Structural and Optical Characterization of CdS Nanoparticles Grown in Different Solvents

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Abstract: *In the present work a chemical method is followed to grow CdS nanoparticles at room temperature by varying the growth time as well as solvents. Anhydrous CdCl₂, Sulphur powder,sodium borohydride powders are used as reactants. The reactions are carried out in variety of solvents and the effect of the solvent on the product quality is investigated. The room temperature synthesis produces high quality nanocrystals as revealed by electron microscopy, optical and photoluminescence measurements. Particle size increases with increase of growth time in both medium. It is observed that nanoparticles are less agglomerated in medium EDA compared to THF. The structural and optical properties show quantum confinement of CdS grown in medium THF and EDA.*

Keywords: *CdS nanoparticles, Structural properties,Optical properties,Photoluminescence*


I. Introduction

The semiconductor nanoparticles exhibit structural, optical, luminescence and photo conducting properties that are very different from their bulk properties [1-6]. It is very attractive because of their possible application in solar cell, photo detector, laser, LED, high density magnetic information storage and many others in semiconductor industries. $A_{II}B_{VI}$ semiconductor nanoparticles play an important role having application in nanodevices [7-12]. CdS (bulk band gap 2.42 eV at 300 K) has huge potential in this aspect. Their growth techniques are relatively cheap. Their characteristic absorption of light is in the visible range. There are various methods to prepare CdS nanoparticles [13-19]. Some of the above mentioned methods have some draw backs. Used precursors are unstable causing environmental hazards and required very high temperatures. These methods are not cost effective also. In the present work a chemical method is followed at room temperature [20]. Sodium borohydride is used to initiate the reaction between $CdCl_2$ and sulphur at room temperature. The method used is simple and cost effective.

II. Experimental

Anhydrous $CdCl_2$ (805.28 mg), Sulphur powder (128 mg) and stoichiometric amount of sodium borohydride were taken to prepare different samples. Tetrahydrofuran was taken as solvent for reaction medium and having very low dielectric constant ($\varepsilon/\varepsilon_0 = 7.58$). Sodium Borohydride is used to initiate the reaction between $CdCl_2$ and Sulphur.Thus sodium borohydride acts as a reducing agent.The stirring was continued at room temperature at a particular speed using a magnetic stirrer. The reaction was carried out seperately at three growth times 3h,7h and 14h at constant stirring speed. The grown samples were centrifuged and finally dried.
The following reaction is take places:
$CdCl_2 = Cd^{++} + 2Cl^-$
$NaBH_4 + 2Cl^- = NaCl + B_2H_6 + 2H + 2e^-$
$2H + S = H_2S$
$H_2S + Cd^{++} + 2e^- = CdS + H_2$
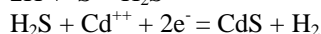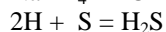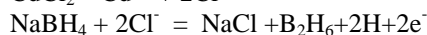
For microstructural study, as prepared CdS nanoparticles were dispersed in ethanol by ultrasonification. The Transmission Electron Micrograph (TEM) of the prepared nanoparticles was acquired using JEOL-JEM-200 operating at 200 kV. The Selected Area Electron Diffraction (SAED) patterns of the said nanoparticles were also carried out. The X-ray Diffraction (XRD) patterns of the said samples are obtained by using Rigaku MiniFlex-II X-ray diffractometer. The optical absorption spectrum of the samples was taken by using Shimadzu-Pharmaspec-1700 UV–Visible spectrophotometer .The photoluminescence spectrum of the as prepared samples was obtained by using PerkinElmer LS55 PL-Spectrometer.

III. Result and Discussions

The XRD pattern of CdS nanoparticles with different synthesis times 3, 7and 14 hours in medium EDA and THF are shown in Fig. 1(a,b) , 1(c,d) and 1(e,f) respectively. From the XRD pattern we see that the nanoparticles are formed in hexagonal phase by comparing with ICDD data.

The planes identified are compared with standard powder diffraction data. It is observed that nanoparticles are CdS nano-crystals. This is valid both for samples grown in THF and EDA. Half width of the peak decreases with increase of growth time which indicates that size of the crystal increases.

The average crystal sizes are determined from the micrograph pattern. Fig. 2(a, b, c) and 2(d, e, f) are TEM and TED pattern in medium THF. Fig. 3(a, b, c) and 3(d, e, f) are TEM and TED pattern in medium EDA.

Also from micrograph pattern it is clearly observed that with increase of growth time the crystal size increases.

This is in agreement with the process called Ostwald Ripening. In Ostwald Ripening smaller particles in solution dissolve and deposit on larger particles in order to reach a more thermodynamically stable state. In medium THF the grown nanoparticles of CdS are agglomerated. In EDA at lower growth times CdS nanoparticles are agglomerated. But as the growth time increases CdS nanoparticles is separated out as shown in figure-2c .SAED pattern for CdS nanoparticles grown in THF medium indicates that with increase of growth time single crystality is reduced. But SAED pattern of CdS grown in EDA indicates that single crystality is enhanced with growth time. EDX analysis shows the atomic % of the constituents Cd and S in CdS. At smaller growth time there is excess of Cadmium. As the growth time increases Cd and S are found to be in equal proportions. The result of EDX is same in medium THF and EDA.

UV-VIS absorption spectra were recorded using a SHIMADZU UV-VIS Spectrophotometer with a 1cm quartz cell at room temperature. Colloidal solution in ethanol was prepared ultrasonically for the UV-VIS measurement. Optical absorption for each sample was taken in the wavelength range 200-900 nm. From the Absorption spectra optical absorption coefficient is determined at each wavelength.
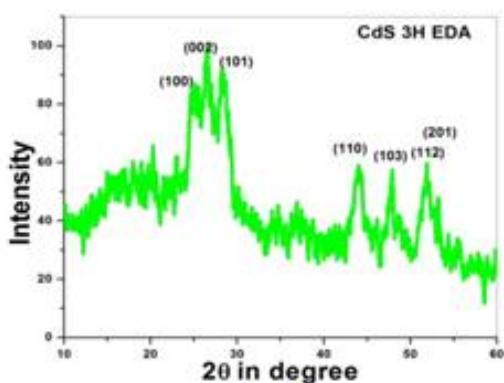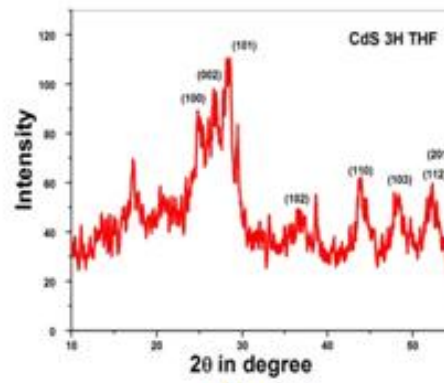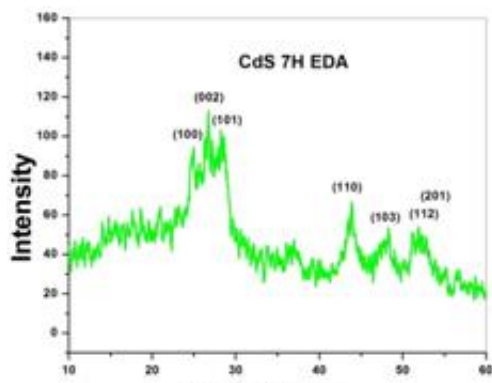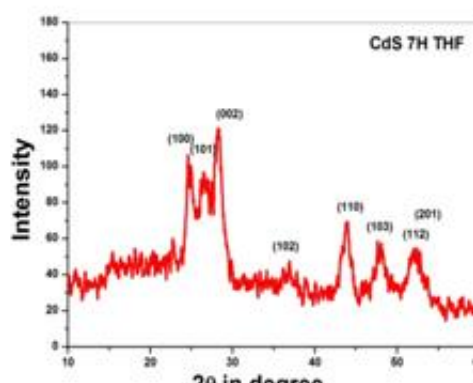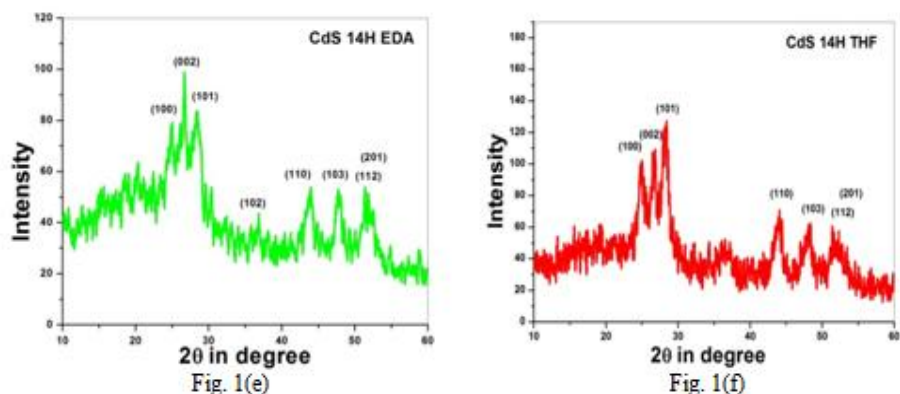

Fig. 1(a)

Fig. 1(b)

Fig. 1(c)

Fig. 1(d)

Fig. 1(e)

Fig. 1(f)

Fig. 1 (a,b,c,d,e,f) XRD pattern of CdS nanoparticles with different synthesis times 3, 7and 14 hours in medium EDA and THF
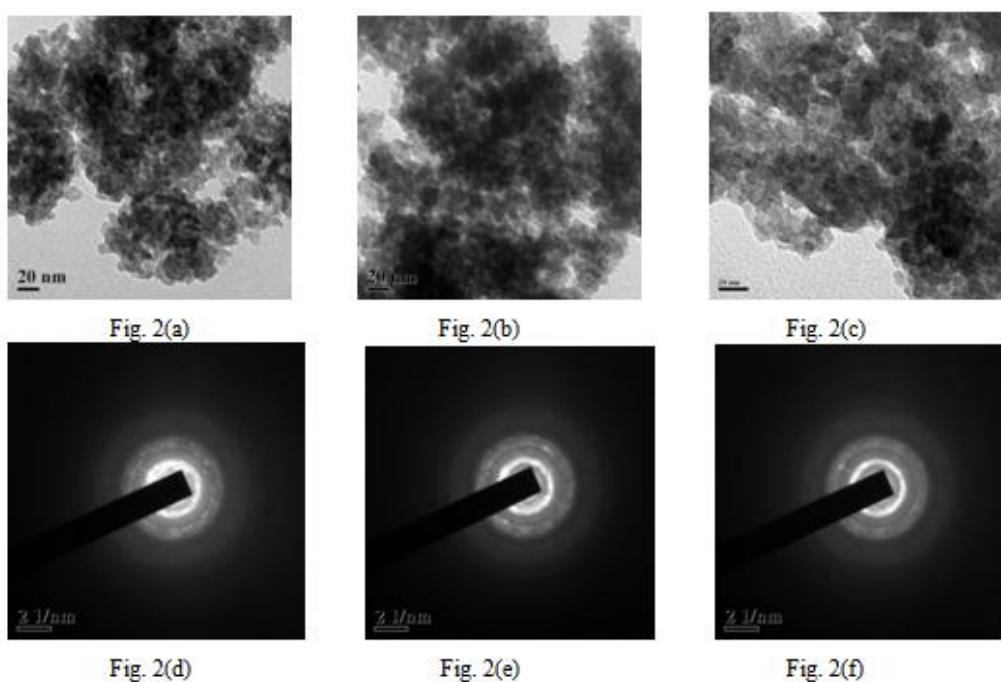

Fig. 2(a)

Fig. 2(b)

Fig. 2(c)

Fig. 2(d)

Fig. 2(e)

Fig. 2(f)

Fig. 2 (a,b,c,d,e,f) TEM and TED pattern of CdS nanoparticles in medium THF

Fig. 3(a)

Fig. 3(b)

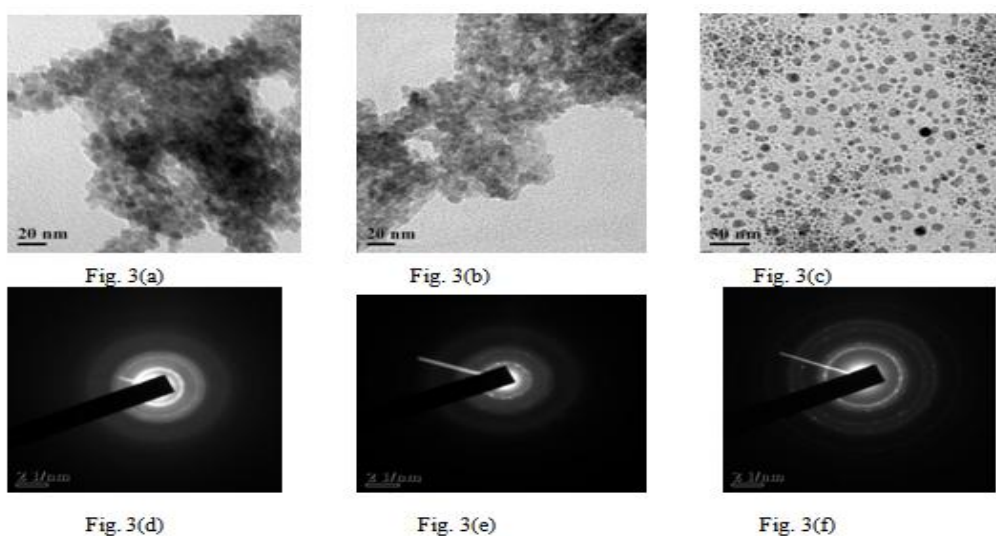

Fig. 3(c)

Fig. 3(d)

Fig. 3(e)

Fig. 3(f)

Fig. 3 (a,b,c,d,e,f) TEM and TED pattern of CdS nanoparticles in medium EDA
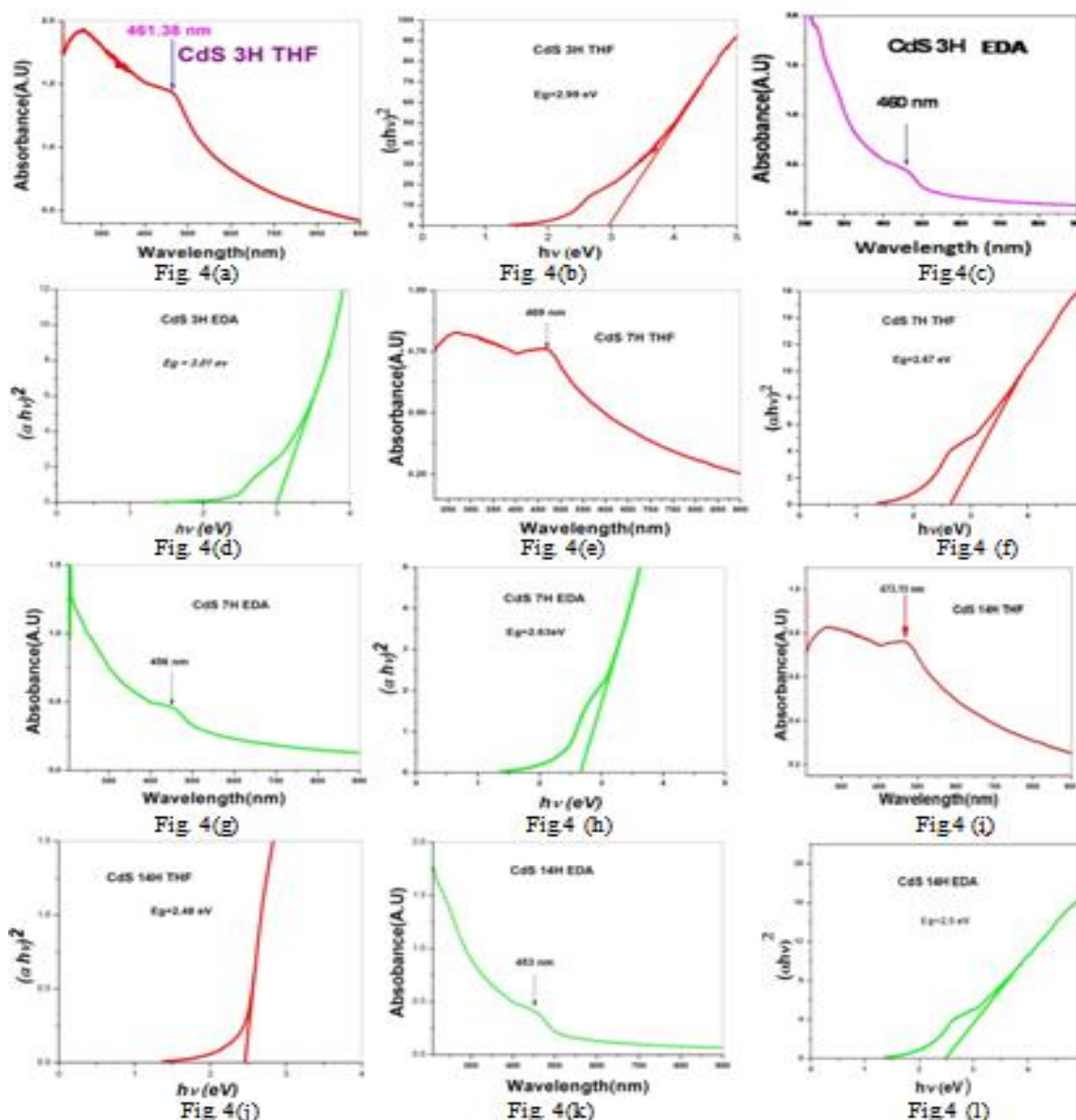
Fig.4 : (a-l) Absorbance and band gap determination plot for different synthesis time 3h,7h and 14h respectively in medium THF and EDA.

Fig [4(a,b),4(c,d),4(e,f),4(g,h),4(i,j),4(k,l)] show absorbance and band gap analysis for different synthesis time 3h,7h and 14h respectively in medium THF and EDA.

The band gap is determined using $(\alpha h\nu)^2$ vs hν plot. Extrapolation of the line to hν axis gives the band gap. Band gap is more compared to the bulk value.

$$(\alpha h\nu)^2 = \text{constant } (h\nu - E_g)$$

The above relation is applied for the band gap which is of direct nature.

The band gaps corresponding to the absorption edges for all four CdS samples are listed in table 1. The band gap of bulk hexagonal W-type CdS is about 2.42 eV. . From the plot of $(\alpha h\nu)^2$ vs hν graph, we can calculate the value of band gap for the three different growth time 3, 7, 14 hours respectively of the samples. Band gap energy decreases as we increase the synthesis time of formation of CdS nanoparticle. The blue-shift in the band gap in nanoparticles due to quantum confinement has the quantitative form. The size of the nanocrystals is greater than the Bhor radius of CdS which is about 3nm.Therefore the confinement potential is much less compared to the coulomb potential between the e-h system. The energy expression can be written as

$$E_n = E_{bulk} - E_{ex} + \frac{h^2\pi^2}{2MR^2}n^2$$

Where R is the center of mass and M is the reduced mass of the e-h pair. E $_{bulk}$ is the band gap of the bulk material, E_{ex} is the excitonic binding energy, n being the quantum number of different energy levels.

Table 1: Comparison Table

Medium	Growth time (Hour)	Crystal Size (nm)	Band gap (eV)	Cd/S in % from EDX
THF	3	7.5	2.9	55.36/44.64
	7	9.0	2.6	50.50/49.5
	14	11.25	2.49	49.22/50.78
EDA	3	8	3	55.36/44.64
	7	13	2.7	59.87/49.13
	14	20	2.5	38.78/61.22

Fig. 5(a)

Fig. 5(b)
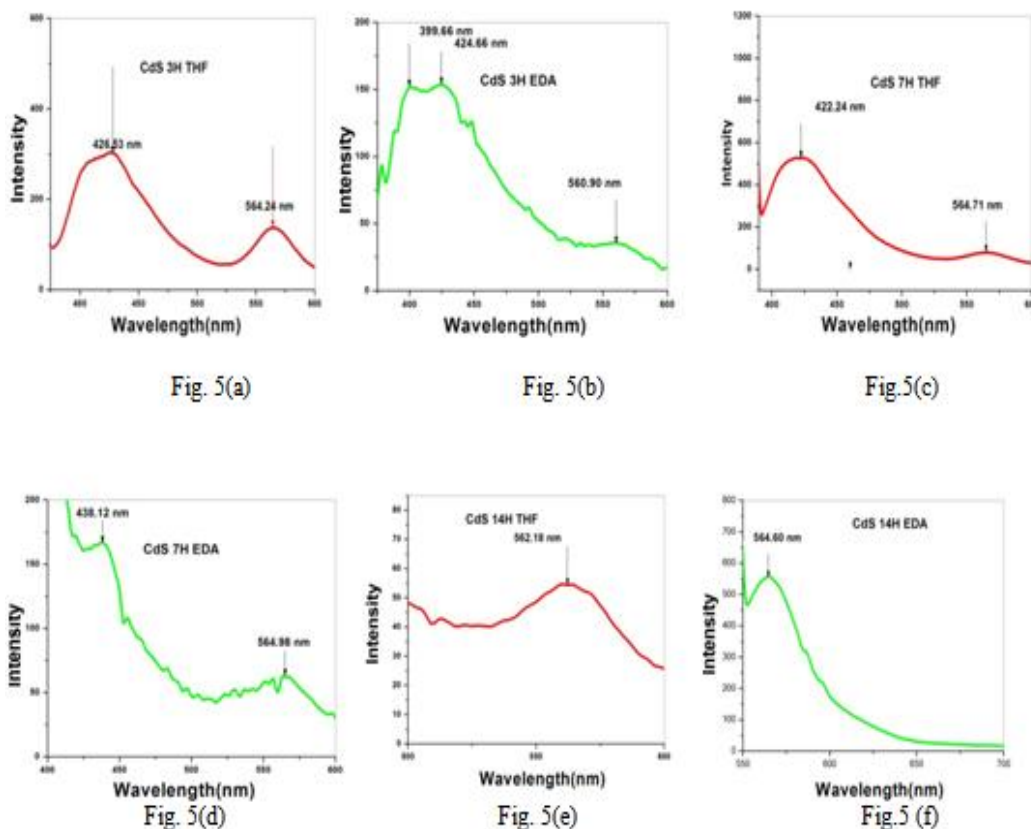
Fig.5(c)

Fig. 5(d)

Fig. 5(e)

Fig.5 (f)

Fig.5 : Photoluminescence spectra of CdS nanoparticles.

PL peak at lower wavelength corresponds to band edge luminescence and it shifts towards higher wavelength with increase of synthesis time as shown in the Fig.5. In both medium band edge luminescence intensiy decreases with increase of growth time. PL peak at higher wavelength centered between 560-660 is commonly attributed to the recombination of charge carriers within surface states (20). In both medium Pl peak intensity at longer wavelength increases with increase of growth time.

IV. Conclusion

CdS nanoparticles are grown by chemical means in different medium like THF and EDA. The growth time is also varied. In both medium the formation of nanoparticles are confirmed. It is observed that in THF the naoparticles are agglomerated but stoichometry is well maintained for different growth time samples. In medium EDA the nanoparticles are all seperated with increase of growth time. This process is cost effective to grow good quality of nanoparticles .These nanoparticles can be applied to fabricate devices like Hetrojunction solar cell as well as in Dye Sensitized Solar cell..Thus the work is important since the process is simple and cost effective to fabricate such important devices.

Acknowledgements

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