

A STUDY OF CRYSTAL GROWTH, CRYSTALLITE STRUCTURE, AND STABILITY OF CdS: Mn NANOCRYSTALS UNDER VARIOUS SYNTHESIS AND ANNEALING CONDITIONS

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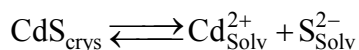
In this research, we synthesized CdS: Mn nanocrystals and studied crystal growth at different stages of the synthesis and aging processes. The effect of doping, synthesis temperature and annealing on the crystallite structure has been investigated. Annealing of nanocrystals improved the crystallites. The X-RD pattern indicated that the crystalline phase of the nanocrystals shifts from hexagonal to cubic when the temperature is raised. The crystalline phase of the samples did not change by varying the doping concentration. The particle size increases when the synthesis time is enhanced. There is a regular growth of particle size as a function of time at high Thioglycerol concentration. The aging process shows stability at low precursor concentrations and instability at high concentrations.

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1. Introduction

The synthesis and characterization of doped semiconductor nanocrystals (NCs) have attracted considerable attention in recent years. Dopants within nanocrystals have been used as probes of microscopic structural parameters. The synthetic challenges of doping semiconductor nanocrystals have also provide grounds for investigation of the basic chemistries of homogeneous nucleation and crystals growth in the presence of impurities. Our discussion focused on Mn^{+2} as dopant and CdS semiconductors as host. The optical and electrical properties of NCs are different from those of the corresponding bulk material because in the nano-size regime solids are gradually losing their bulk behavior due to quantum confinement. NCs exhibit interesting physical properties like blue shift of the absorption band gap with decrease in crystallite size, high oscillator strength and optical nonlinear effect. Among the different synthesis methods, the aqueous solution method has been widely used [1, 2] because of their synthesis quantum dots (QDs) have strong stability. Synthesis methods might offer possibly the ideal conditions for nucleation and crystal growth. It would help to produce ideal structure crystals after Ostwald ripening process [3-6]. Controlling the size of the NCs depends on the ability to stop the crystal growth above equilibrium relation [1]



This can be achieved by selecting an appropriate reactant, capping agent and solvent. In this research, we synthesized CdS: Mn NCs by the aqueous solution method and studied crystal growth at different stages of the synthesis and aging processes. The effect of doping, synthesis temperature and annealing process on crystallite structure was investigated.

2. Experimental details

CdS: Mn NCs were synthesized by the aqueous solution method under different conditions as follows:

Samples in Fig. 1-4: were synthesized with 0.1M of cadmium sulfide, 0.1M of sodium sulfide and 0.2M of Thioglycerol (TG) as capping agent were added to a mixture of 120cc ethanol in addition to 40cc distilled water at room temperature. The synthesis time was about 2 hour. The pH was adjusted to about 2, 4 and 6, respectively, corresponding to figures 1, 3, 4, by adding an appropriate amount of NaOH.

Samples in Fig. 5-7: were synthesized with 0.1M of CdCl_2 and Na_2S with 3 atom% Mn^{2+} dopant, with pH=2 at 54°C by varying the TG concentration from 0.1 M-0.3 M.

Samples in Figs. 8 and 9 : Fresh and aged (after 5 months) samples were synthesized with 0.02M of CdCl_2 and Na_2S and using TG as a capping agent with 0.1M and 0.2M at pH=2, respectively prepared at 50°C and RT.

Sample in figure 10: was synthesized with 0.1M of CdCl_2 and Na_2S and TG=0.2M with 3atom% Mn^{2+} dopant, at pH=6 and prepared at room temperature.

Sample in Fig. 11: was synthesized with 0.1M of CdCl_2 and Na_2S , 0.1M of TG with 3atom% Mn^{2+} dopant, prepared at pH=2 and 54°C .

The optical absorption spectra of CdS: Mn nanocrystallites dispersed in ethanol were measured using a UV-VIS spectrophotometer (Cary 100). The luminescence spectra were obtained using about 370 nm wavelength to excite the CdS: Mn nanocrystals in LF-5 Perkin Elmer and RF-5000 Shimadzu. The X-ray diffraction pattern was measured with an X-ray diffractometer (Philips) using Co radiation of wavelength $\lambda = 1.78\text{\AA}$ in the scan range $2\theta=20-80^\circ$

3 Results and discussion

As shown in Fig. 1, there exists a small red shift and broadening in the absorption spectra of doped CdS with increasing Mn^{2+} concentration. X-ray diffraction measurement (Fig. 2) on the same samples in Fig. 1 shows the crystalline phase is hexagonal at room temperature (27°C). From Fig.2 it can be observed that the XRD pattern of doped CdS NCs with different concentration of Mn^{2+} ions did not change.

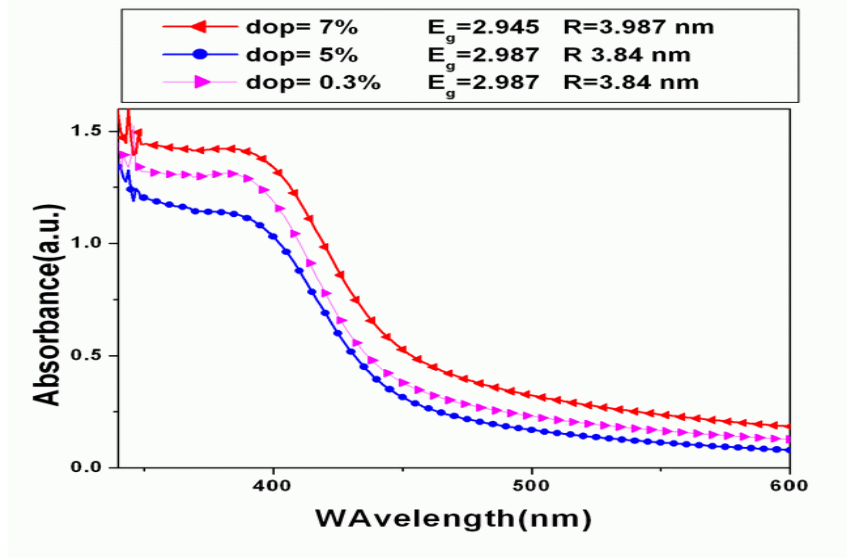


Fig. 1. Absorption spectra of samples by varying doping concentration, for pH $\approx$ 2 and TG=0.2 M.

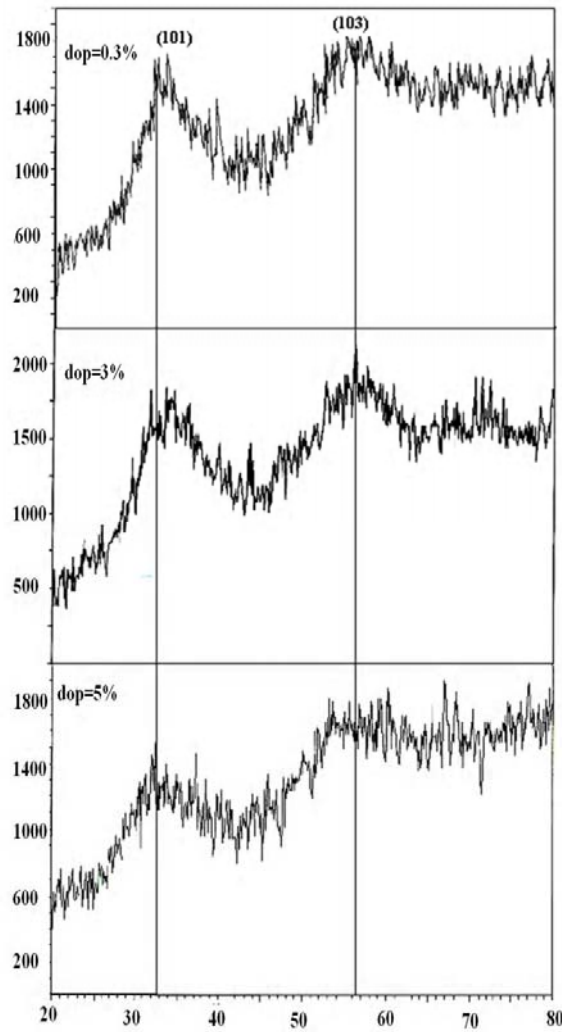


Fig. 2. XRD patterns of samples in Fig. 1

In Figs. 3 and 4 it is indicated that the size of the particles changed non-monotonically as a function of dopant percentage. As shown in Fig.3-a, optical absorption intensity varied with increasing Mn^{2+} doping concentration and position of absorption shift towards higher wavelengths. This small shift suggests that there is direct energy transfer between the semiconductor excited state and the 3d shell levels of Mn^{2+} ions that are coupled by energy transfer processes [7]. Within the size distribution, Mn^{2+} ions are more easily incorporated into "large" particles than small ones, since the lattice deformation due to doping may be more easily adjusted in large particles [8]. Thus, these "large" doped particles mainly contribute to the emission from Mn^{2+} ions.

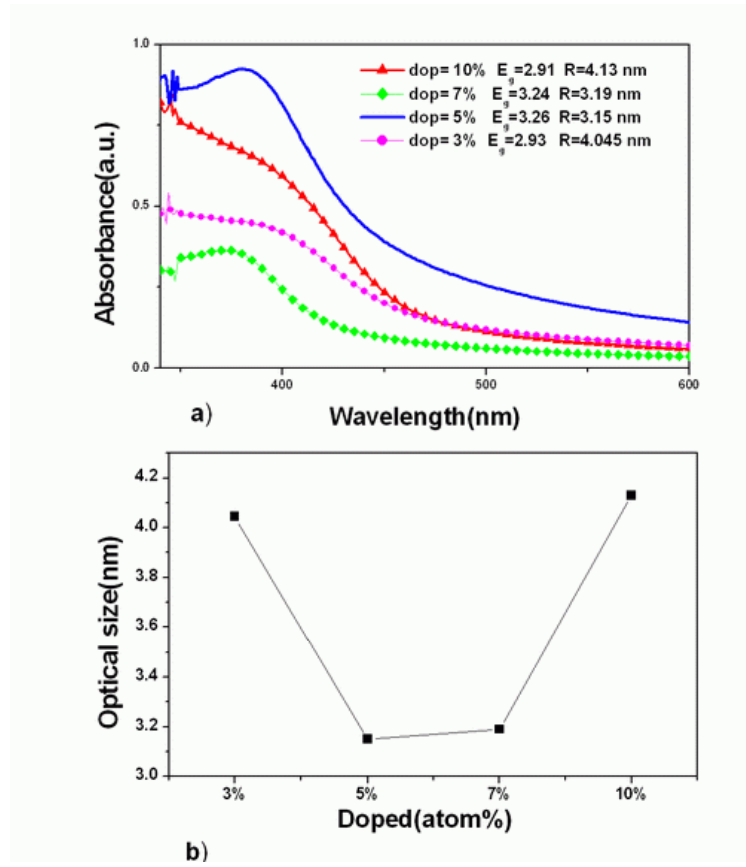


Fig. 3 a) Absorption spectra of samples by varying doping concentration b) optical size of samples in Fig. 3a, for $pH \approx 4$ and $TG = 0.2$ M.

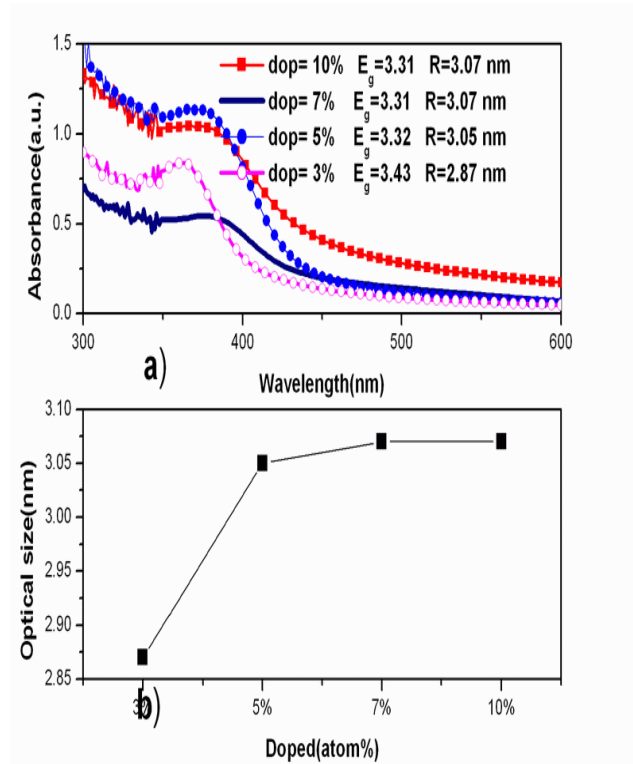


Fig. 4. a) Absorption spectra of samples by varying doping concentration b) optical size of samples in figure 4a, for $pH \approx 6$ and $TG = 0.2$ M.

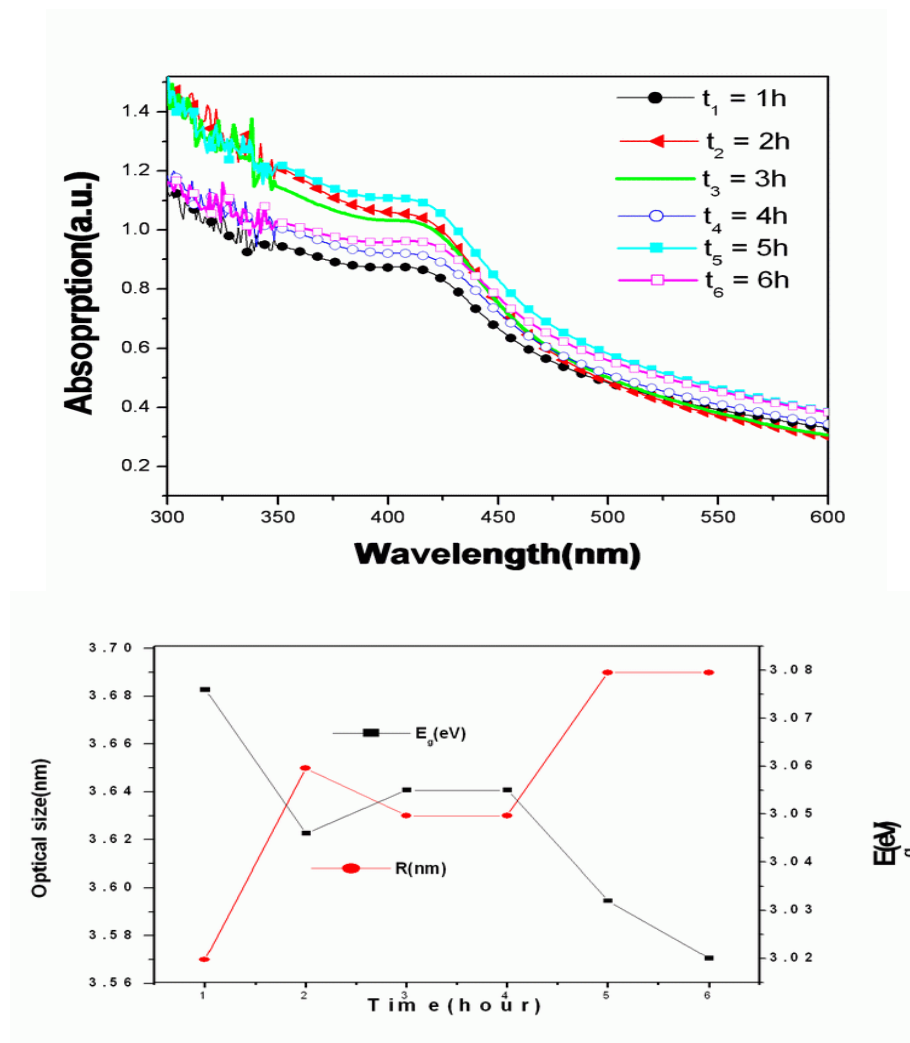


Fig. 5. a) Absorption spectra of samples by varying synthesis time b) Variation of optical size and band gap of sample as a function of time, for $pH \approx 2$ and $TG=0.1$

At high temperature, chemical reaction reduces the defects of NPs, and high-quality NPs can be obtained [9]. Therefore we synthesized nanoparticles at high temperature and investigated their crystallites. Figs 5, 6 and 7 present examples of the absorption spectra of CdS: Mn NPs as a function of synthesis time. These figures show a typical example of clear red shift in comparison with the previous absorption spectra. We found an irregular crystal growth with varying synthesis time at low TG concentration (Fig. 5) and a regular growth of nanoparticles with varying synthesis times at high TG concentration, as shown in figures 6b and 7b.

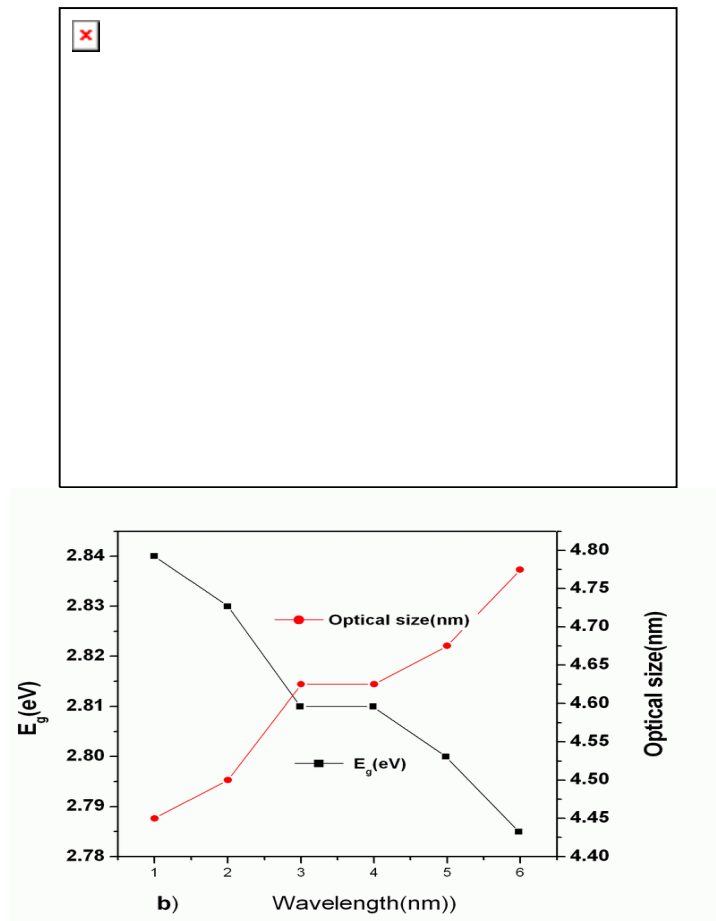


Fig. 6. a) Absorption spectra of samples by varying synthesis time b) optical size and band gap of sample as a function of time, for pH ≈ 2 and TG = 0.2 M.

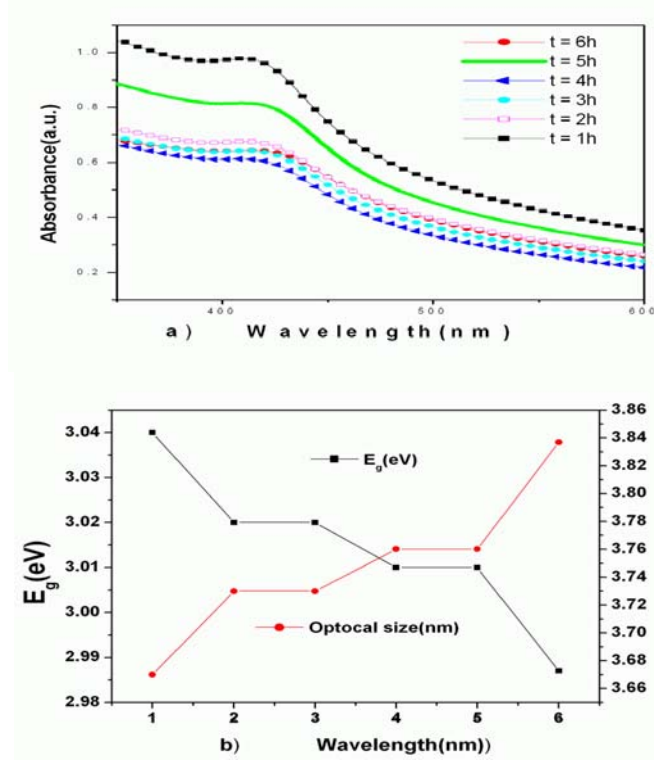


Fig. 7 a) Absorption spectra of samples by varying synthesis time b) optical size and band gap of sample as a function of time, for pH ≈ 2 and TG = 0.3 M.

The absorption spectra of fresh and aged samples are presented in Fig. 8. The aged sample shows a red shift compared to the fresh sample and there exists a good excitonic peak after 5 months. It seems that Ostwald ripening had a good affect [3] on broad size NPs to achieve a narrow size distribution after 5 months.

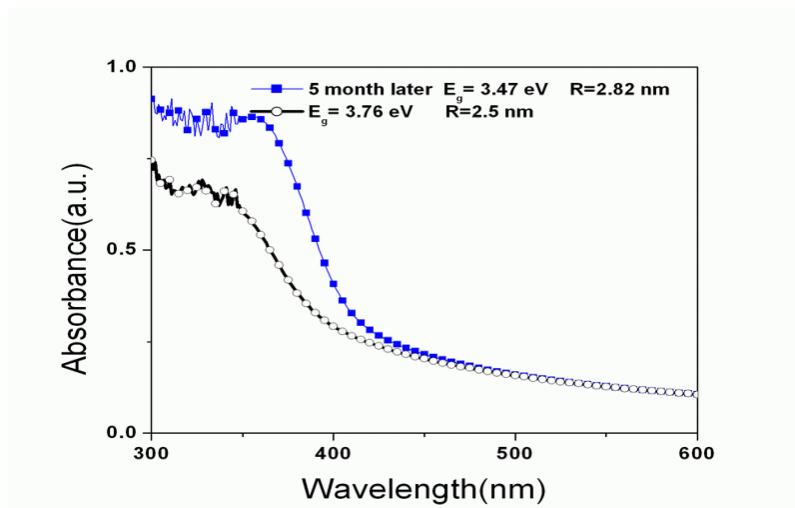


Fig. 8 Absorption spectra of CdS: Mn nanoparticles with low precursor concentration prepared at room temperature 5 months later for $pH \approx 2$ and $TG = 0.2$ M.

However, Fig. 9 shows an unfavorable effect of Ostwald ripening that result in a broad size distribution, in addition to increasing the particle size.

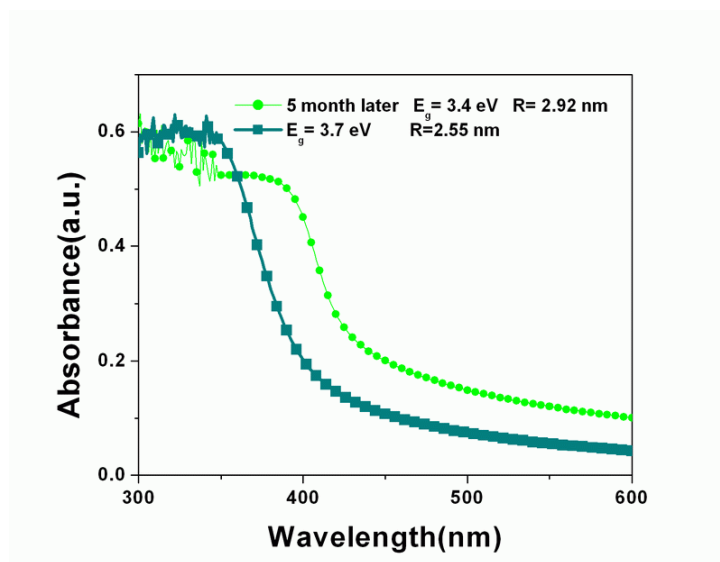


Fig. 9 Absorption spectra of CdS: Mn nanoparticles with low precursor concentration prepared at $50^\circ C$, for $pH \approx 2$ and $TG = 0.1$ M, 5 months later.

The size distribution of NPs changed after 3 months (Fig. 10) in samples with a high precursor concentration, because much interaction existed between NPs. Therefore, it is expected that Ostwald ripening has a non-interesting affect.

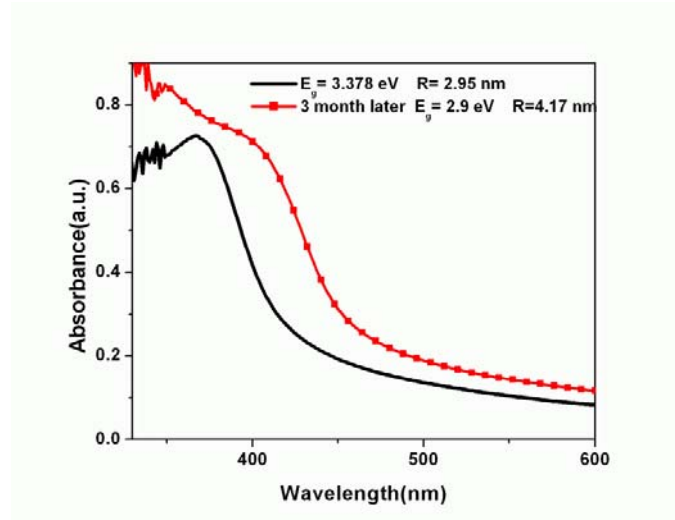


Fig. 10. Absorption spectra of CdS: Mn nanoparticles with high precursor concentration prepared at room temperature, after 3 months for $\text{pH} \approx 6$ and $\text{TG} = 0.2 \text{ M}$.

There is good stability in the absorption spectra after 3 months (Fig. 11) and there is no change in the absorption maxima and in the size distribution. This stability can be the result of suitable precursor solubility at high temperature, sufficient time for crystal growth and suitable TG concentration.

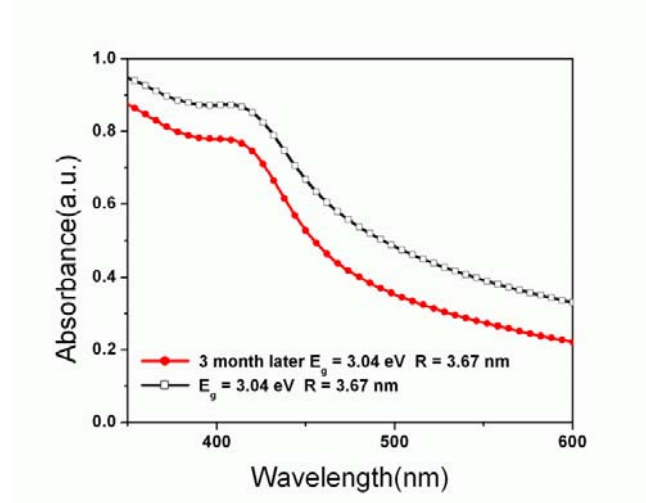


Fig. 11. Absorption spectra of CdS: Mn nanoparticles with high precursor concentration prepared at 54°C , 3 months later, for $\text{pH} \approx 2$ and $\text{TG} = 0.1 \text{ M}$.

The broadening of the diffraction peaks in all XRD patterns indicates the nanostructure nature of the sample. There are two main peaks for the hexagonal phase of CdS at 32.9° and 56.5° (referring to (101) and (103)), and three main peaks for the cubic phase at 30.8° , 51.47° and 61.1° (referring to the (111), (220) and (311) planes) [10]. The XRD pattern in figure 12 shows the hexagonal phase at RT and the cubic phase at high temperature. The absorption spectra and size of these samples are indicated respectively in figure 13 and table 1. We found that the particle size increases with increasing synthesis temperature in both calculation method of effective mass approximation (EMA) [11-12]

$$E_{g(\text{np})} = E_{g(\text{bulk})} + \frac{\hbar^2 \pi^2}{2R^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.8e^2}{\epsilon R} - 0.248 E_{Ry}^* \quad (1)$$

and the Scherrer formula [13, 14]

$$\beta_{hkl} = \frac{0.89\lambda}{L_{hkl} \cos \theta} \quad (2)$$

Where $E_{g(np)}$ is the band gap energy of the CdS nanoparticles, $E_{g(bulk)}$ is the band gap energy of bulk CdS, R is the particle radius, m_e^* and m_h^* are the subsequent electron and hole effective masses and E_{Ry}^* is the Rydberg exciton energy. λ is the wavelength of the x-rays, β_{hkl} the full width at half maximum (FWHM), L_{hkl} the mean crystallite size of the CdS particles and θ is the angle of diffraction.

Table1. Optical size and crystal size of CdS: Mn nanocrystals samples in figure 13

Synthesis temperature	Crystal size (nm)	Optical size (nm)
RT (27°C)	1.64	3.3
54°C	2.43	3.38
76°C	2.81	3.5

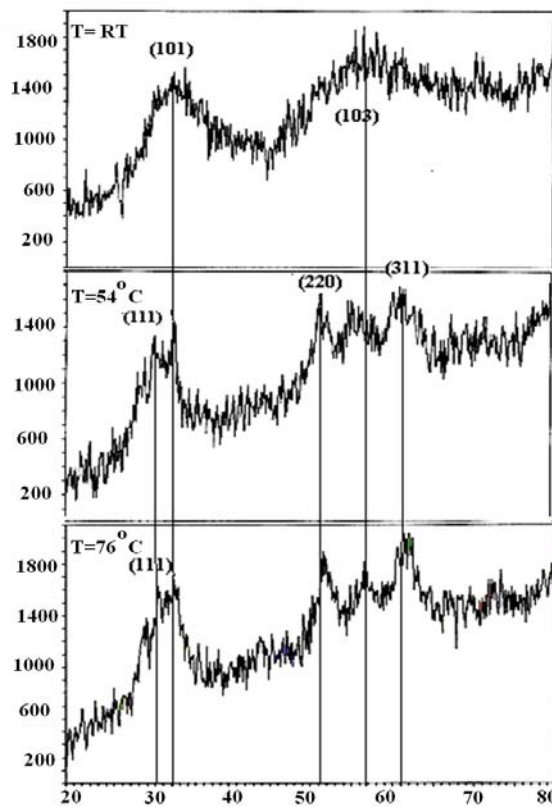


Fig. 12. X-ray diffraction patterns for CdS: Mn nanocrystals prepared by varying synthesis temperature. Other synthesis parameters are the same as sample in Fig. 11.

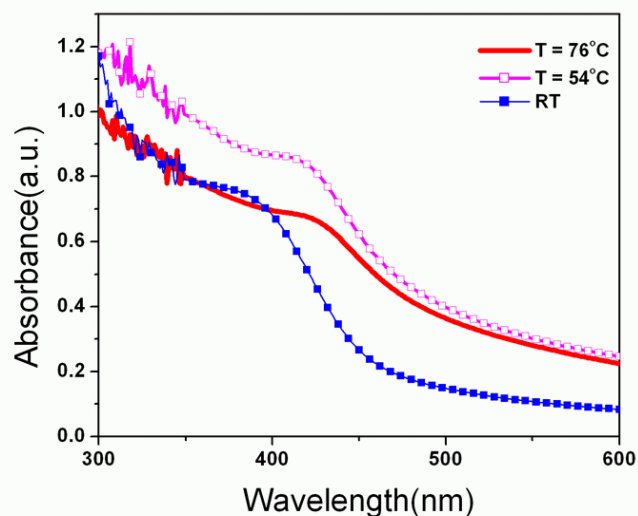


Fig. 13. Absorption spectra for CdS: Mn nanocrystals prepared by varying synthesis temperatures (For samples in Fig. 12).

The samples in Fig. 12 were annealed at 300°C in two steps. First the temperature rose up to 100°C and remained 30 minutes at this temperature, and then rose till 300°C. After annealing the crystal phase of samples synthesized at RT shifted from hexagonal to cubic and the crystal size increased (Fig. 14). Also, after annealing, the crystalline nature of the materials improved. Due to annealing, the phase of the synthesized sample at 54°C became cubic, but the crystal size increased with increasing temperature. The effect of annealing on the estimated particle size is presented in Table 2.

Table2. Optical size and crystal size of CdS:Mn nanocrystals before and after annealing

Sample	Crystal size(nm)	Temperature	Crystal phase
a)	1.64	RT (27°C)	hexagonal
Annealed a)	3.27	300°C	cubic
b)	2.43	54°C	cubic
Annealed b)	2.91	300°C	cubic

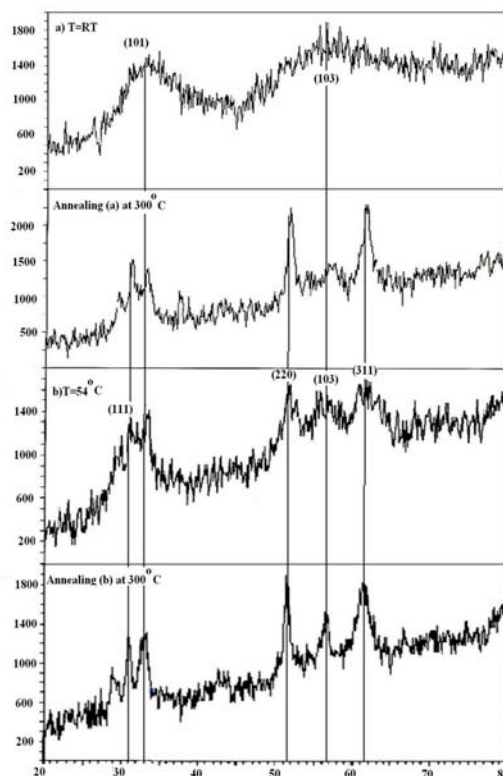


Fig. 14. X-ray diffraction pattern for CdS: Mn nanocrystals before and after annealing for sample in Fig. 12.

4. Conclusion

We prepared CdS: Mn nanocrystals by the aqueous solution method under different conditions. At low temperature, the samples show a hexagonal phase, while the samples at high temperature show the cubic phase. By increasing the reaction time, the crystal growth increases. In the samples with high Mn concentrations, the size of the NCs mostly increased. Also, the results indicated that Ostwald ripening has a favorable effect only on the properties of some samples which were prepared under different conditions. In addition, the crystal structure of the NPs was improved by annealing.

Acknowledgements

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