Characterization of CdS nanocrystals grown from newly organic salt

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Abstract—Two CdS nanocrystals were grown by using the newly organic salt named Potassium *N'*-[4-(*N'*-dithiocarboxy-hydrazino)-4-oxo-butyryl]-hydrazinecarbodithionate which dissolved using different solvents, (200 ml water) and (100 ml water and 100 ml ethanol). The synthesized nanocrystals were characterized using X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM) and UV-visible spectrophotometry. The yield, elemental analysis, lattice parameters, crystallite sizes, microstrains, transmittance, absorbance and the band gap energy were compromised for the two CdS nanocrystals. The obtained CdS nanocrystals show ~ 53.2 % and 52.3 % transmittance.

Index Terms— Quantum dots, nanocrystals, CdS, microstrain and optical properties, organic salt.

1 INTRODUCTION

Nanocrystalline materials have high surface energy due to the large no of surface atoms. These materials exhibit unique physical and chemical properties that depend on their particle size. A large number of studies concerning synthesis, characterization and applications of nanocrystalline materials are present [1-5]. The characteristics of a nanocrystalline material are greatly influenced by the preparation method and conditions. Nano-size Cadmium sulfide (CdS) is among the most important semiconductors materials, which has applications in many fields [6-8]. Many reports are available concerning the synthesis of CdS by different methodologies [1, 6, 9-12] and the field of research for new methods and routs for manufacturing CdS is promising. In this context, physical methods of preparing the nano-particles are well established. However, the biological methods [13, 14] and the chemical methods which can be applied for synthesizing nano-materials by controlling different conditions and by using a variety of precursors are important. Parameters may be adjusted for better crystallinity, shape and size distribution of certain product. Homogeneous precipitation, in which some reactants can be generated by the action of some variables like heat, and also the hydrothermal methods (or generally, solvothermal methods), where the reactions are performed at controlled temperature and pressure are simple and well established.

In this present work, an attempt has been made to study the structural and optical properties of the CdS grown by procedure starts from Potassium *N'*-[4-(*N'*-dithiocarboxy-hydrazino)–4–oxo-butyryl]-hydrazinecarbodithionate as a precursor for CdS formation.

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2 EXPERIMENTAL

2.1 Preparation of CdS nanocrystalls

2.1.1 Synthesis of Potassium *N'*-[4-(*N'*-dithiocarboxy-hydrazino)-4-oxo-butyryl]-hydrazinecarbodithionate (2):

Carbon disulfide (0.1 moles) was added to a solution of potassium hydroxide (0.1 moles), absolute ethanol (100 ml) and the appropriate succinic acid dihydrazide (**1**) (0.05 moles). This mixture was diluted with absolute ethanol (100 ml) and agitated for 12 hours. It was then diluted with dry ether (100 ml) and the product was filtered off and dried. The salt prepared was used freshly without further purification in 83% yield; m.p.= 280ºC; IR (KBr): ν 3450, 3330 cm^{-1} (NH), 1650 cm^{-1} (C=O), 1275 cm^{-1} (C=S); MS: m/z= 374 (0.3%), [313 (3.7%), 299 (2.1%), 94 (25%) 75.9 (100%)] for $C_6H_8N_4O_2S_4K_2$.

2.1.2 Synthesis of CdS (1):

$Cd(NO_3)_2$. $2H_2O$ (0.001 mole, 1.33 g) and the Potassium salt (**2**) (0.001 mole) were dissolved in 200 ml water. A white precipitate was formed at first and then the reaction mixture was heated under reflux for 3 hours. The yellow precipitate formed of CdS was filtered off, washed with water and dried at 100 °C. Elemental analysis: Calc. for CdS: Cd, 77.78%; S, 22.22%. Found: Cd, 62.2%; S, 37.8%.

2.1.3 Synthesis of CdS (2):

$Cd(NO_3)_2$. $2H_2O$ (0.001 mole, 1.33 g) and the Potassium salt (**2**) (0.001 mole) were dissolved in a mixture of (100 ml water and 100 ml ethanol). A white precipitate was formed at first

and then the reaction mixture was refluxed for 3 hours. The yellow precipitate formed of CdS was filtered off, washed with ethanol and dried at 100 °C. Elemental analysis: Calc. for CdS: Cd, 77.78%; S, 22.22%. Found: Cd, 62.8 %; S, 37.2%.

2.2 Characterizations

The grown CdS nanocrystals were analyzed by energy dispersive x-ray analysis, x-ray diffractograms and high resolution transmission electron microscopy.

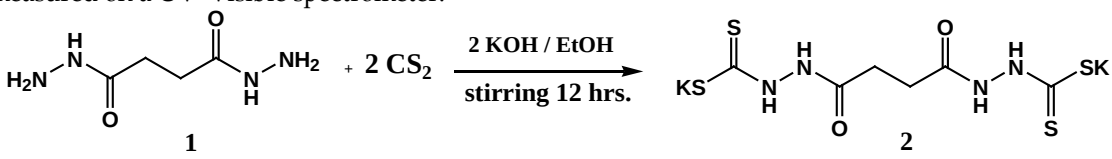
The X-ray diffractograms were measured stepwise with angle/second value of 0.02° at ambient temperature with a model D 5000 Siemens diffractometer (Germany). High resolution transmission electron microscopy (HRTEM) images were recorded using a JEOL JEM 2100 microscope (Japan). The chemical composition of the samples was determined using an energy dispersive x-ray analysis (EDX) spectrometer (Elemental Analyzer EDXRF, JSX3222, JEOL, Japan) attached to the scanning electron microscope. The UV–VIS absorption spectra were measured on a UV–Visible spectrometer.

3 RESULTS AND DISCUSSION

3.1 Crystal growth

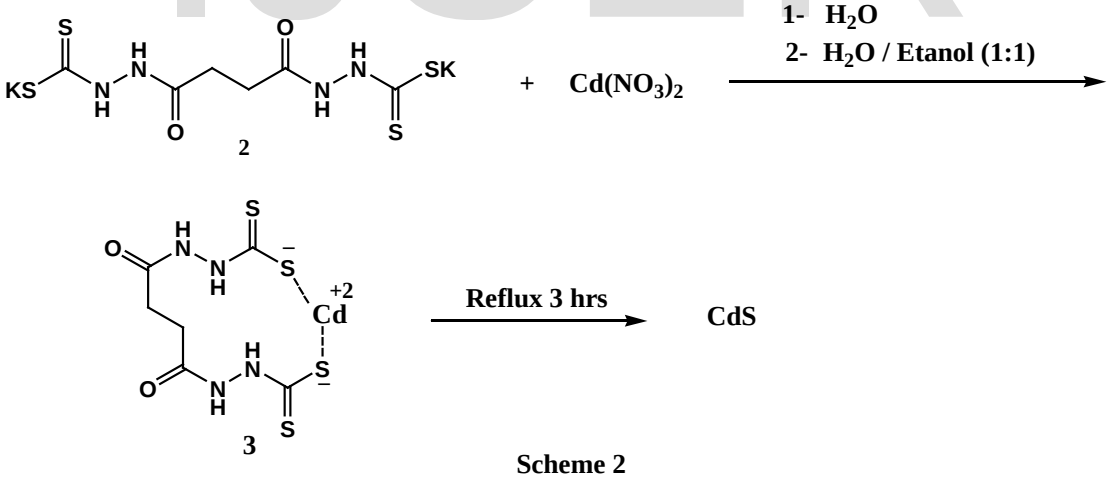
In our earlier study [12] we investigated the effect of using complexing agents on the structural and optical properties. Best results were obtained for CdS nanocrystals which were grown without using complexing agents.

In this work, we describe the synthesis of cadmium sulfide nanoparticles using the newly organic salt named Potassium *N'*-[4-(*N'*-dithiocarboxy-hydrazino)-4-oxo-butyryl]-hydrazine carbodithionate (**2**), which prepared by stirring of succinic dihydrazide (**1**) [15, 16] with carbon disulfide and potassium hydroxide in ethanol for 12 hrs, at room temperature as shown in **(scheme 1)**:



Scheme 1

When the potassium salt (**2**) and cadmium nitrate were dissolved in different media such as water or water/ ethanol (1:1), a white precipitate of the cadmium salt (**3**) was formed at first, then the reaction mixture was heated under reflux for 3 hrs, cadmium sulfide nanoparticles was obtained as shown in **(scheme 2)**:



Scheme 2

3.2 Nanostructural and X-ray diffraction studies

Figure 1 presents a typical HRTEM images for CdS (**1**) and CdS (**2**) samples respectively. The average crystal-sizes obtained by HRTEM are 1.98 nm and 1.3 nm for CdS (**1**) and CdS (**2**) respectively.

Figure 2 depicts the X-ray diffractograms for the prepared CdS nanocrystals. The spectra confirm the crystalline nature of the prepared samples. The XRD analysis confirmed the synthesis of cubic CdS with prominent peaks from (111), (220) and (311) planes. XRD measurements showed agreement with Cross-Ref PDF No. 00-047-1179.

The lattice parameter *a* can be calculated from the known equation for cubic geometry [17], it is preferable to determine a value of *a* from each diffraction line and plotting it on a graph against an angular function [18]. Figure 3 shows the relation between the lattice parameters *a* for CdS nanocrystals vs. angular function *F(θ)*. From this figure, the lattice

parameters for the obtained crystals are a = 5.87 and 5.89 Å for CdS (**1**) and CdS (**2**) respectively, where the lattice parameters for the standard CdS is 5.83 Å, [19]. These results verify the identity between the grown crystals and the standard one.

To estimate the crystallite size using X-ray powder diffraction measurements, the Scherrer equation is the most used method [12, 17, and 20]. The crystallite size (D) can be calculated using the Scherrer equation [21], the average crystallite size obtained is 3.15 and 2.13 nm.

Peak broadening in the X-ray diffraction was generally caused by two factors, apart from the instrumental broadening. One is due to finite size of the crystallites and the other is due to inhomogeneous strain. The Scherrer equation gives us a rough estimate of crystallite size. Despite the accuracy of this method, it neglects the importance of the microstrain, ε, and its effects in the powder diffraction pattern [22].

A simple method to separate the contributions of crystallite size and microstrain to the line broadening in the XRD patterns is the Williamson–Hall (WH) plotting [23].

Figure 4 shows the WH plotting for nanocrystalline CdS samples. This WH plotting method proved that average crystallite size D = 3.5 and 2.09 nm and microstrain is about 0.022 and 0.008 for CdS (**1**) and CdS (**2**) respectively. The positive signal of the microstrain indicates a lattice expansion [12, 24].

The nanostructural parameters have been compared as shown in Table 1.

3.3 Optical properties

Figure 5 shows the transmission spectra of the nanocrystalline CdS samples vs. wavelength recorded in the range 200 – 1100 nm. These show ~ 53.2 % and 52.3 % transmittance for CdS (**1**) and CdS (**2**) respectively.

The fundamental absorption, which corresponds to electron excitation from the valence band to conduction band, can be used to determine the nature and value of the optical band gap.

The relation between the absorption coefficients (α) and the incident photon energy ($h\nu$) can be written as [25],

$$(\alpha h\nu)^{1/n} = A\,(h\nu - E_g)$$

where A is a constant and E_g is the band gap of the material and exponent n depends on the type of transition. For direct allowed n=1/2, indirect allowed transition, n=2, and for direct forbidden, n = 3/2.

The direct band gap (see **Table 1**) was determined from $(\alpha h\nu)^2$ vs. $h\nu$ plots (as shown in Fig. 6). The direct band gap values of the nanocrystalline CdS samples is 4.4 and 4.8 eV for CdS (**1**) and CdS (**2**) respectively which are higher than that of bulk value of CdS (2.42eV) [26] because of quantum confinement of CdS nanocrystals [12]. The obtained band gaps for CdS nanocrystals is the biggest value between all published values [27 - 32], we suggest that this is due to the obtained crystallite size value for CdS nanocrystals in this work is the smallest value between all published values [27 - 32].

Comparing the absorption edge of bulk CdS with that of CdS (**1**) and CdS (**2**) samples, it is seen from Fig. 7 that a blue shift in the onset of absorption is observed in these samples. The absorption edge of samples CdS (**1**) and CdS (**2**) is about 400 and 380 nm. Compared with the absorption edge of bulk materials (515 nm), the amount of blue shift is 115 and 135 nm respectively. The main reasons for the blue shift are the quantum dimensional effect of the nanocrystals [12].

The blue shift of band gap might also be utilized in determining the crystallite radius (r) using relation [33]

$$\Delta E_g = E_{g(nano)} - E_{g(bulk)} = [h^2/8M\,r^2]$$

Where h is Planck's constant and M is the effective mass. From the above equation, the crystallite sizes have been determined and these are equal to 2.4 and 2.1 nm.

The properties of nanocrystalline materials are changed from their corresponding bulk properties due to the crystallite size become comparable to the Bohr excitonic radius (r_B) [34].

$$r_B = h^2\varepsilon[1/m_e^* + 1/m_h^*]/\pi e^2$$

where ε is the permittivity of the sample, m_e^* =0.21 m_0 and m_h^*=0.80 m_0 are the effective mass of electron and hole in CdS, respectively, where m_0 is the mass of a free electron. From the above relation the Bohr radius of CdS has been calculated to be 2.8 nm [28]. The values of the crystallite size of samples CdS (**1**) and CdS (**2**), as determined from that of XRD studies, are comparable to the Bohr excitonic radius supporting the quantum size effect.

CONCLUSION

- CdS nanocrystals were prepared from Potassium *N*'-[4-(*N'*-dithiocarboxy-hydrazino)-4-oxo-butyryl]-hydrazinecarbodithionate for the first time.
- The average crystal-sizes obtained by HRTEM are 1.98 nm and 1.3 nm for CdS (**1**) and CdS (**2**) respectively.
- The values of the crystallite size as determined from that of XRD studies are 3.15 and 2.13 nm for CdS (**1**) and CdS (**2**) respectively, are comparable to the Bohr excitonic radius supporting the quantum size effect. Also microstrain is about 0.022 and 0.008 for CdS (**1**) and CdS (**2**) respectively.
- CdS (**1**) and CdS (**2**) show ~ 53.2 % and 52.3 % transmittance respectively.
- The direct band gap value is 4.4 and 4.8 eV for CdS (**1**) and CdS (**2**) respectively.
- The amount of blue shift is 115 and 135 nm for CdS (**1**) and CdS (**2**) respectively.

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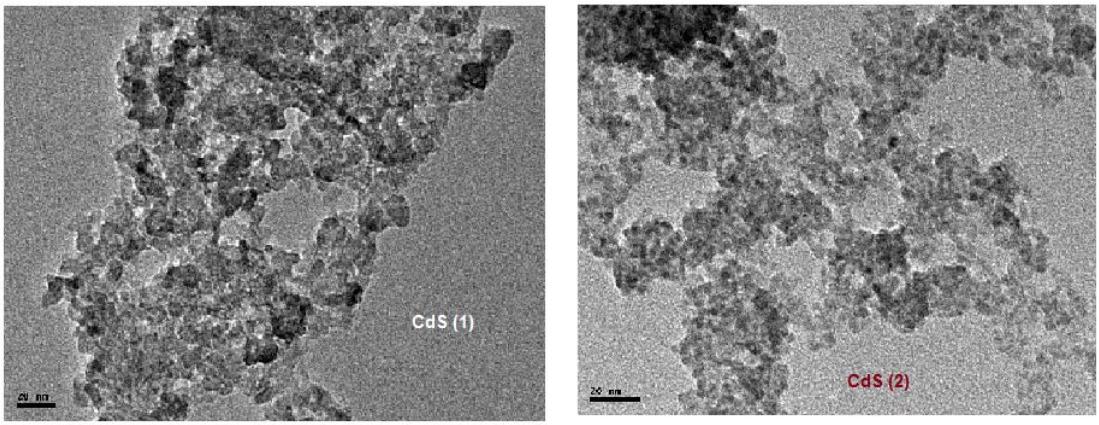

Fig. 1: The HRTEM image of CdS nanocrystals

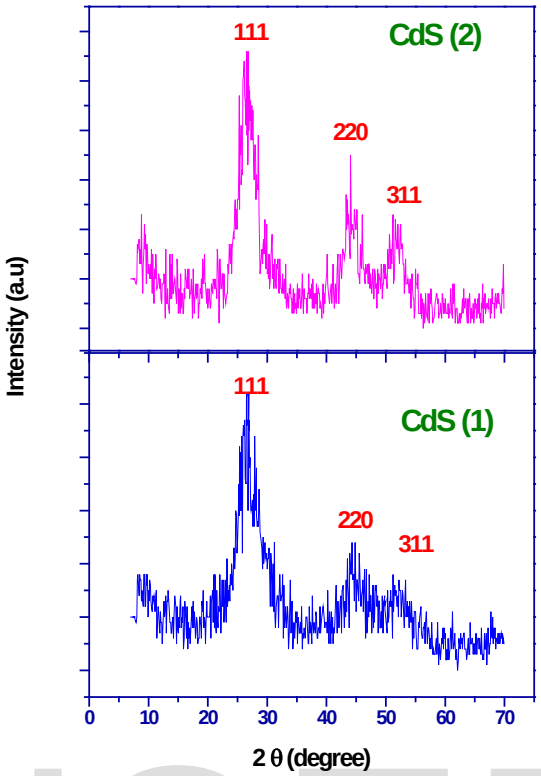

Fig. 2 : X ray powder diffraction pattern of CdS nanocrystals

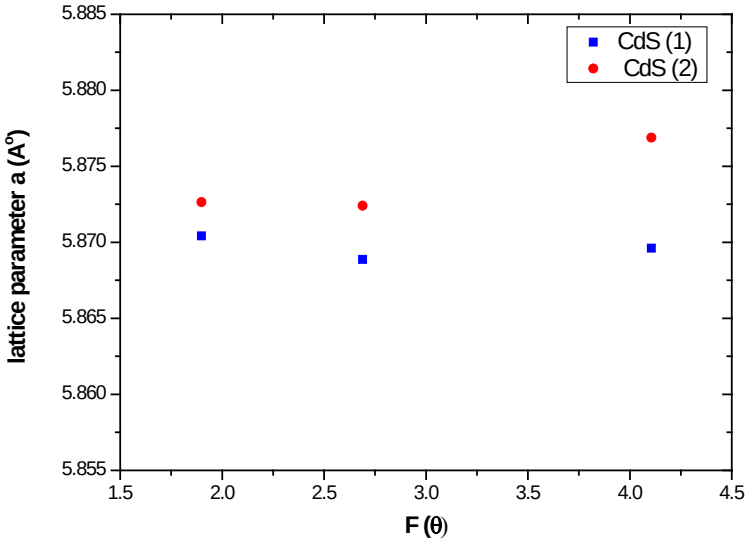

Fig. 3: The relation between the lattice parameters and F(θ)

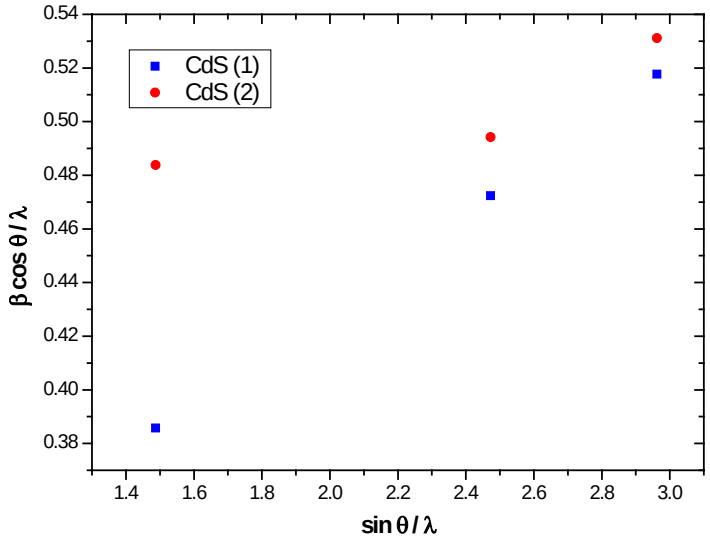

Fig. 4: Williamson – Hall plotting

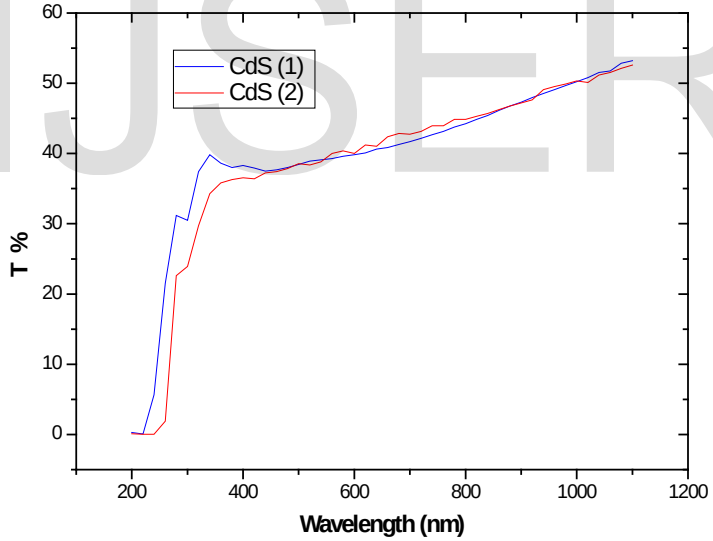

Fig. 5 : The transmission spectra vs. wavelength for nanocrystalline CdS samples

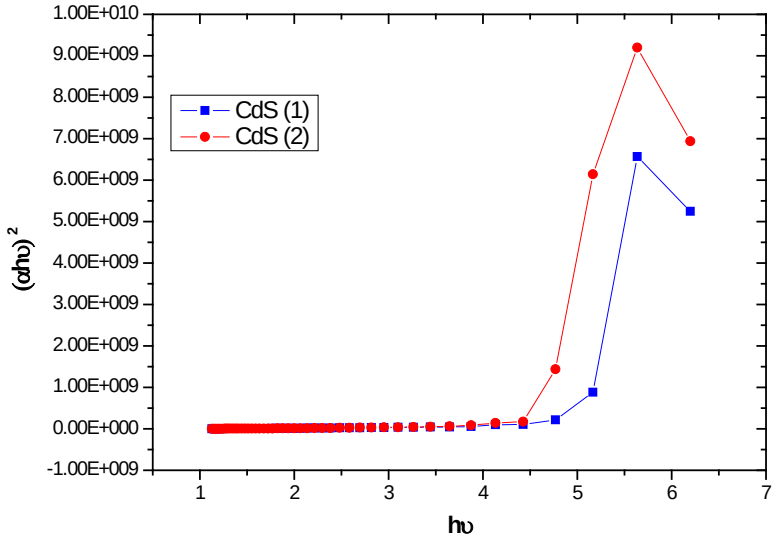

Fig. 6: The relation between (αhν)2 vs. hν

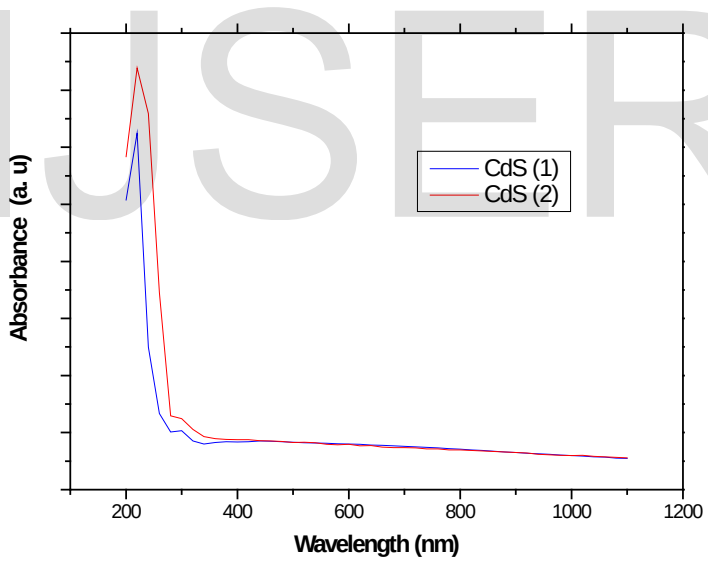

Fig. 7: UV–Visible absorbance spectra

Sample	Crystallite size (nm)				Lattice Parameter (Å)	Microstrain	Eg (eV)
	HRTEM	Scherrer	WH plot	Blue shift of band gap			
CdS (1)	1.98	3.15	3.5	2.4	5.87	0.022	4.4
CdS (2)	1.3	2.13	2.09	2.1	5.89	0.008	4.8

Table1: Nanostructural and Optical properties for grown CdS nanocrystals