

## **Synthesis and Characterization of CdS Ink Comprised of Nanoparticles**

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### **ABSTRACT**

CdS nanoparticles are synthesized by cost effective and application oriented sol-gel technique. Ethylene glycol and de-ionized water were used as solvents, whereas cadmium chloride ( $\text{CdCl}_2$ ) and sodium sulphate ( $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ ) were used as cadmium and sulphur sources. CdS sol was prepared by refluxing the product at  $40^\circ\text{C} - 70^\circ\text{C}$  for 0 – 75 minutes. Solution was centrifuged at 10,000 rpm for 10 minutes. Resultant precipitates were annealed at 50 -  $100^\circ\text{C}$  for different time intervals. CdS hexagonal nanoparticles with crystallite size  $\sim 10\text{nm}$  were confirmed by X-Ray Diffractograms. SEM results show diameter of  $\sim 25\text{ nm}$  at a low synthesis temperature of  $50^\circ\text{C}$ . Size was tuned to  $\sim 18\text{ nm}$  by changing the synthesis conditions and refluxing time. Previous studies show preparation of CdS nanoparticles in ultrasonic waves, whereas in this research work simplest route of nanoparticle synthesis is explained. Optimized nanoparticles were dispersed in absolute ethanol and pyridine to prepare nanocrystalline ink. CdS ink was then spin coated onto a glass substrate for optical measurements.

### **1. INTRODUCTION**

Semiconductor nanoparticles exhibit unique optical and electronic properties that are strongly dependent on their size, shape and surface modification. Because of these novel properties nanoparticles can find applications in nano-metric sized devices such as nano LEDs (Rogach 2008, Mueller 2005, Tekin 2007) and nano solar (Kongkanand 2007).

Cadmium sulphide (CdS) has been extensively studied for optoelectronic application since it has a direct band gap of  $\sim 2.5\text{eV}$ , ideal to be used for solar cell (Saikia 2011, Han 2010, Wang 2007), photo-catalyst (Yang 2011) and cell imaging (Rempel 2011).

In the past few decades, a variety of wet chemical methods have been used to prepare CdS nanoparticles such as hydrothermal method (Lu 2011), solvothermal method (Zhong 2010), micro-emulsion (Ghows 2010) and chemical precipitation method (Lee 2009). In most of these synthesis methods capping agents are used to prevent agglomeration of particles; this helps to control the size of nanoparticles (Jamali 2007). When these nanoparticles are extracted as free-standing powders, they can be exploited in thin film preparation for device formation application. Capping agents, however, are not always

desirable since for many applications efficiency of nanoparticles is affected by the surfactant molecules that are covalently bond with the surface atoms of nanoparticles. For example, for organic photovoltaic hybrid solar applications, where charge transfer between nanoparticles and conjugated polymer are required, surfactant may cause hindrance in the charge transfer. Therefore, often the exchange or removal of ligands from the surface of nanoparticles is essential step (Verma 2009).

In this study efforts are made to synthesize surfactant-free nanoparticles by controlling their size via refluxing through a simple chemical method. During our experiments it was observed that refluxing time has great influence on particle size. The effect of refluxing time on samples has been analyzed. Five samples were prepared  $S_1, S_2, S_3, S_4$  and  $S_5$  with reflux time of 15, 30, 45, 60 and 75 min.

## 2. EXPERIMENTAL

### 2.1. Chemicals

Cadmium chloride ( $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ ), sodium sulphide ( $\text{N}_2\text{S} \cdot 9\text{H}_2\text{O}$ ), distilled water and methanol were of analytical grade and used directly as purchased without further purification.

### 2.2. Synthesis of cadmium sulphide nanoparticles

In this study, we have used cadmium chloride ( $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ ) as an  $\text{Cd}^{+2}$  ion source and sodium sulphide ( $\text{N}_2\text{S} \cdot 9\text{H}_2\text{O}$ ) as a sulfur  $\text{S}^{-2}$  ion source, respectively. For the synthesis of cadmium sulphide nanoparticles, 50mL aqueous solution of (0.1M)  $\text{CdCl}_2$  and 50mL aqueous solution of (0.1M)  $\text{N}_2\text{S}$  were prepared. The freshly prepared aqueous solution of  $\text{N}_2\text{S}$  was added drop wise into the  $\text{CdCl}_2$  aqueous solution in a three-necked flask at  $85^\circ\text{C}$ .

The solution was refluxed at 400rpm for 2hrs. As the reaction started, the mixture gradually changed from transparent to bright yellow and after the completion of reaction this turned to reddish orange. The temperature was kept constant at  $85^\circ\text{C}$  and aliquots were removed after every 15 min. Excess methanol was added in each aliquot and centrifuged at 10,000 rpm for 10 min. The resultant precipitates were dried in desiccators for 48hrs.

### 2.3. Spin Coating

Films were spin coated onto  $1 \times 1 \text{cm}^2$  glass slides using a Süss Microtech Delta 6RC spin coater at 3000 rpm for 30 sec. The glass slides were firstly washed with detergent and then ultrasonically cleaned in acetone and IPA for 10 and 15 minutes respectively.

### 2.4. Characterization

X-ray diffraction patterns of dried nanoparticles and films were studied by using Rigaku D/Max II-A X-Ray Diffractometer (XRD). Size and morphology of nanoparticles were observed by using Hitachi S-3400N Scanning electron microscope. Optical properties were measured by JA Woollam's variable angle spectroscopic ellipsometer (VASE).

### 3. RESULTS AND DISCUSSION

#### 3.1 XRD Analysis

XRD patterns of as-synthesized CdS nanoparticles are shown in Fig 1. These patterns show three definite peaks at angles ( $2\theta$ ) of  $26^\circ$ ,  $28^\circ$  and  $51.8^\circ$ , which could be interpreted as diffraction from (0 0 2), (1 0 1) and (1 1 2) planes, of wurtzite hexagonal crystal lattice, respectively with the lattice parameters of  $a= 4.12 \text{ \AA}$  and  $c=6.72 \text{ \AA}$ .

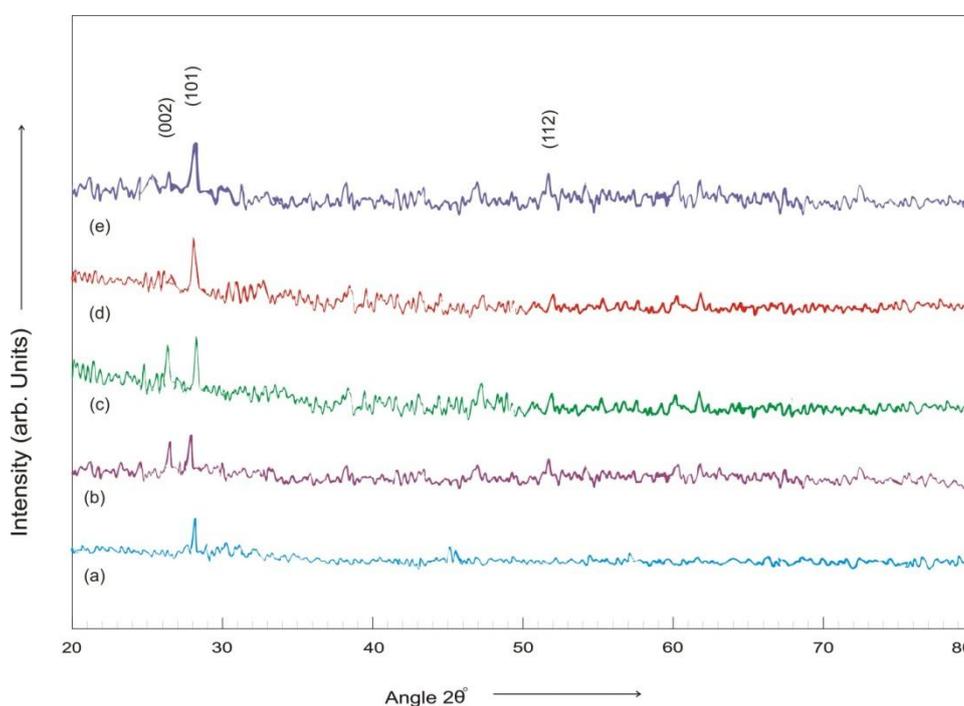


Fig. 1 XRD patterns of CdS nanoparticles at different reflux times

These results match quite well with the international centre for diffraction data (JCPDS card num 75-1545). The as-prepared CdS is found to be polycrystalline in nature. The diffraction peaks become sharper and crystallinity is improved with the increase in refluxing time. The equation used to find the lattice parameters for hexagonal system of CdS is:

$$1/d_{hkl}^2 = 4/3a^2(h^2 + hk + K^2) + l^2/c^2 \quad (1)$$

Crystallite size of CdS nanoparticles is estimated to be  $\sim 10\text{nm}$  by using Scherer equation:

$$D = K\lambda/B.\cos \theta \quad (2)$$

Where K is a constant that is equal to 0.94, lambda is the X-ray wavelength  $\lambda = 1.5405\text{\AA}$  and B is the full width at half maximum of the XRD selected diffraction peak on the  $2\theta$  scale where  $\theta$  is the diffraction angle.

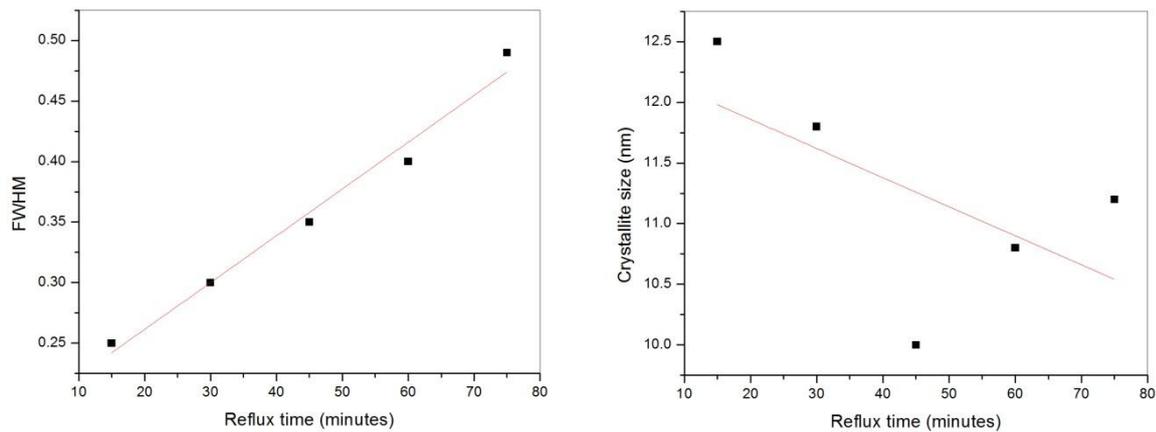


Fig. 2 (a) FWHM and (b) Crystallite size variation of CdS nanoparticles with different reflux time

FWHM linearly increases with the reflux time; as the reflux time increases from 15min to 75min the FWHM increases from  $0.24^\circ$  to  $0.5^\circ$  [Fig. 2a]. Crystallite size is inversely related to the FWHM of the individual peak i.e. the more narrow the peak the larger the crystallite size. Fig. 2(b) shows a graph of crystallite size values (calculated from Scherer equation) versus reflux time. The graph shows that crystallite size decreases by increasing the reflux time. At 15min reflux time the grain size is 12.5 nm that decrease to 10 nm at 45min reflux time.

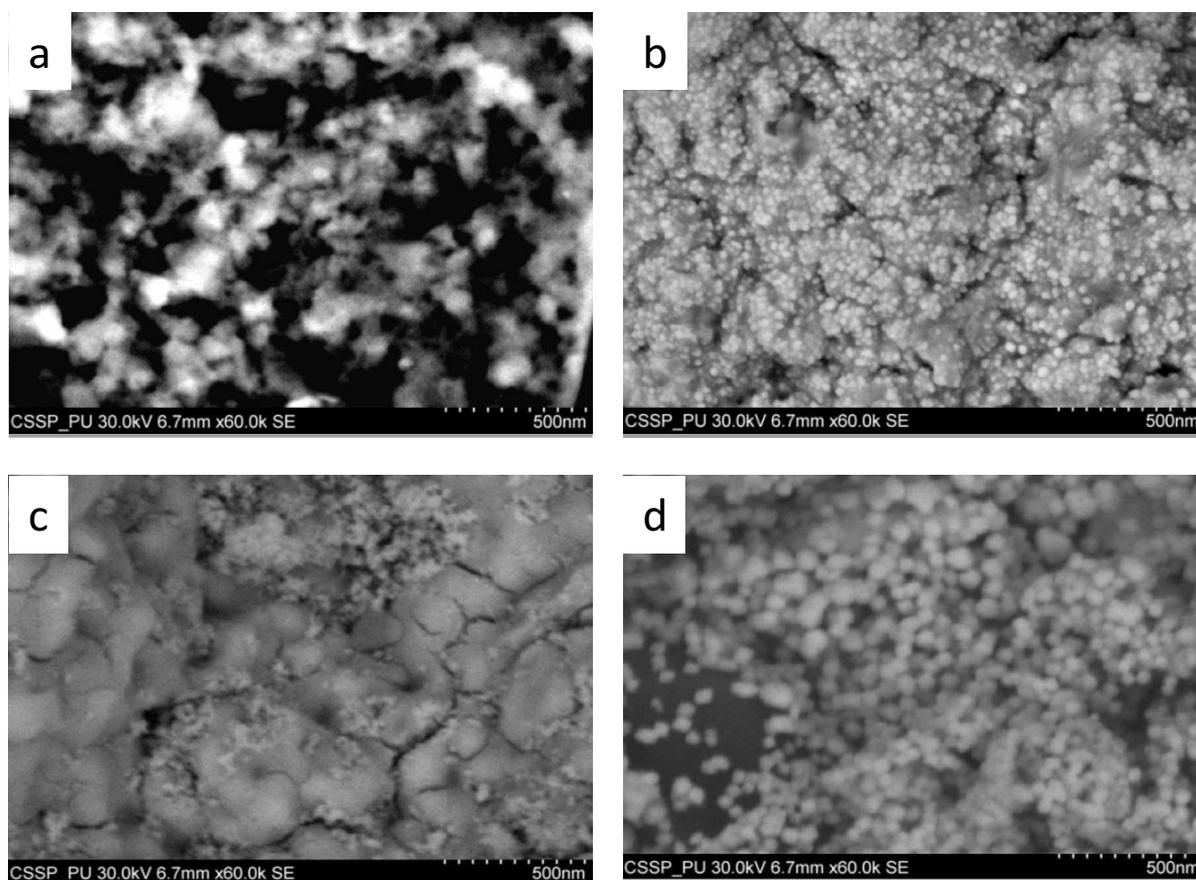
Variation in growth of crystallites can be indexed to the relaxation and stresses produce in the films, as well. The stress/strain ratio varies strongly as a function of grain growth since the films provide accommodation to the high temperature stresses in the grains. Grain growth is driven by neighboring grains that posses different energies due to the curvature of energetic grain boundaries and different amounts of accumulated strain energy. By differentiating the Braggs law the micro strains are calculated as:

$$b = \Delta 2\theta = -2 \frac{\Delta d}{d} \tan \theta \quad (3)$$

The uniform strain is observed in the films and this fact is evident from the shapes and shifts of the peaks of reflection planes when compared with the standard shapes. (Cullity 1978).

### 3.2. SEM Characterization.

SEM results of the samples  $S_1, S_2, S_3, S_4$  and  $S_5$  of as-synthesized CdS nanoparticles are shown in Fig 3. SEM images of 15min sample shows spherical particles with an average size of  $\sim 60\text{nm}$ . When the reflux time is increased to 30min ( $S_2$ ) the particle size diameter decreases to  $\sim 25\text{nm}$ . At 45 minute reflux time, size of nanoparticles decreases to  $18\text{nm}$ . From the micrograph it is observed that after further increase in time the particle size diameter kept growing from  $\sim 50\text{nm}$  to  $\sim 85\text{nm}$  for samples  $S_4$  and  $S_5$ , respectively. This shows that as the reaction time increases the particle size also increases due to the Ostwald ripening growth mechanism i.e. during the growth the total amount of particles decreases slowly due to dissolution of small ones and the larger particles will continue to grow resulting in a defocusing of size distribution. Fig. 3(f) shows the plot between diameter and reflux time, which illustrates the fluctuation in particle size with respect to time.



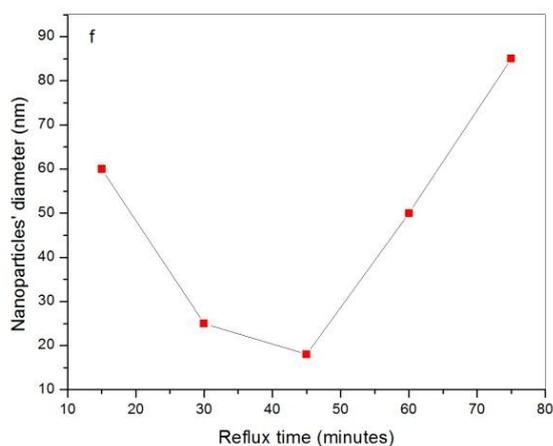
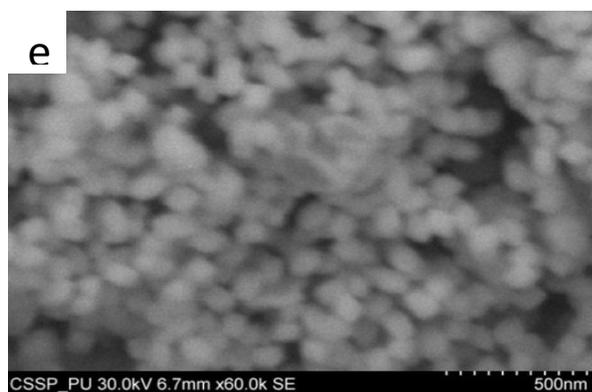


Fig. 3 SEM micrographs of CdS nanoparticles refluxed for (a) 15 min (b) 30 min (c) 45 min (d) 60 min (e) 75 min and (f) Plot between nanoparticles' size and Reflux time (min).

### 3.2 Optical properties

Fig. 4 shows the transmission versus wavelength plots of CdS nanoparticles prepared at different reflux times. Maximum transmission of 93% is observed for the particle size diameter of 25nm at 30min reflux time. The sharp fall in transmission near the fundamental absorption edge is indicative of good crystallinity of the films. The rise and fall in transmittance for wavelengths greater than 500nm may be constituent to the interference of light transmitted through thin film and the substrate (Sanap 2010).

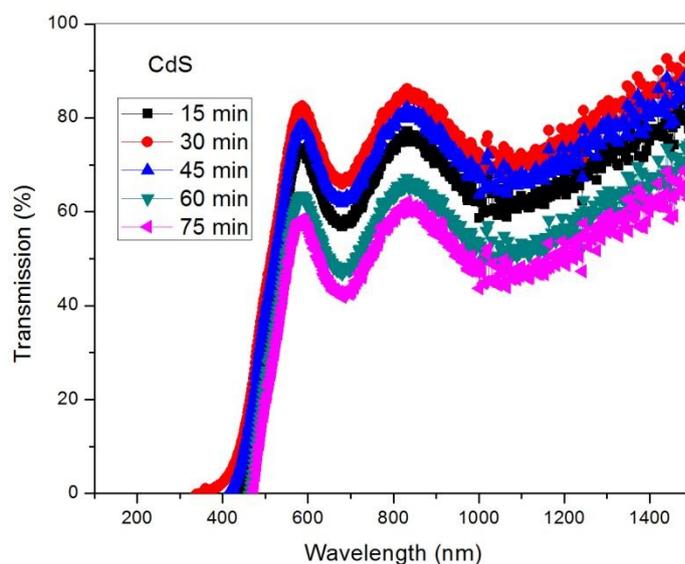


Fig. 4 Transmission spectra of CdS nanoparticles at different reflux times

Optical band gap of cadmium sulfide nanoparticles is obtained from absorption spectra by plotting  $\alpha^2$  versus photon energy  $h\nu$ . Linearity of the plots for CdS nanoparticles films indicates that the material is of direct band gap nature [Fig. 5]. The linear part of the plot has been extrapolated towards energy axis giving the energy band gap of the film material. The intercept value of the energy axis has been found to be 2.43eV for 15 min and decreased to 2.42 for 45 minutes reflux time. On further increasing the reflux time, band gap of the films increases to 2.46 eV. Relatively larger band gap of cadmium sulphide, for 60 and 75 minutes reflux time might be due to quantum confinement effect of particles i.e. when the size of the crystal is smaller than or in the order of the exciton Bohr radius.

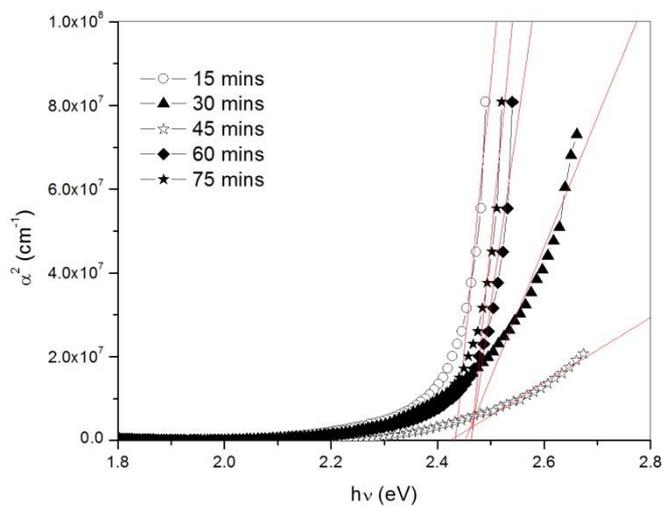


Fig. 5 Energy band gap plots of CdS nanoparticles for different reflux time

Band gap energy and transmission with respect to particle size is given in Table - I. All particles were found to be spherical. The red shift is observed in band gap value for the particle having size of 18nm while the blue shift is observed for the particles having sizes of 25, 50, 60 and 85 nm as compared to band gap of bulk CdS (2.42eV) indicating quantum confinement effect in nanoparticles. The sample with particle size of ~25 nm is found to have maximum transmission percent (93%) as compared to the rest of the samples.

Table - I: CdS nanoparticles' size, shape, band gap energy and transmission

Sample	Reflux Time (minutes)	Nanoparticles' Diameter (nm)	Nanoparticles' Shape	Transmission (%)	Band Gap (eV)
S1	15	60	Spherical	80.09	2.43
S2	30	25	Spherical	93.02	2.45
S3	45	18	Spherical	89.52	2.42
S4	60	50	Spherical	74.14	2.46
S5	75	85	Spherical	68.52	2.46

## CONCLUSION

In summary, the spherical shaped wurtzite hexagonal cadmium sulfide (CdS) nanoparticles have been successfully synthesized through simple surfactant free chemical method by using cadmium chloride and sodium sulfide as precursors. Sizes of the nanoparticles were controlled in the 18 – 85 nm range by adjusting the reflux time. Nanoparticle of 18 nm with a band gap of 2.42 eV were observed for the reflux time of 45 minutes. Maximum transmission was observed for the nanoparticle of 25nm diameter with the reflux time of 30 minutes. Blue shift is investigated in the transmission spectrum which was due to the quantum confinement effect in nanoparticles.

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