

Synthesis, optical and structural characterization of CdS nanoparticles

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Abstract

Cadmium sulfide nanoparticles were grown using wet chemical method by dissolving the reactants of cadmium acetate and sodium sulfide in the presence of thioglycerol (TG) as capping agent in ethanol solvent. Different nanoparticle sizes and size distribution were obtained through varying the molarities of thioglycerol. At higher TG concentration, synthesis provides a nearly monodisperse nanoparticles. Also this method reveals high stability of nanoparticles in ethanol solvent. Samples properties were investigated using UV-VIS absorption, photoluminescence spectroscopy and X-ray diffraction (XRD) methods.

Keywords: Cadmium sulfide, Nanoparticles, Chemical synthesis, Photoluminescence (PL), Aging effect, Hexagonal structure

1. INTRODUCTION

The synthesis of semiconductor nanoparticles (NPs) in colloidal solutions has attracted many researchers, due to their unique optoelectronic properties and quantum confinement effects from the bulk materials [1-3]. The potential applications of semiconductors in optical switching, single charge memories, single electron transistors, etc are most investigated. The physicochemical properties of semiconductors are greatly affected by the consequences of low dimensionality when the radius of the particle is comparable to the Bohr radius of the exciton versus the bulk material. Modification in the electronic levels occurred very strongly due to the limited number of atoms in the particles. Such materials in these regime exhibit novel physical and chemical properties due to the large surface to volume ratio as well as size quantization effect in semiconductor nanoparticles [4-7]. There are several methods of forming and controlling the size of NPs in liquid phase. Capping agents and surfactants prevent uncontrolled growth and agglomeration of the NPs [8-15].

The aim of this work is preparing the colloidal nanoparticles of II-VI semiconductors such as CdS to obtain particles in different sizes through changing synthesis parameters and to reveal optical and electronic size dependent properties of CdS nanoparticles.

2. EXPERIMENTAL DETAILS

CdS nanoparticles were prepared through dissolving of cadmium acetate and sodium sulfide in the presence of an organic solution of thioglycerol which stabilizes the particle surfaces formed during the reaction. Argon gas has been used for deoxygenating reaction vessel. The reaction time was about 48 minutes. Thioglycerol solution in ethanol was used with concentrations of 0.01 M and 0.02 M at a fixed precursor concentration of 0.02 M and also by varying TG concentration from 0.001M to 0.007 M at a fixed precursor concentration of 0.005 M at pH= 5. The precipitate was air-dried to get powder of CdS nanoparticles. The prepared solution through dispersing the powders in double distilled water has been used to study

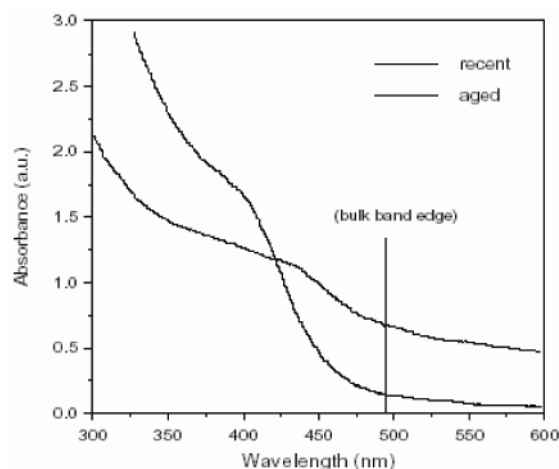


Figure 1: UV-vis absorption spectra of recent and aged colloidal CdS particles were prepared with 2:1: Cd $(\text{NO}_3)_2 \cdot (\text{NH}_4)_2\text{S}$ [13].

the optical absorption of nanoparticles. Optical absorption studies were carried out with UV-VIS spectrophotometer (Shimadzu UV-3500). The Photoluminescence spectra were obtained using the 254 nm wavelengths to excite CdS nanoparticles in Shimadzu spectro-fluorophotometer RF-5000. To obtain the X-ray diffraction pattern of the powder sample, the Cu-K α (1.54 \AA) radiation was used from Philips APD Expert diffractometer.

The process of nanoparticles syntheses in liquid phase is initiated by nucleation of NPs in the solution and is continued by growing the produced monomers. The mechanism of mass transferring from smaller crystals to bigger one is known as "Ostwald" ripening. The higher surface energy of small crystalline makes it less stable than larger crystalline with respect to dissolution in the solvent. The net result of this stability gradient within dispersion is a slow diffusion of material from small particles to the surface of larger particles [13-14]. The "Ostwald" ripening process decreases through time and permits a longer lifetime for the bigger crystals. Pal et al [13] produced NPs without surfactant that are shown in Figure 1, where it can be seen a clear shift of band edge in the colloidal particles from the bulk CdS at 490 nm due to quantum confinement effects. The growth of particles continues versus time, and the band edge

shifted towards the lower energy.

A similar shift of band-edge has observed with the increase of CdS crystalline size [1-15]. The peak of "exciton" transition appeared in all the optical absorption spectra. The excitonic peak position shifted through the particle size increases, which depends on the concentration of the ions in the mixture for a finite time.

3. RESULTS AND DISCUSSION

3.1. TG effects on size and distribution of particles

As shown in Figure 2, increasing the TG concentration from 0.001 M to 0.007 M, reduces the size of nanoparticles. It becomes apparently the shift of excitonic peak to smaller wavelength (blue shift) in absorption spectra. Furthermore, the sharper peak leads us to the nanoparticles of narrower size distribution for higher TG concentrations. This phenomenon relate to more confinement for excitons which result to increase the oscillator strength.

For higher TG concentration from 0.01M to 0.02M the size and size distribution of nanoparticles reduce as shows in Figure 3. The low absorbance intensity of sample with 0.01M TG is due to immediate precipitation and supernatant of CdS nanoparticles in quartz cell.

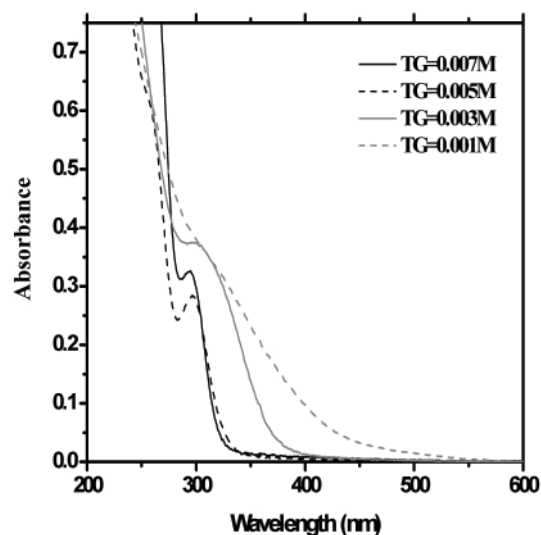


Figure 2: UV-vis absorption spectra for samples were prepared in different TG concentration (0.001M, 0.003M, 0.005M, 0.007M) in ethanol solvent.

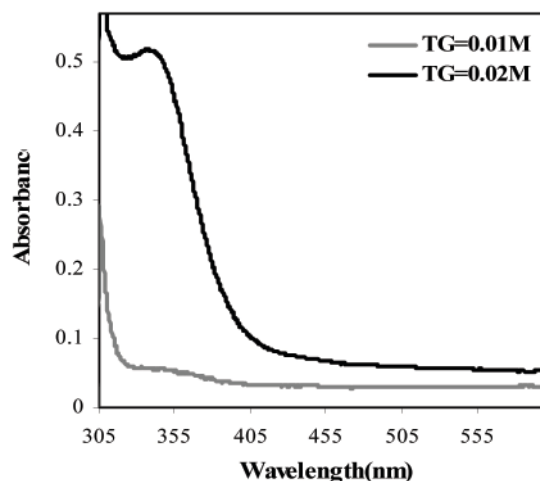


Figure 3: UV-vis absorption spectra for samples were prepared in TG concentration of 0.01M and 0.02M in ethanol solvent.

3.2. Optical size measurements of CdS nanoparticles

Hua Tong et al [8] produced CdS nanoparticles based on low-temperature thermolysis of one single-source organometallic precursor in noncoordinating (ethanol) or coordinating (oleic acid) solvent. The absorption spectrum for CdS nanocrystals was prepared in ethanol at 60 °C for 10 hours was shown in Figure 4. The relation between $(\alpha h\nu)^2$ and $h\nu$ satisfies the equation (1) for $n=0.5$. It was known that $n = 0.5$ is for direct transitions and 2 for

an indirect one [8, 14], therefore CdS nanoparticle is a direct band gap semiconductor. The intercepts of photon energy axis show the band gap energies of the samples as were shown in inset of Figure 4 and in Figure 6.

$$\alpha h\nu = \text{const}(h\nu - E_g)^n \quad (1)$$

The trend of band gap changes can be translated into NP size change through effective mass

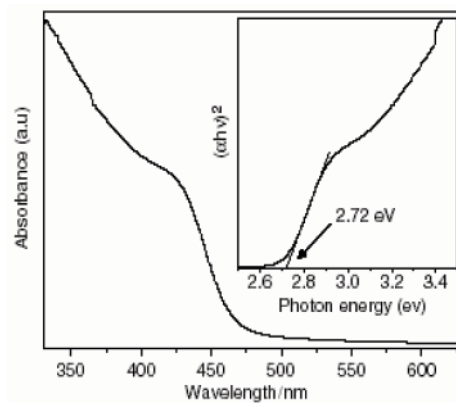


Figure 4: UV–vis absorption spectrum for CdS nanocrystals were prepared in ethanol at 60 °C for 10 h. The inset shows the relation between $(\alpha hv)^2$ and hv [8].

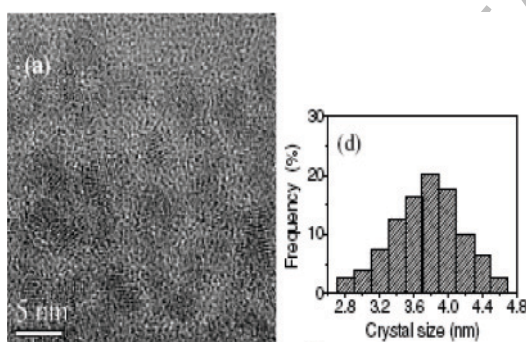


Figure 5: a) HRTEM results of CdS nanocrystals were prepared in ethanol at 60 °C for 10 h , d) histogram of crystal size distribution [8].

approximation (EMA) method (equation (2)) [12]. The estimated size from this model can be regarded as the ‘optical size’ and took it as a measure of the NP size as d.

$$d = \left[2\pi^2 \hbar^2 \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \frac{1}{\Delta E_g} \right]^{\frac{1}{2}} \quad (2)$$

Here ΔE_g is the difference between nano and bulk band gap edges. It has been demonstrated that EMA overestimates the size of NPs for the particles smaller than 5 nm [12]. However, optical size remains a good and easy indication of the NP growth process. As shown in Figure 5 HRTEM and TEM sizes are considered as the true sizes for nanoparticles [8]. From the EMA method the

nanoparticle sizes were obtained about 5.3 nm while from HRTEM method the mean size is 3.8 nm. This high overestimation leads us to use the stronger theoretical methods like tight-binding approximation (TBM).

Lippens et al. [16] did the calculations for CdS and ZnS particles using tight binding parameters and found better agreement with the experimental data for clusters larger than 20 Å (Figure 6). The nanoparticles size of typical sample by TBM method reach to 3.5 nm that shows good agreement with experiment data from HRTEM. Figure 7 shows the change of NPs band gap edges with TG concentrations. The particle sizes of different samples were calculated using EMA and TBM approximation that are shown in table 1.

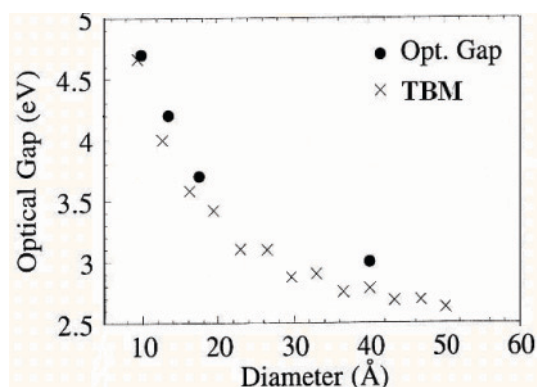


Figure 6: A comparison of TBM method for the size confinement effect in cubic CdS nanoparticles with experimental data by TEM (shown by black circles) [16].

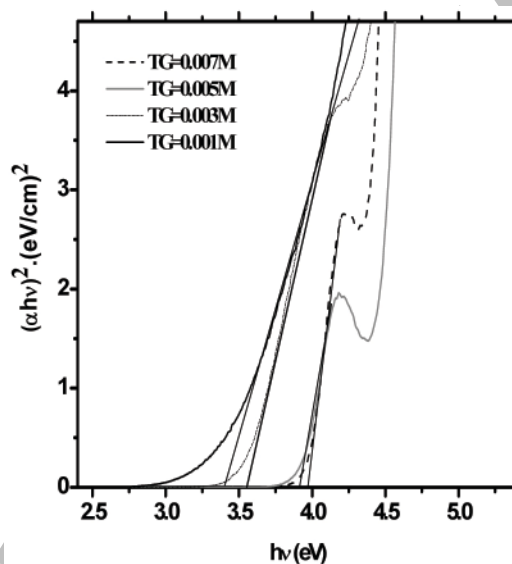


Figure 7: The relation between $(\alpha hv)^2$ and $h\nu$ for CdS nanocrystals was prepared in different TG concentration at pH=5.

Table 1: Optical sizes for prepared samples in different TG concentrations.

TG Conc. (M)	pH	Optical size (nm) EMA	Np size (nm) TBM
0.007	5	2.4	1.2
0.005	5	2.4	1.2
0.003	5	2.8	1.7
0.001	5	3.0	2
0.02	5	2.8	1.7
0.01	5	3.3	2.2

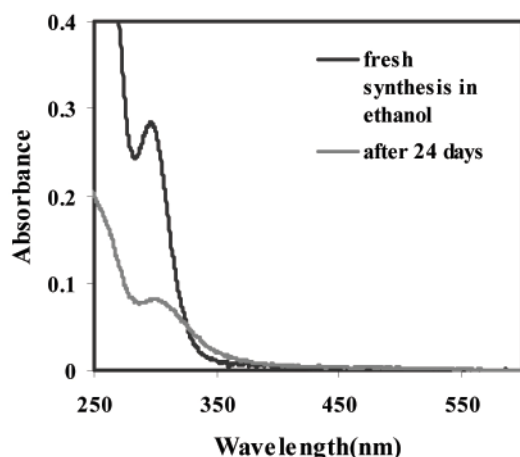


Figure 8: UV-vis absorption spectra of fresh and aged synthesis (after 24 days) for sample prepared in the same TG concentration of 0.005M at pH=5.

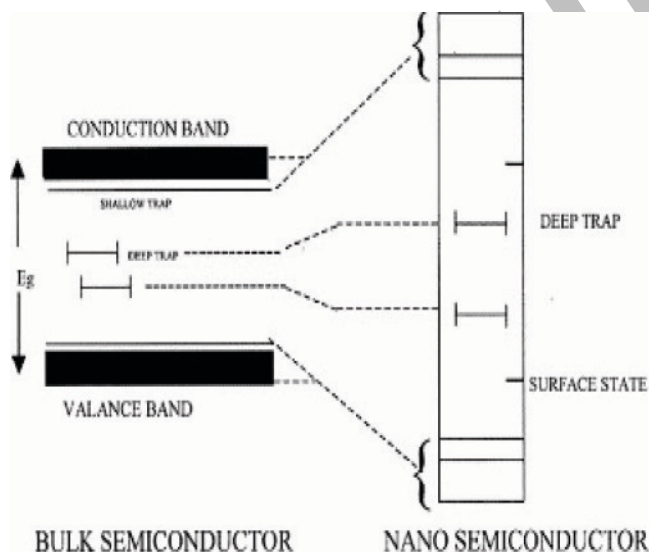


Figure 9: The energy levels diagram of a bulk and a nanocrystalline semiconductor [15].

3.3. Stability of CdS nanoparticles

The absorption spectra of fresh and aged synthesized sample (after 24 days) of the same TG concentration of 0.005 M at pH = 5 were studied. Figure 8 shows that the CdS nanoparticles have good stability in ethanol solvent. At higher TG concentration, there is no change in the absorption maxima but there is a little change in the size distribution.

Figure 8 UV-vis absorption spectra of fresh and aged synthesis (after 24 days) for sample prepared in the same TG concentration of 0.005M at pH=5.

3.4. Photoluminescence spectra of CdS nanoparticles

The energy levels diagram of a bulk and a nanocrystalline semiconductor are shown in Figure 9. Surface states arising due to increased surface-to-volume ratio in nanocrystals are also shown in Figure 9.

The results of absorption and PL spectra for a series of CdS nanocrystal samples were prepared by Hua Tong et al [8] in oleic acid at 160 °C for different reaction time are shown in Figure 10.

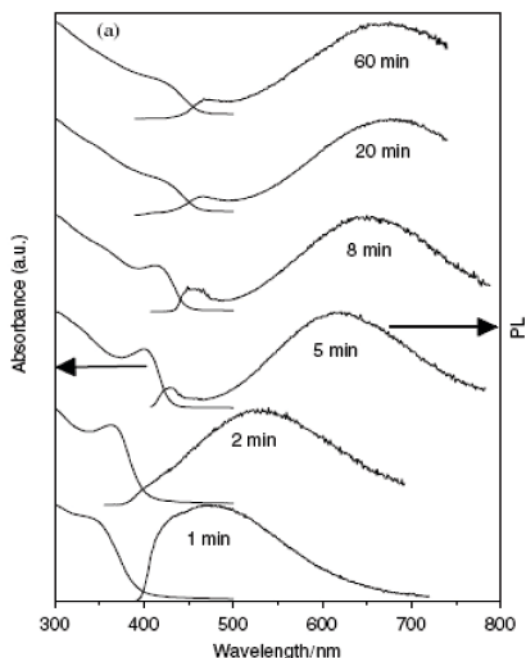


Figure 10: UV–VIS absorption and PL spectra for a series of CdS nanocrystal samples were prepared in oleic acid at 160 °C for different reaction times [8].

The intense PL emissions have been shown in Figure 1. However, the broad deep-trap emission overwhelms the near-band emission due to the high density of the deep-trap state and the high ratio of surface atoms in CdS nanocrystals. The near-band emission is red-shifted with increasing reaction time, indicate that the sizes of CdS nanocrystals increase through the reaction time. Furthermore, the broadening of the near-band emission peak with increasing reaction time implies widening of the crystal size distribution. The deep-trap emission is also red-shifted with increasing reaction time [8]. As it was shown the smaller particle sizes were obtained in higher TG concentration because of more TG molecules cap the surface of the particle. In the other word, decreasing TG concentration results to more surface trap and this effect apparently is shown in the photoluminescence's spectra of Figure11. The broadening of band emission reveals the broad size distribution of nanoparticles [9-10]. Figure 11 shows that for TG concentration of 0.005 M the narrow band emission peak wavelength occurred at 361.6 nm whereas for TG concentration of 0.003 M it occurred at 368.0 nm.

In addition, it contributed with high intensity and broad surface trap peak at 452.8 nm which has a

shoulder at 398.4nm. The broad band emission peak wavelength for TG concentration of 0.001M occurred at 363.1 nm and the broad surface trap peak wavelength occurred at 468.8 nm which shows that TG molecules were not sufficient for capping CdS nanoparticles in the reaction vessel. It was found that decreasing TG concentration from 0.005 M to 0.003 M leads to increase the band emission wavelength which reveals that the nanoparticles sizes increase. From Figure 11 for TG concentration of 0.001M it is clear that the band emission wavelength decreases but its broadness shows the broad size distribution of nanoparticles that some of them are smaller and some of them are larger than the nanoparticles were produced in TG concentration of 0.003 M.

3.5. Crystal structure of CdS nanoparticles

Our studies show that the CdS nanoparticles could possess either the hexagonal or the cubic structures and in many cases the phases cannot be resolved due to the similarity of the cubic and hexagonal peaks and the broad peaks that appear for CdS nanocrystalline. The hexagonal phase of CdS has two main peaks at 28.3° and 48.1° (referring to (101) and (103) planes) and cubic phase has three main peaks at 26.5°, 43.9° and 51.9° (referring to (111), (220) and (311)

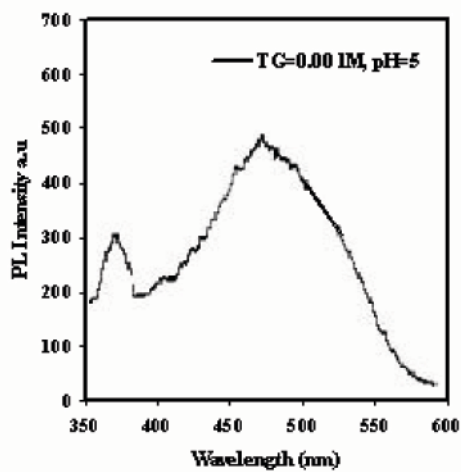
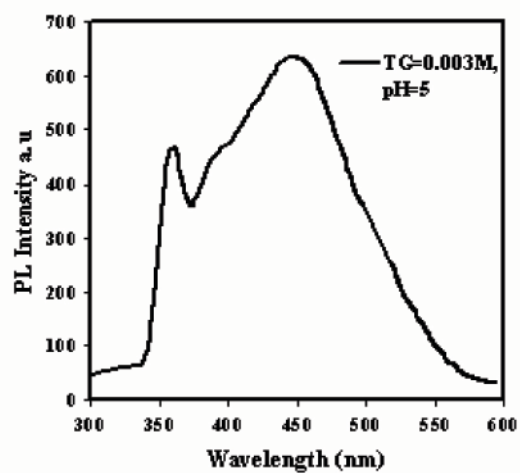
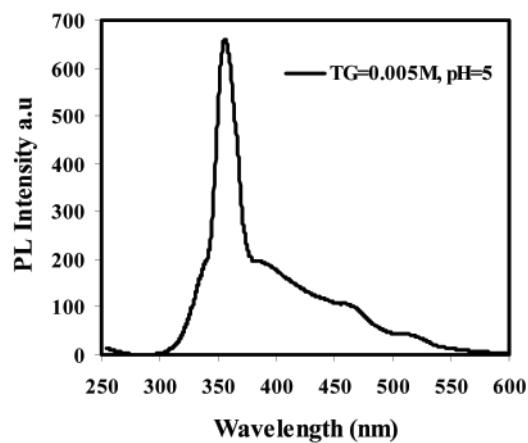


Figure 11: Photoluminescence's Spectra for samples were prepared in TG concentration of 0.005 M, 0.003 M and 0.001 M in pH=5.

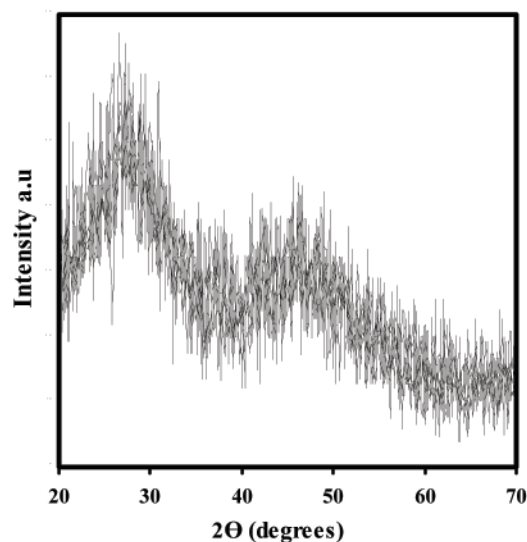


Figure 12: Powder X rays diffraction pattern for CdS nanocrystals were prepared in the TG concentration of 0.003 M at pH=5

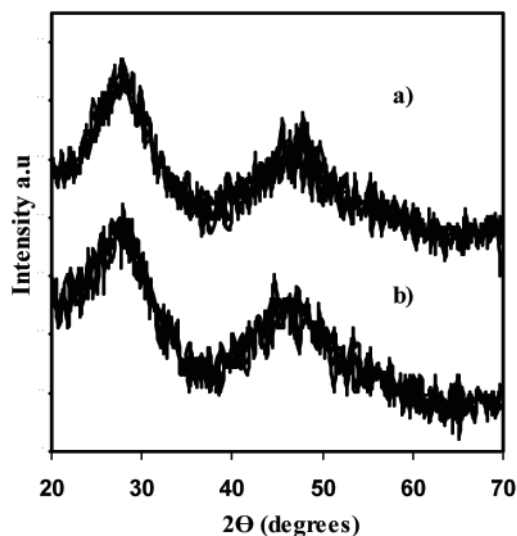


Figure 13: Powder X rays diffraction pattern for CdS nanocrystals were prepared in different TG concentration a) 0.02M , b) 0.01M at pH=5.

planes) [8]. Figure 12 shows the x-ray diffraction spectrum of the sample which is prepared in TG concentration of 0.003 M at pH of 5. Two broadened peaks that observed in the spectrum are belonging to hexagonal structure of CdS nanocrystals. The prepared sample at the room temperature and low reactant's concentration shows that the peaks were not so clear therefore by increasing the reactant's concentration (i.e. for TG concentrations of 0.02M and 0.01M at a fixed precursor concentration

of 0.02M) the peaks become more clear to show the hexagonal phase as preferable phase for CdS nanoparticles in ethanol synthesis (Figure 13). The sizes of CdS nanoparticles were calculated using the x-ray diffraction spectrum and Debye Scherer formula [15] for the samples which are prepared in different TG concentrations. In this method the size of the particles are obtained as 1.57nm, 1.65nm and 2.17nm for the TG concentrations of 0.003 M, 0.02 M and 0.01 M respectively.

4. CONCLUSION

The synthesized nanocrystalline samples were prepared through precipitation of cadmium sulfide from ethanol solution of cadmium and sulfur salts. The clusters were capped by TG molecules. Our investigations show that increasing the concentration of TG, cause a blue shift in the UV-VIS absorption spectra of CdS nanoparticles. This is concurrent with the blue shift of the band emission peak in PL spectra. Furthermore, by increasing TG concentration the broad peak that relates to surface trap in PL spectra was disappeared. Good stability of CdS nanoparticles was observed in TG concentration of 0.005M. The x-ray diffraction results indicate that the preferable phase for typical samples of CdS nanoparticles is hexagonal phase.

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