Size analysis of CdS nanoparticles for the synthesis of polymer nanocomposites

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In this emerging era, polymer nanocomposites proved to be cornerstones for sustainable environment and energy applications like solar cells, optoelectronic devices, efficient drug delivery. Polymer combined with Inorganic semiconductor material provides the advantages of both constituting compounds providing high stability and enhanced electrical and optoelectrical properties. CdS has attracted the attention of many researchers, being a N-type semiconductor, it possesses wide energy band gap value 2.42eV and thus making it worthy material in optical switches, lasers, photoconductive devices and much more. In the present work, uniform thin films of CdS of varying thickness at different time interval (5min, 10 min and 15 min, respectively) have been synthesized and analyzed for the dependency of reaction time on the size of nanoparticle. These films were analyzed using different characterization tools such as X-Ray Diffraction (XRD), UV-Visible spectroscopy and atomic force microscopy (AFM) which tells about crystallographic structure, absorption spectra and morphological features of sample respectively. It was found that the size of nanoparticles deposited on substrates have been increased with increase in reaction time from 5 min to 15 min. The monodispersed particle has been deposited on the substrate obtained after 5 minutes of reaction time resulting in good quality thin film. Thus, it can be used to synthesize polymer nanocomposites for various electrical, optoelectrical and biological applications.

Keywords: Nanocomposites, Sustainable, Cadmium sulfide, Drug delivery

INTRODUCTION

In the recent times, polymer nanocomposites have been extensively used in various fields like for medical purposes, sustainable energy, and environmental applications due to their high-performance and unique physical and chemical properties [1, 2]. Nanocomposite are formed by the combination of different materials to have the best properties of the materials added in which at least one of them is of the nano regime [3, 4]. The inorganic(semiconductor) and organic (polymer) nanocomposites have fascinated many researchers or various applications such as solar cells, Light emitting diodes, transistors, and biological imaging [5]. The organic polymers engrossing the inorganic nanomaterial provides stability by passivating defects and dangling bonds, flexibility and the functional tunability. However, the inorganic semiconductor material enhances their optoelectronic properties with long lifetime [6, 7].

Amongst many inorganic semiconductors materials, cadmium sulfide (CdS) nanoparticles have been investigated by many researchers due to its good thermal stability and chemical resistance. Moreover, its physical and chemical nature changes significantly with size. It is the II–VI, direct band gap semiconducting nanomaterials having auspicious potential in the field of optics, electronic, optoelectronic, and medical applications[8]. Cadmium sulfide, a yellowish pigment, has many applications such as optical, electrical, optoelectrical. CdS (n-type semiconductor) has a wide energy band gap of 2.42 ev [9,,10].

The physical, chemical, biological, electronic, and optoelectronic properties of the nanocomposites can be varied by making changes in the shape, size and size distribution of nanomaterials incorporated [11-13]. The nanoparticle can be synthesized by different methods like chemical methods - chemical bath deposition, sol–gel method, electrodeposition and vacuum-sputtering [14, 15]. Based on literature survey, chemical methods are founds to be of low cost, very simple and quick. Also, they are very easy to change the parameters like temperature of reaction, pressure of reaction, reaction time, etc., which play an important role in the determination of the size and size distribution [11]. In the present work, the effect of size variation of CdS nanoparticles was analyzed. The CdS nanoparticles were synthesized by the chemical bath deposition (CBD) method. It is a method based on controlled precipitation of desired constituents from compound solution. The thin films synthesized with this method are uniform, pin-hole free, as ions are the basic building blocks. It is a fast, simple, and economical approach with desired particle-size, shape, composition, and aggregation of particles.

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Three thin film samples were deposited with the variation in reaction time for 5 minutes, 10 minutes and 15 minutes, respectively. The samples deposited were characterized for structural, morphological, and optical characterisics.

MATERIAL AND METHOD

Material required and characterization

The chemicals used to synthesize CdS are purchased from Aldrich and used without further purification. CdS has been obtained from 3mM cadmium sulfate ($CdSO_4$) as a cationic precursor. Ammonia (NH_4OH) solution was used to maintain pH of the solution, 20mM thiourea (CH_4N_2S) was an anionic precursor. Distilled water, acetone, and 2-propanol were used.

The CdS samples synthesized using the CBD method were characterized using Philips X-ray diffractometer (XRD). The crystalline structure of CdS nanoparticles was determined by the spectra measured in the range of 20°-60° with copper Kα radiation at 1.5418Å wavelength. The optical characterization was done using the UV-Visible spectrometer (Shimadzu-UV1650PC) in the wavelength range of 425 to 750 nm. The morphological measurements were performed using an atomic force microscope (AFM). The images were obtained using a Multimode V NSV, Veeco instrument. The imaging was done in tapping mode at the resonant frequency of 300 kHz with a force constant 40 N/m.

Synthesis

The thin films of CdS nanoparticles were synthesized using a common bath deposition method (CBD) with some modifications [16]. In a beaker, some distilled water was taken and thiourea was mixed in it. In another beaker, distilleed water was taken and $CdSO_4$ was mixed in it. These two solutions were then sonicated for 10 min to ensure uniform mixing. Then, ammonium solution was added to the $CdSO_4$ solution and stirred for 10 sec. The thiourea solution was mixed to the $CdSO_4$ solution and the final solution was prepared. The solution was then heated on a hot plate with continuous stirring at a temperature of 65°-80° C. After that, the samples substrates were loaded in the beaker keeping mixture at low speed and waited for some time depicted in Fig. 1. The samples of CdS thin film were collected for an interval of 0 min, 5 min, 10 min and15 min.

The deposition process includes slow release of Cd^{2+} and S^{2-} ions through controlled setting of appropriate chemical equilibrium. The scheme of CdS thin films obtained after various time intervals of 0 min, 5 min, 5 min and 10 min is depicted in Fig. 2.
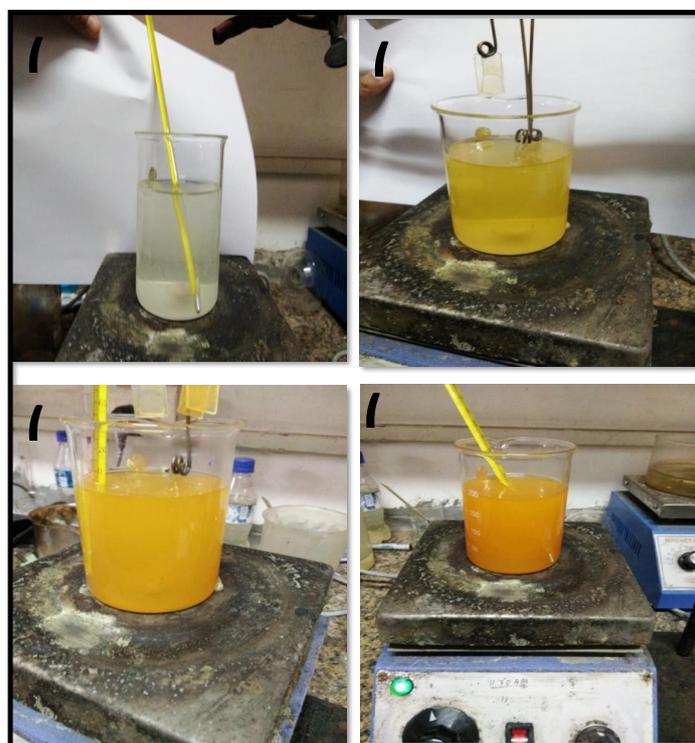

Fig. 1. Experimental steps for CdS thin film preparation: (a) 0 min; (b) 5min; (c) 10 min and (d)15min, respectively.
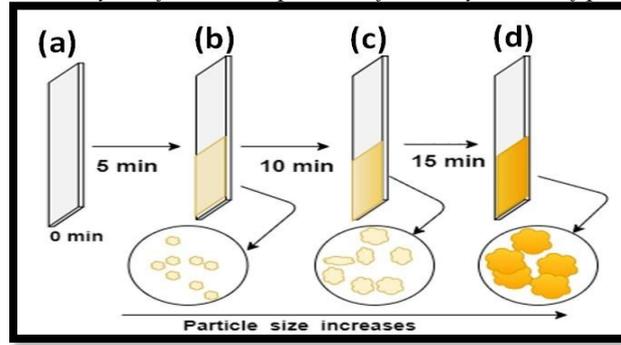
Fig. 2. CdS thin films obtained after specific intervals: (a) 0 min; (b) 5 min; (c) 10 min and (d) 15 min.

RESULTS AND DISCUSSION

Structural characterization

X-ray diffraction (XRD) analysis

Fig. 3 shows the XRD pattern of different CdS thin films synthesized *via* common bath deposition (CBD) technique. Fig. 4(A) shows the diffraction peak at 29.7 which is attributed to the (200) planes of CdS thin film. Similarly, Figs. 4(B) and 4(C) show the peaks at 26.7 and 29.7∘ which are assigned to (111) and (200) planes of CdS, respectively. It matches well with the standard JCPDS (10-0454) suggesting that the thin films are in cubic (zinc blend, ZB phase) form and in good agreement with the literature on CdS [17, 18]. The absence of other peaks corresponding to other phases confirms the pure phase synthesis of thin film.

It was observed that the peak intensity (Table 1) of CdS thin film decreases when reaction time increases from 5 minutes to 15 minutes. This decrease in intensity shows a decrease in crystallinity of the thin film. The FWHM values of the XRD peak provide the value of crystallite size of nanomaterials. The particle size decreases with increasing FWHM [19]. The crystallite size was calculated using Scherer's equation [20] and tabulated in Table 1.

$$D = k\left(\frac{\lambda}{\beta \cos\theta}\right) \qquad (1)$$

where, K = a constant of value equal to 0·89, λ = wavelength of X-ray (0·154 nm), β = full width at half maximum, θ = half diffraction angle.

The increase in crystallite size can be observed with the decreased value of FWHM. The estimated X- ray crystallite size of CdS varies from ~12 nm to ~31 nm as the time of reaction increases from 5 minutes to 15 minutes.

Lattice constant for the CdS nanoparticles forming the thin film can be calculated using equation (2) [21].

$$d^2 = a^2/(h^2+k^2+l^2) \qquad (2)$$

where a = lattice constant, (h, k, l) = Miller indices (MI). Lattice constant calculated was found to be 0.60 nm for our sample (CdS), which matches well with the earlier reported value for cubical CdS thin film [18].

Optical characterization

UV-Visible analysis

The optical studies of the CdS thin films were carried out using the absorption spectra in the visible range. Figs. 4 (A), (C) and (E) show the absorption spectra of the as fabricated CdS thin films. However, Figs. 4 (B), (D) and (F) show the corresponding Tauc's plots. The optical band gap (BG) energy of the nanomaterials which allows direct transition can be governed using the following equation (3) [22]:

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \qquad (3)$$

where, E_g = band gap energy; α = absorption coefficient, ν = incident photon frequency and h = Planck's constant.
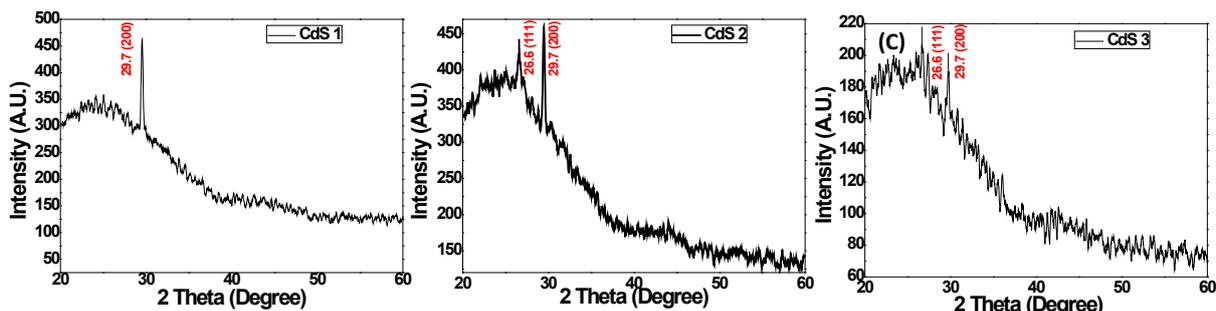
Fig. 3. XRD pattern for: (A) CdS 5 minutes (B) CdS; 10 minutes; (C) CdS 15 minutes, respectively

Table 1. Particle size as calculated from XRD analysis

Sample	2 theta (Degree)	(hkl)	Peak Intensity (A.U.)	FWHM (β)(Degree)	D (nm)
CdS 1 (5 minutes)	29.7	200	462	0.732	~12
CdS 2 (10 minutes)	29.7	200	459	0.285	~30
	26.6	111	442	0.351	~24
CdS 3 (15 minutes)	29.7	200	201	0.273	~31
	26.6	111	218	-	-

The optical band gap can be observed by extrapolating the linear region of the plot $(\alpha h\nu)^2$ *versus* photon energy ($h\nu$) and having intercept on the x-axis [23]. Decrease in band gap from 2.55 eV to 2.46 eV was observed in CdS thin films as the time of reaction increased from 5 minutes to 15 minutes (Figs. 4(B) and (F)). This blue-shift in the values of energy band gap w.r.t bulk CdS reflects the quantum confinement in the as synthesized CdS nanoparticles in thin film form. Furthermore, dual band gaps can be observed in CdS thin film synthesized with the reaction time of 10 minutes. These two bandgaps indicate the presence of different-sized nanoparticles which signifies polydispersity.

The effective mass approximation (EMA) proposed by Brus can be used to find the particles size as given by equation (4) [12] for different band gap CdS:

$$E_n = E_g^{bulk} + (\hbar\pi^2)/(2R^2)(1/(m_e^*)+1/(m_h^*)) - ((1\cdot 8e^2)/(4\pi\varepsilon_0\varepsilon R)) \qquad (4)$$

where,

R = radius of the nanoparticle,
m_e^* = effective mass of (e-)electron (0.19me),
m_h^* = effective mass of hole (0.80me),
m_e = mass of electron,
ε = dielectric constant of material (for CdS = 5.7) and
εo = permittivity of free space.

Applying EMA, the size (radius) of CdS nanoparticles was calculated as 14 nm, 31 nm and 43 nm, respectively with reaction time of 5 minutes, 10 minutes, and 15 minutes. Thus, the decrease in the band gap was observed with increasing particle size as the time of reaction varies from 5 minutes to 15 minutes which is in good agreement with the XRD analysis. Furthermore, the lower band gap of 2.0 eV observed in a CdS thin film synthesized after 10 minutes reaction time indicates bulk or very large sized nanoparticles and confirms the polydispersity as obtained above by XRD. Thus, the film obtained after reaction time of 10 minutes is not favorable for

polymer nanocomposites and thus, for many device applications like photovoltaics and photocatalysis.

Morphological characterization

Atomic force microscopy (AFM)

The high uniformity and smoothness of thin film are very important properties as they provide a good interface with less lattice mismatch and pin hole defects [24]. The uniformity and other morphological characteristics of the CdS thin films were investigated by atomic force microscopy (AFM) in the present study.

Fig. 5 shows the AFM images of CdS thin films in 2-dimension and 3-dimension, respectively. Figs. 5(A), (C) and (E) represent the 2-dimensional view of CdS thin films, which shows the shape and particle size distribution of CdS nanoparticles. It shows spherical-shaped CdS nanoparticles in all cases. However, there is an increase in particle size as the reaction time increases from 5 minutes to 15 minutes. Fig. 5(C) shows that a CdS thin film obtained after 10 minutes of reaction has polydispersity which is in good agreement with XRD and UV analysis.

The different particle size of CdS nanoparticles in different films results in morphological variation of the thin film. Figs. 5(B), (D) and (F) show the 3-dimensional view of thin films corresponding to different-sized CdS nanoparticles. The RMS roughness value of these films was found to be 21.0, 28.2 and 32.3, respectively. From these it can be observed that increasing particle size results into an increase in roughness of films. This leads to an increase in non-uniformity of the films and defects in the thin film. These defects may cause bad interface contacts with other films in the device which results into bad quality device. Thus, for good quality of film and thus, of nanocomposites, nanoparticles should be monodispersed with small size, which can be obtained with a shorter reaction time.
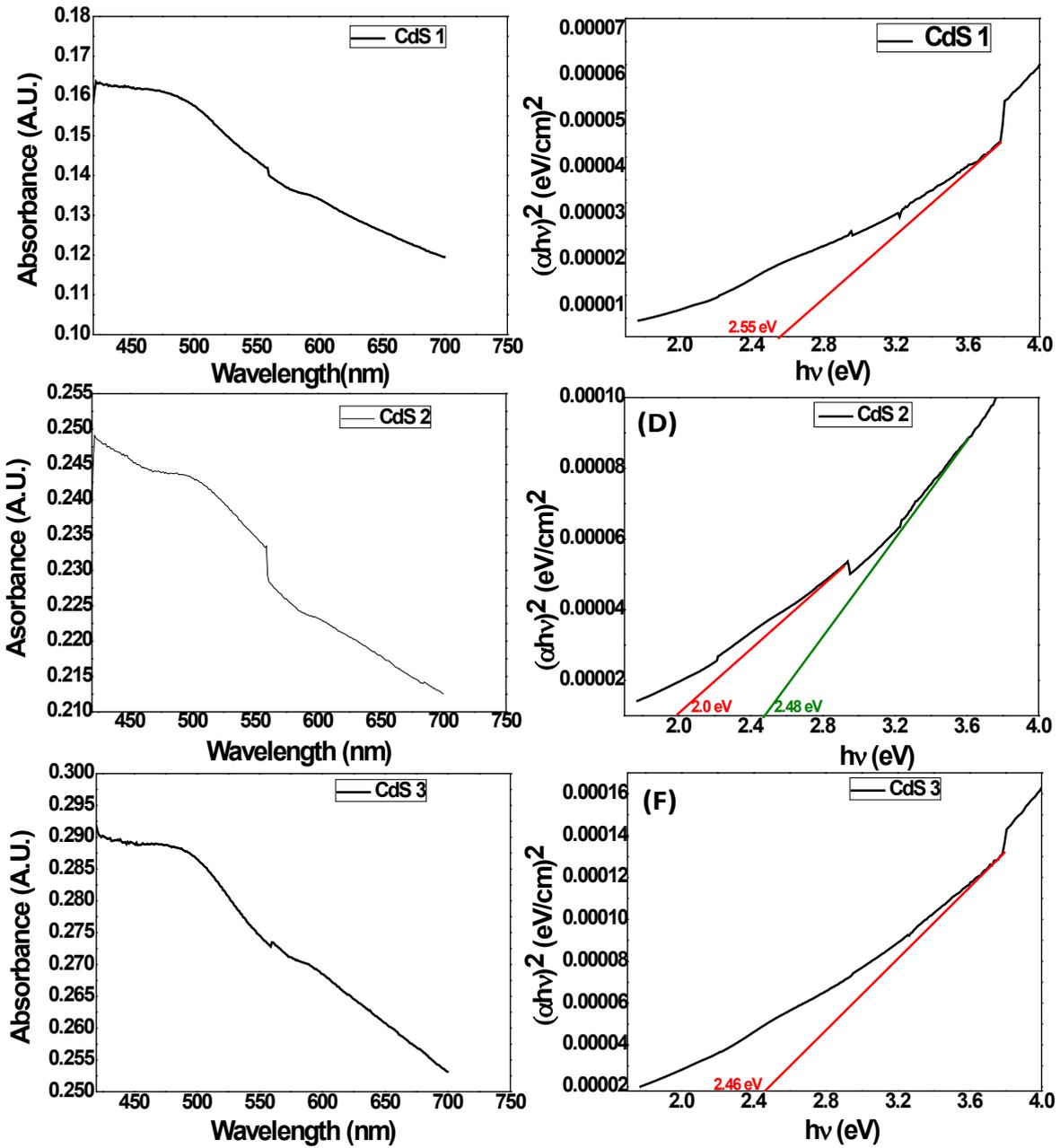
Fig. 4. Absorbance curve and corresponding Tauc's plot for (A & B) CdS 5 minutes, (C & D) CdS 10 minutes and (E & F) CdS 15 minutes, respectively
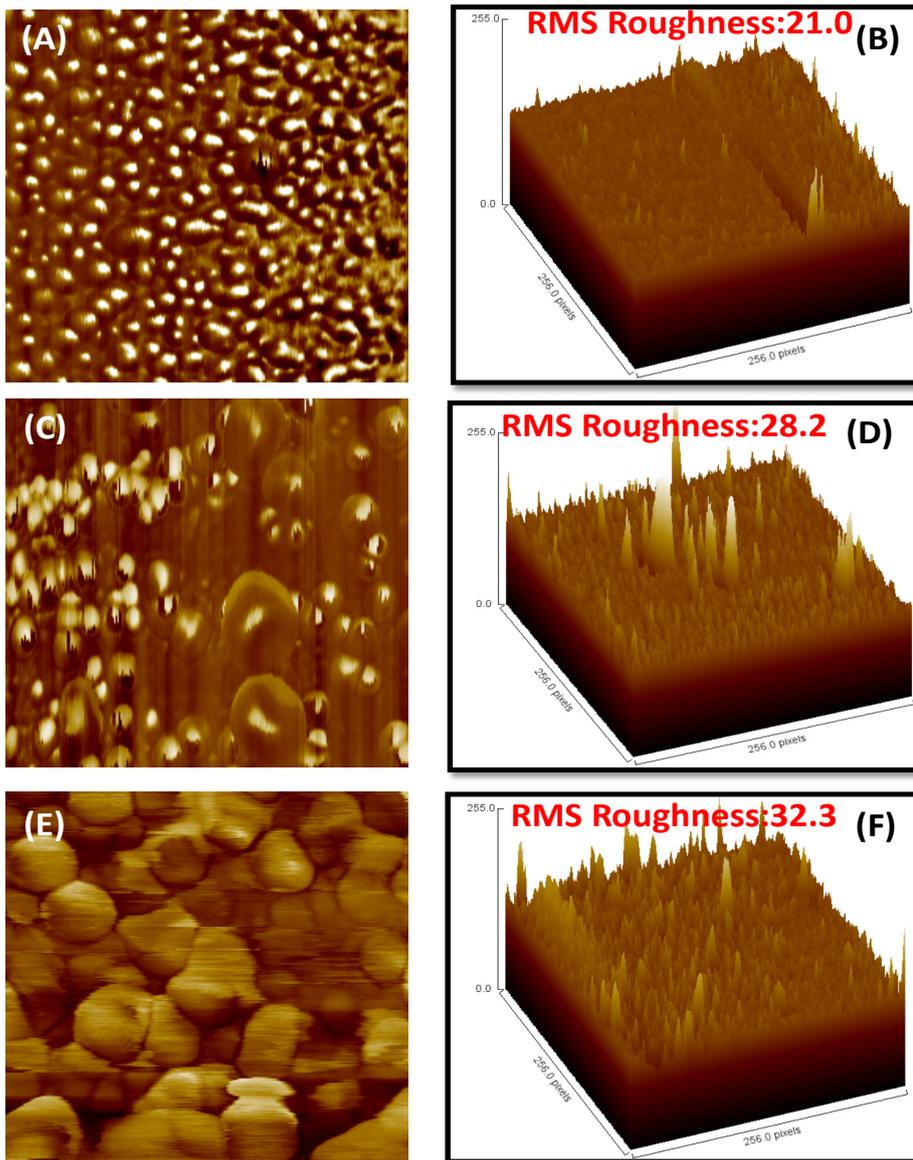
Fig. 5. AFM images for (A & B) CdS 5 minutes, (C & D) CdS 10 minutes and (E & F) CdS 15 minutes

CONCLUSION

An investigation was carried out on CdS thin films for the formation of polymer nanocomposites. The CdS thin films were synthesized using a chemical bath deposition (CBD) method. This method proves to be cost-effective, time saving and easier to grow CdS thin films. This method allowed us to collect thin films of different thickness with variation in reaction time during synthesis. The structural, morphological, and optical characterization of CdS thin films were carried out using various techniques such as XRD, UV- visible spectroscopy and AFM. XRD confirmed its crystalline nature and the diffraction peaks obtained at specific angles confirmed the cubic structure of CdS. The crystalline size calculated from Debye'-Scherrer equation confirmed the increase in size of nanoparticles with increase in reaction time. Optical characteristics of thin films were measured in the visible region and confirmed the decrease in bandgap with increase in particle size. This blue-shift in absorption edge indicates the quantum size effects as the reaction time increases from 5 minutes to 15 minutes and verifies the results obtained by XRD. AFM provided a topographical view, roughness, uniformity defects and surface profile of the fabricated thin films. It was observed that for the procurement of a monodispersed thin film of good quality, the reaction time in CBD method should be short. Thus, the characterization of thin films by XRD, optical UV-visible spectroscopy and AFM confirmed that the nanoparticles or the thin film obtained after reaction time of 5 minutes can be used for the synthesis of polymer nanocomposites.

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