# Study of optical properties (linear and nonlinear) and structures for CdS thin film preparation in Spray pyrolysis technique

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**Abstract**
We observed strong nonlinear absorption in the CdS nanostructure in the range 50-100 nm when irradiant with femtosecond pulsed laser at 800 nm and 120 GW/cm$^2$ irradiance intensity. The repetition rate and average power were 250 kHz and 30 mW respectively. The CdS nanostructures were prepared by chemical spry pyrolysis technique with substrate temperature 300 $^o$C. The structure of the prepared CdS nanostructure was tested and its optical properties were investigated. The structure of the CdS nanostructure was tested with X-Ray diffraction and it was found to be a polycrystalline with recognized peaks oriented in (100), (002), (101), (102), (110), (103), (112), and (004). The measured nonlinear absorption coefficient was found to be about 116 cm/GW which is about ten times higher than the bulk value.

**Keywords:** Multiphoton processes, CdS nanostructures, Nonlinear optics, Two photon absorption

## 1. Introduction
The CdS nanostructure compound of extensive interest at the present. This is due to high potential uses of this material as sensitive photodetectors, heterojunction diodes, and solar cell semiconductor devices. The nanostructure semiconductor materials with large nonlinear coefficients have attracted more attention in recent year [1-5]. This interest is due to their different optical properties when their size decreased from bulk to few nanometers. Such unusual properties may have technological applications such as optical switching devices, Q-dot laser, and it is great potential in biophotonics [6-7]. The linear optical properties of the semiconductor nanoparticles depends strongly upon the particle size [8]. The nonlinear optical properties were observed in nanoparticles semiconductor CdS material [9-11]. The two photon (2PA) in semiconductor nanostructure has been widely investigated [12-13]. The dynamic of the CdS excited state have been studied by femtosecond laser and by the photoluminescence (PL) analysis [14-16]. In this work the two-photon absorption in CdS nanostructures illuminated by intensity 120 GW/cm$^2$ Ti-Sapphire laser is observed.

## 2. Experimental:
The CdS nanostructure was prepared by mixing a 0.5 M aqueous solution of thiourea ($NH_2CSNH_2$) and 0.5 M aqueous solution of cadmium chloride ($CdCl_2$) as starting solution. Spray pyrolysis was a used to prepare the CdS nanostructure. With spray pyrolysis, the solution is sprayed directly onto the substrate. A stream of nitrogen gas can be used to help the atomization of solution through the nozzle. In the study, CdS nanostructure was deposited by the spray pyrolysis technique on glass substrates [17]. Table (1) summarizes the optimized thermal pyrolysis deposition condition for the preparation of CdS nanostructure that is employed in our work.

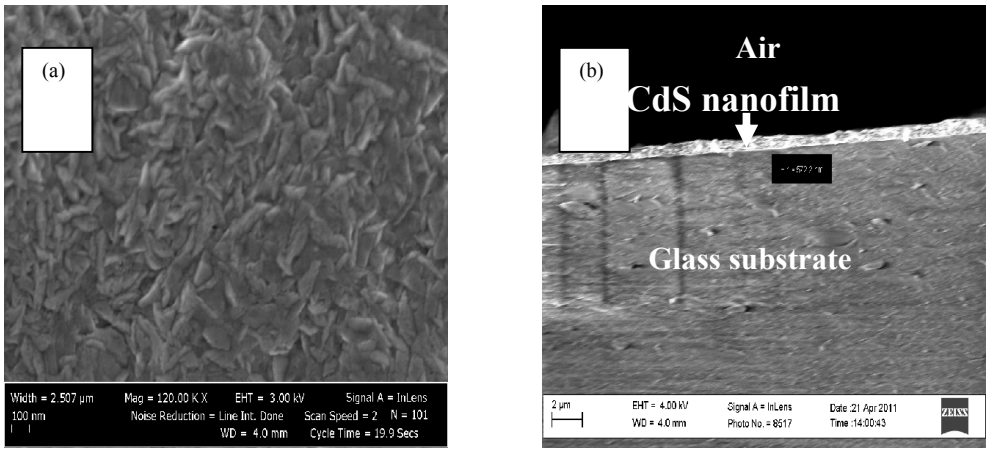
**Table (1):** Optimum thermal spray pyrolysis deposition condition for the preparation of CdS nanostructure.

| Spry parameter | value |
|---|---|
| Substrate temperature | 300 $^o$C |
| Spray rate | 5 ml/min |
| Carriers gas pressure | 1 bar |
| Nozzle-substrate distance | 28 cm |
| diameter of nozzle | 0.8 mm |

The formation of the CdS nanostructure on the heated substrate may follow the following reaction.

$$Cdcl_2 + (NH_2)_2 CS + 2H_2O \rightarrow \downarrow CdS + \uparrow 2NH4Cl + \uparrow CO_2 \quad (1)$$

During the chemical reaction gas and water vapor is obtained from this reaction due to the high temperature of the substrate. At the end of the reaction a yellow prepciption of CdS material. After deposition the film, the material was cooled to room temperature gradually.
The topography study of the prepared nanofilm surface was carried on using Scanning Electron Microscopy (SEM) type ULTRA 55 as shown in figure 1. The results show that the CdS nanoparticles were formed in a layer of 522nm deposited on the glass substrate.




The figure show nanostructure of size 5-100 nm. The micrographs reveled that the particles were hexagonal in shape. The X-ray diffraction (XRD) pattern of CdS nanostructure was recorded by (XDR 2000). The X-Ray diffractometer use copper tube radiation line of wavelength 1.54A in 2θ range from $20^o$ to $60^o$. The UV-VIS absorption and transmission spectra of the sample were recorded by Hitachi U-4100 spectrometer covering (200-1100nm). The nonlinear absorption study carried out using single beam femtosecond open aperture z-scan technique (OA). The z-scan setting is illustrated by schematic diagram shown in figure 2.

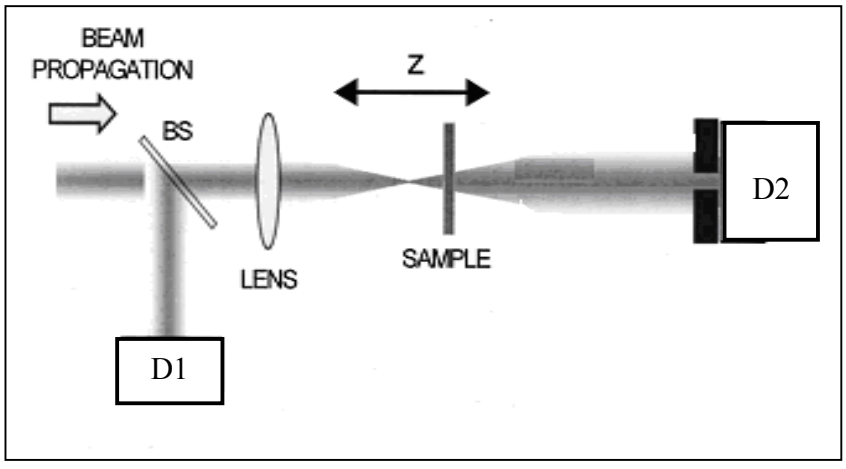



**Figure (2):** Schematic of the z-scan set up; D1 reference photodetector and D2 transmittance photodetector

A femtosecond laser of pulse duration 60 fs and of power 30 mW was used as a laser source. The pulse duration was measured by autocorrelation system and the energy was measured by pyroelctric energy prob. The beam profile was adjusted by spatial filter leading to spatial intensity profile near Gaussian with beam quality of $M^2 \approx 1.36$. The laser beam was focused by a lens of 15 cm focal length to produce a waist of 20.89 μm. The sample was translated along the beam axis (z-axis) through the Rayleigh distance 1700 μm

**3. Results and discussion:**

The (XRD) pattern was recorded for CdS spray deposited film as shown in figure 3.

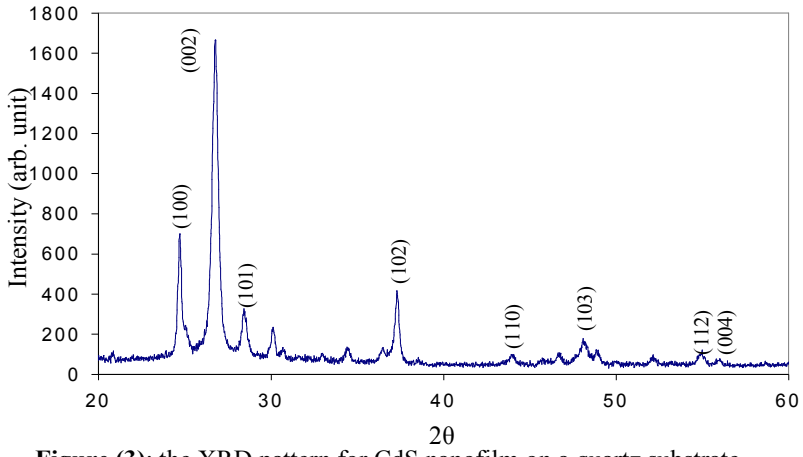



**Figure (3)**: the XRD pattern for CdS nanofilm on a quartz substrate.

The spectrum through $2\theta=20^o$ to $2\theta=60^o$ indicates that the CdS nanofilm formed with polycrystalline structure. The observed values of the X-Ray diffraction peaks are compared with American Society for Testing and Materials (ASTM) data for hexagonal CdS. The figure shows broad peaks which give evidence of the formation of the nanostructure. Using the width of (002) peak which appears at angle $26.78^o$ on 2θ scale in Scherrer relation [18]:

$$d=0.9\lambda / \beta \cos\theta \qquad (2)$$

where $d$ is the grain size, $\lambda$ is the wavelength, $\beta$ represents the full width at half maximum (FWHM) in degree and $\theta$ is the diffraction angle, the size of the formed nanoparticles was found to be about 20 nm. Scan rate was 1deg/min. wavelength was 1.54 $^o$A.

The absorption spectrum of the nanoparticles CdS shows high absorption in the UV up to 550 nm in visible, and it shows low absorption beyond the range; as shown in figure 4.

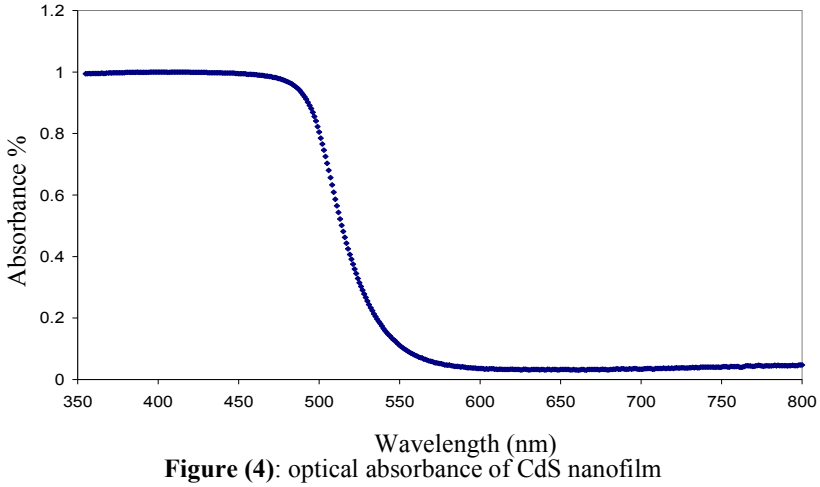



**Figure (4)**: optical absorbance of CdS nanofilm

Referring to the data extracted from the absorption spectrum the absorption coefficient was calculated as function of wavelength. Assuming allowed transition, the dependence of $(\alpha h\upsilon)^2$ with $h\upsilon$ is plotted in figure 5.

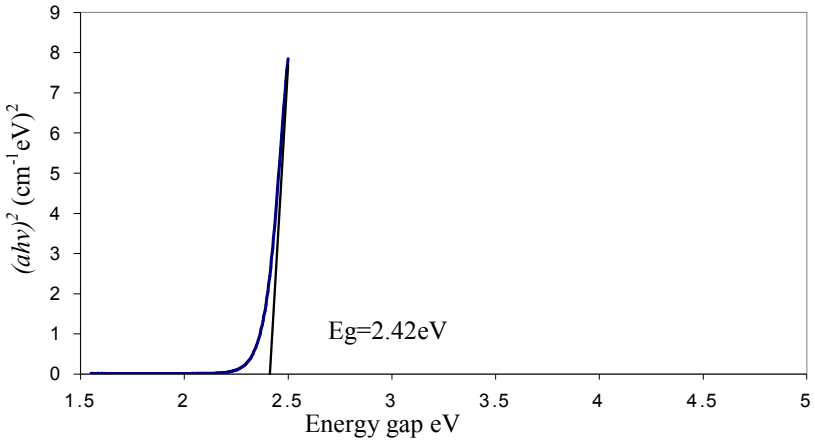



**Figure (5):** $(ahv)^2$ versus energy gap

The extrapolation of the linear part of the plot $\alpha h\upsilon=0$ give rise to estimate the energy gap value of the nanoparticles CdS which was found to be 2.42eV. This value is comparable to the values found by other workers [19]. The optical transmittance spectrum of CdS nanofilm is shown in figure 7. It can be noticed from this figure that the transmittance is high in the visible region with sharp increasing beyond the 520 nm, this indicate that the CdS nanofilm show high absorption below this value because of the occurrence of the nonlinear absorption.

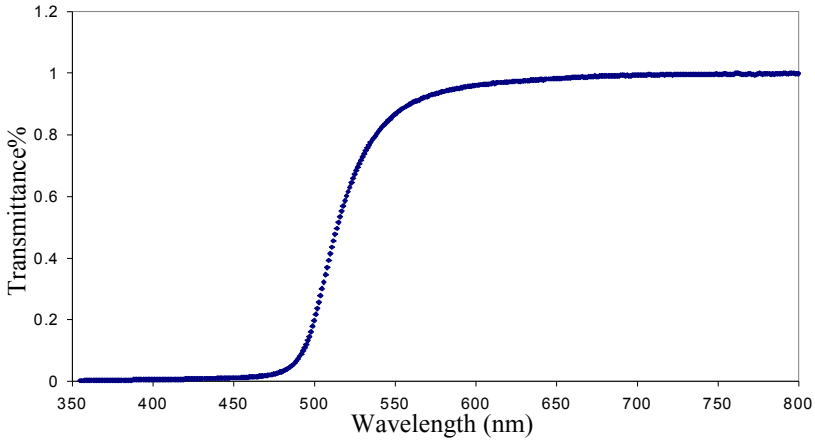



**Figure (6):** Optical transmittance of CdS nanofilm.

Figure (7) shows the variation of extinction coefficient as a function of wave length for CdS Thin film. It is observed from this figure that the extinction coefficient increase with increasing of wavelength until wavelength 500 nm. Also, it is observed from this figure that the extinction coefficient at wavelength 500 nm decreases with the wavelength. Finally the extinction coefficient increase slightly with increasing of wavelength after 600 nm.

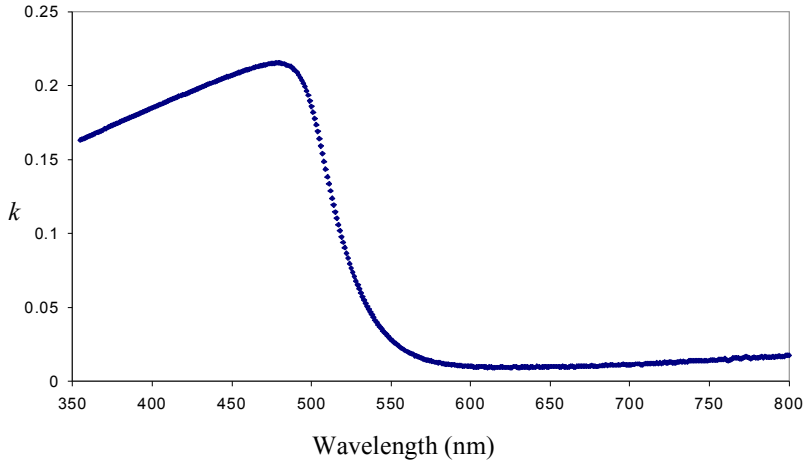



**Figure (7)**: The Extinction coefficient for CdS thin films at room temperature.

The surface trapping peaks are attributed to the formation of the surface state in the energy gap due to nanostructure of the prepared CdS. The locations of the surface state are determined by a model based on the spatial variation of the potential at the grain boundary [20]. The presence of such state contributed the linear absorption which may reduce the nonlinear absorption cross section. Thus our tested samples in z-scan were prepared with low defect formation.

The z-scan transition curves at different excitation intensities are recorded for the nanoparticles CdS nanofilm and it can show in figure 8. The normalized transmittance of the open aperture Z-scan is given by [21]:

$$T(z) = \frac{1}{\pi^{1/2} q_o} \int_{-\infty}^{\infty} \ln[1 + q_o \exp(-x^2)] dx \qquad (3)$$

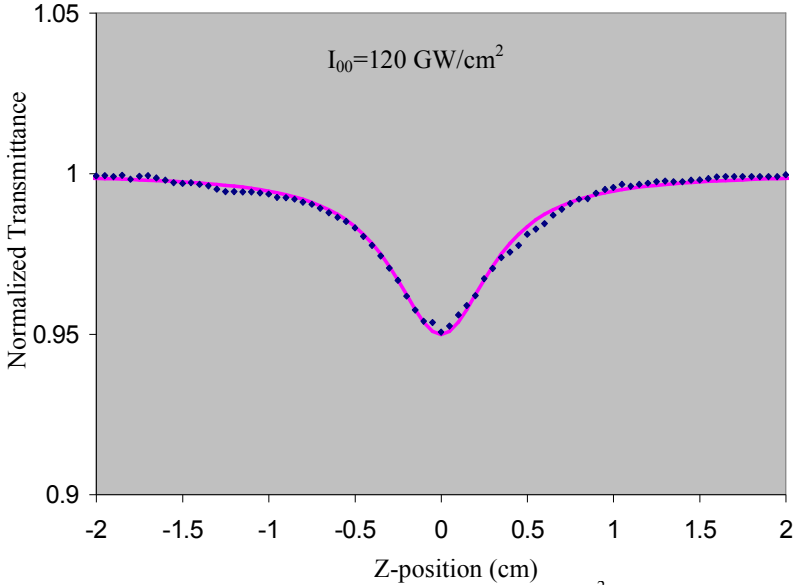



**Figure (8):** OA Z-scan measured at 120 GW/cm$^2$ excitation irradiance, wavelength of 800nm, a pulse duration 60 fs, and repetition rate of 250 kHz. The solid lines are the fitting curves by employing the z-scan theory, described in the text, on 2PA.

Where $q_o=\beta\ I_o\ L_{eff}$, $I_o=I_{oo}/(1+z^2/z^2_o)$ is the excitation intensity at the position $z$; $z_o=\pi\omega_o^2/\lambda$ where $z_o$ is the Rayleigh range; $\omega_o$ is the minimum beam waist at focal point (z=0); $\lambda$ is the laser free-space wavelength; $L_{eff}=[1\text{-}exp(-\alpha_o\ L)]/\alpha_o$ is the effective sample length for 2PA processes; $L$ is the sample length and $\alpha_o$ is the

linear absorption coefficient. The 2PA coefficient can be extracted from the best fit between the above equation of the Z-scan and the OA Z-scan curve. The results show the value of $\beta$ is in order of 116 cm/GW. This value is in a good agreement with values mentioned by [22].refereeing to the Z-scan theory for 2PA [23]. The transmission as a function of the incident intensity is given by:

$$T = 1 - \frac{\beta I_o L_{eff}}{2^{3/2}} \tag{4}$$

**4. Conclusions:**

The CdS nanostructures were prepared by the chemical spray pyrolysis technique. The nonlinear absorption coefficient was measured by fully computerized Z-scan unit. The measurements show that the nonlinear absorption coefficient for the nanocrystallites is one order of magnitude higher than that of the bulk CdS material. This increasing in the nonlinear responsivity when the crystalline size approach the nano dimension may be attributed to the defect formation in this type of material which is highly improve the nonlinear dynamic of the CdS nanocrystallite. The above formed surface states may highly contribute to the nonlinear scattering of the incident laser radiation leading to low value of the TPA coefficient.

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