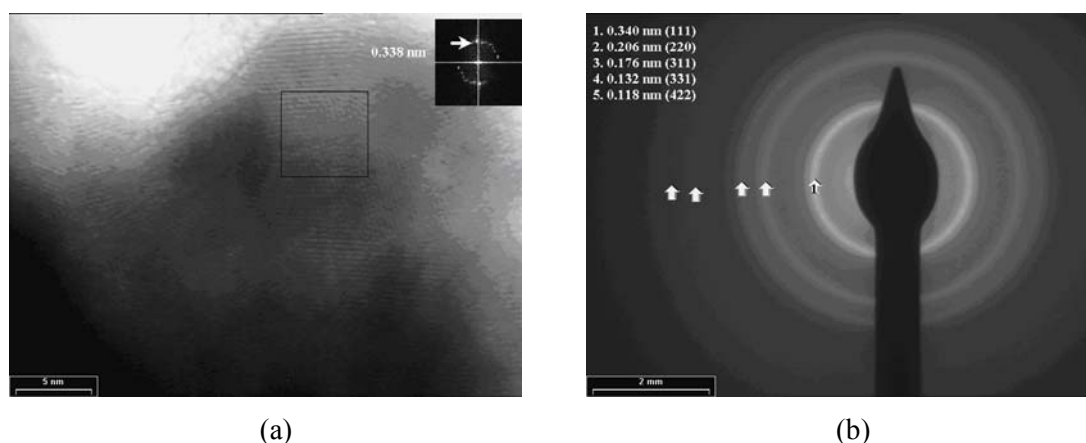


Fig. 5. HRTEM image of CdS (2) single crystal (a); SAED pattern for CdS (2) (b).

HRTEM image for CdS (1) shows a nanoparticles agglomerating, and two particles were selected for Fast Fourier Transform (FFT) analysis. Inset presents Fourier representations with measured values for parallel line found in image. Those lines are assigned to diffraction on (111) planes. On CdS (2) FFT analysis exhibits a large number of particles, oriented so that the interference fringes from (111) planes are visible and form a ring (typical from diffraction on polycrystalline material).

3.4. UV-Vis absorption spectra

Optical properties of the CdS powders were investigated by UV-Vis spectra, as shown in Fig. 6. It can be seen from this figure that intensive absorptions are present in the ultraviolet - visible range of about 300 – 490 nm.

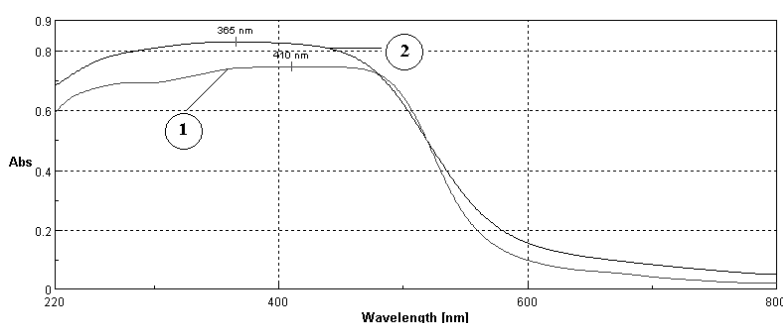


Fig. 6. UV-Vis absorption spectra of CdS (1) and CdS (2).

The UV-Vis absorption spectra showed that the absorption peaks of analysed CdS particles are at 410 nm for CdS (1), respective 365 nm for CdS (2), relative blue-shift to the band gap of bulk cubic CdS (515 nm) [39]. The peaks positions can be related with the mean diameter of particles, smaller diameter meaning lower wavelength. The results showed the effect of quantum confinement (quantum size effect, QSE). Reference [40] reported that the QSE in direct-gap semiconductors nanocrystals were well understood, such as a shift of the optical absorption edge to higher energies with decreasing size, which can explain the UV-Vis blue-shift effect.

4. Conclusions

We prepared cadmium sulfide by hydrolysis reaction, at room temperature, using thioacetamide as source for sulfide ion, and complex compounds with aromatic diamines (odab and mdab) as precursors. The resulted samples were analysed by XRD, BFTEM, HRTEM, and SAED techniques. The cadmium sulfide was obtained as uniform, fine and spherical particles, which form crystalline aggregates. The mean diameters calculated from Debye - Scherrer equation are 5.34 and 3.85, respective; the mean diameters determined from BFTEM micrographs are 6.82 nm and 6.65 nm, respectively. The electronic spectra of CdS samples can be correlated with the mean diameter of the particles.

These results may illustrate the importance of intermediate metal-ligand complex formation to crystal arrested precipitation growth mechanism and particle stabilization.

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