Enhanced Photoluminescence Properties of Mn Doped CdS Nanocrystals

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Abstract. We II – VI semiconductor nanoparticles are presently of great interest for their practical applications such as zero- dimensional quantum confined materials and for their applications in optoelectronics and photonics. The manganese doped cadmium sulfide (CdS: Mn) particles in the nanometer size regime have been synthesized by chemical route technique. The particles were capped with mercaptoethenol to achieve the stability and avoid coalescence. The presence of the capping agent does not allow the particle size to grow. In the present work the crystal structure and grain size of the particles are studied using SEM along with the study of optical absorption spectra of bulk and doped CdS nanocrystals and photoluminescence spectra studies for various concentration of Mn at room temperature. SEM estimated the crystallite sizes of the order of 40 nm. Optical absorption spectra of nanocrystals are blue shifted and show steps confirming the discrimination of energy levels due to quantum confinement. Two peaks are observed in the photoluminescence spectra of Mn doped nanocrystals, intensity of first peak increases and second peak shifts towards blue by increasing Mn concentrations.

Key words: Nanocrystals, absorption spectra, photoluminescence.

INTRODUCTION

Semiconductor nanocrystals have attracted growing interest during the last four decades [1, 2]. During the past two decades, research on quantum size semiconductor particles has increased enormously due to their exciting novel properties [3- 6]. II- VI semiconductor nanoparticles are currently of great interest for their practical applications such as zero- dimensional quantum confined materials, and in optoelectronics and photonics. Surface chemistry is an efficient tool not only to organize and immobilize the nanocrystals, but also to effectively modify the emission properties. It is also possible to manipulate the synthesized nanocrystals by proper modification of the surface using capping agents, there rendering them compatible in almost any chemical environment and soluble in organic solvents. Therefore, depending upon the size of the particles and the constituting elements, ionization potential, elastic properties, magnetic properties, optical properties, bonding, melting point etc change drastically. The different energy states available between valence and conduction band responsible for radiative recombination are provided by photoluminescence spectra. The nano size quantized particles yield the best external photoluminescence quantum efficiency and luminescence decay time much faster than the corresponding bulk crystals. The luminescent measurements carried out on various nanocrystals show the efficiency increases with decreasing particle size of the nanocrystalline size. Most studied nanocrystalline semiconductors belong to the II- VI groups, as they are relatively easy to synthesize and are generally prepared as particulates and in thin film forms. CdS is an important II- VI compound semiconductor with energy band of 2.4 eV and is used as a window material for solar devices. It has a typical response time of about 200 μs and sense in the wavelength range 1- 3 μm. The synthesis of semiconductor nanoparticles has attracted many researchers, due to their unique optoelectronic properties and quantum confinement effects from the bulk materials [7-10]. In the present paper, CdS:Mn doped nanoparticles were prepared by chemical precipitation technique for various concentration of capping agents. Mercaptoethanol was used as a capping agent in case of manganese doped CdS nanocrystals. Simple and inexpensive routes compared to those reported earlier have been devised. The optical absorption spectra, X-ray diffraction, scanning electron microscopy (SEM) and

photoluminescence emission spectra of impurity doped cadmium sulphide nanoparticles have been studied for different concentrations.

EXPERIMENTAL SECTION

Sample Preparation

Nanoparticles of CdS are synthesized in aqueous medium through chemical precipitation technique that used by Nosaka et al. [11] and reported elsewhere [12] starting from analar grade cadmium salt and sodium sulfide using mercaptoethanol as capping agent. For synthesis of 10^{-2} mole aqueous solution of cadmium chloride ($CdCl_2$), mercaptoethanol (C_2H_5OSH) and sodium sulphide (Na_2S) solutions were prepared. Firstly, mercaptoethanol solution was added drop wise to $CdCl_2$ (+ $MnCl_2$ for doping) solution at the rate of 1 ml per minute, while stirring it continuously so that solution is properly mixed. Then Na_2S solution will be added in a similar manner. The precipitate of CdS is insoluble in water and were thoroughly washed in double distilled water, centrifuged and then air dried. The presence of maecaptoethenol does not allow the particle size to grow in bigger size. Three different samples were prepared at room temperature and different manganese concentration.

Characterization techniques

In order to investigate the surface morphology and particle size with the help of scanning electron microscopy (SEM) of Stereoscan 430 made by Leica Company analyzed the samples. The sample were characterized at Inter University Consortium (IUC) Indore for X-ray diffraction studies with Cu Kα radiation ($\lambda = 1.5418$Å). XRD data were collected over the range 20^0-70^0 at room temperature. The particles size was calculated using the Debye-Scherer formula. Optical absorption spectra and photoluminescence of nanoparticles bulk and doped with different Mn concentrations were investigated using Perkin Elmer Lamda 12 spectrometer and Grating Monochromator HM-104 with Photomultiplier Tube (PMT- RCA- 931). The photoluminescence emission intensity in the range 400-1000 nm was measured with the help of PMT placed at other slit of monochromator.

RESULTS AND DISCUSSION

Figure 1 shows the optical micrographs of Mn doped CdS nanocrystals by scanning electron microscope of stereoscan 430 made by Leica company, fractal feature are observable in sample whose thickness range in between 20 nm to 359 nm by the micrograph under optical microscope the fractals appear but when sample are zoomed to higher magnification they are formed to consists of several crystallites.. The X - ray diffraction patterns of the samples are shown in Figure 2. Three different peaks are obtained at 2Θ values of 26.74^0, 43.86^0 and 51.64^0. This shows that the samples have zinc blende structure. The broaden peaks indicates nanocrystalline behavior of CdS sample. The width of the peak increases as the size of the particle decreases. The size of the particles has been computed from the full width half maximum (FWHM) of the first peak using Debye Scherer formula [6 & 13]. The particles sizes of the entire sample are in the range 2 nm to 4 nm. This XRD pattern confirms the CdS: Mn^{2+} prepared in nanocrystalline form and the size of particle is dependent on the concentration of mercaptoethanol use in synthesis of CdS:Mn. Therefore, the higher the concentrations of mercaptoethanol the smaller will be the cluster size [14]. It can also be seen clearly from figure.3.

The absorption spectra of sample were recorded with the help of the Perkin Elmer Lamda 12 spectrometer. It was observed that with systematic variation of morality of the additive mercaptoethanol concentration, the optical band gap could be varied from a bulk value of 2.4 eV to 3.98 eV for clusters. Figure 3 illustrates this observation. As the mercaptoethanol concentration increases the excitonic peak shifts to a shorter wavelength as it becomes sharper. This indicates the narrow size distribution, increase in energy gap, and creation of sharp excitonic level with increasing additive concentration. As expected, doping did not have any measurable effect on the absorption spectra.

Figure 4 (a)(b)(c) and (d) gives the photoluminescence spectra of CdS: Mn nanocrystalline samples having 0%, 0.1% and 0.2% Mn doped concentrations at room temperatures. The intensity peaks are seen at 460 nm and 740 nm for 0% doping of Mn, 470 nm and 680 nm for 0.1% , 460 nm and 660 nm for 0.2% of Mn and 460 nm and 650 nm step rise in absorption is observed for 0.3% of Mn doped concentration at room temperature. It can be seen that each peak in absorption spectra corresponds to transition at different excited states of the conduction band. In this case, the emission energy is mainly related to electron- photon interaction. The photoluminescence spectrum of

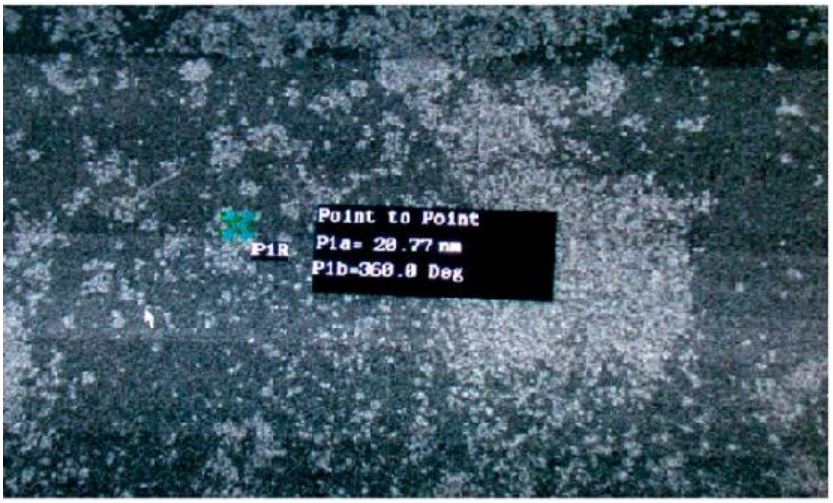

FIGURE 1 SEM Micrograph of CdS nanocrystals

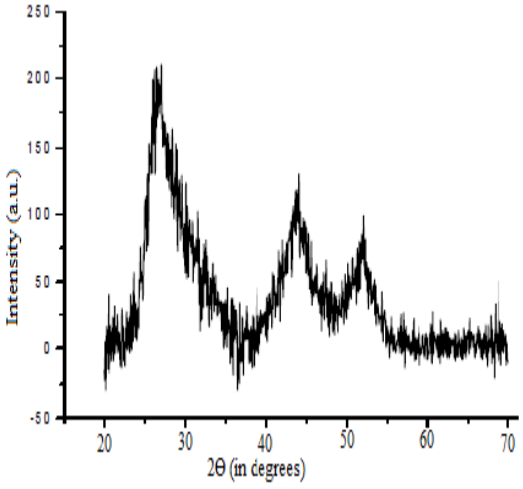

FIGURE 2 XRD pattern of CdS:Mn nanocrystals.

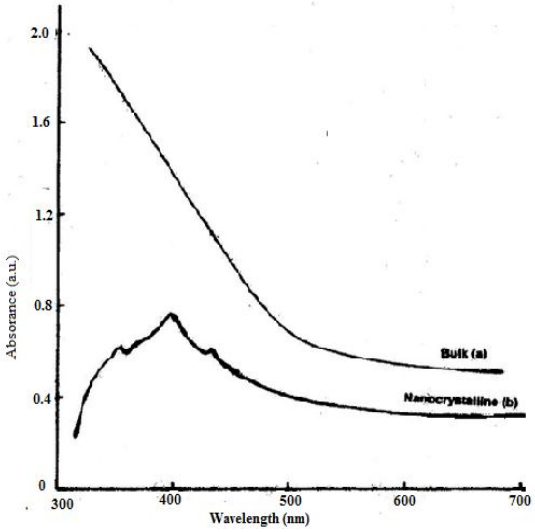

FIGURE 3 Absorption spectra of CdS:Mn nanocrystals & bulk sample (22).

manganese doped cadmium sulfide nanocrystals shows two peaks. The first one, within the range of 460 nm and corresponds to the band in the undoped sample, and therefore this peak has to be assigned to the band gap related photoluminescence of the CdS semiconductor [15-17]. The second peak with a maximum at 650 nm has a higher intensity and is ascribed to the fluorescence of manganese ions embedded in CdS particles. Figure 4 shows the dependency of the PL intensity at 650 nm on the relative concentration of manganese ions. The intensity increases with increasing Mn^{2+} concentration from 0.1% to 0.3% . When raising the concentration the emission at 650 nm is considerably reduced and above this relative concentration no manganese derived emission at all can be observed whereas the wave emission is still present. These finding on the intensity of the manganese emission are in acordnce with previous observations [18, 19] where it was assumed that higher manganese concentration favours nonradiative recombination processes. The observable red emission is caused by manganese ions located within the CdS nanoparticles.

In general, in manganese doped II-VI semiconductors there are complex optical processes, and the direct semiconductor band gap transition and the internal transitions within the 3d orbitals of the Mn^{2+} ions are coupled by energy- transfer processes [20, 21].The Mn^{2+} photoluminescence is caused by emission from the first excited state $^4T_1$ to the ground state $^6A_1$, and the position of the band strongly depends on the host lattice. In our case, we have observed – in addition to the semiconductor band gap related luminescence - a luminescence band caused by

divalent manganese ions with a peak maximum at 650 nm (1.90eV) indicating an environment with distorted tetrahedral or octahedral symmetry. The red emission is strong and can be seen even at room temperature.

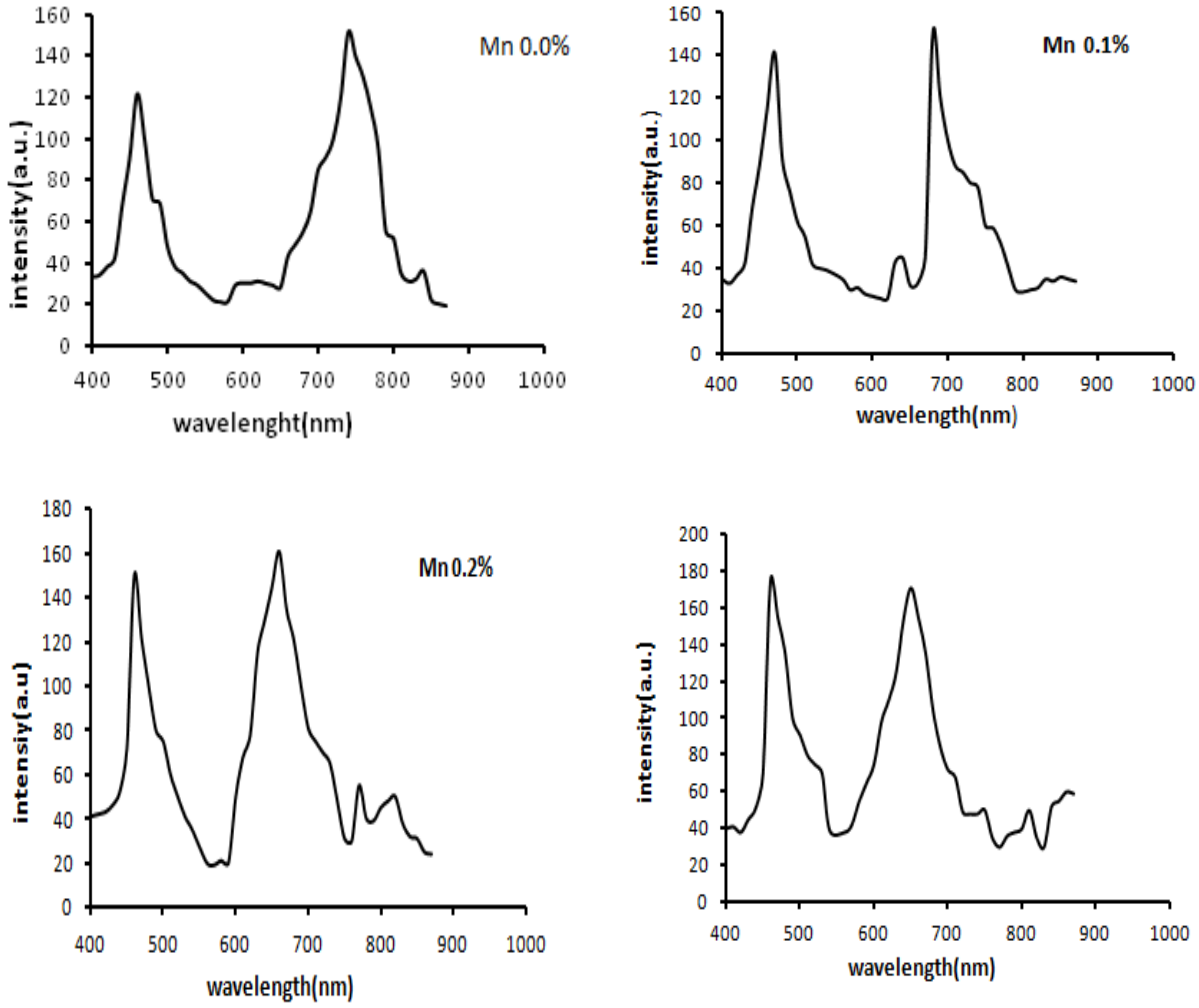

FIGURE 4(a),(b)(c)(d) Photoluminescence spectra of doped CdS nanocrystals for 0.0%,0.1%, 0.2% and 0.3% Mn concentration (23)

TABLE : 1 Crystalline size and PL Peaks of CdS:Mn nanoparticles

Sample	Mn%	PL Peak					
		A			B		
		Int. (a. u.)	WL λ (nm)	Photon energy (eV)	Int. (a. u.)	WL λ (nm)	Photon energy (eV)
a	0.0%	122	460	2.69	152	740	1.67
b	0.1%	141	470	2.63	150	680	1.82
c	0.2%	150	460	2.69	161	660	1.87
d	0.3%	175	460	2.69	171	650	1.90

CONCLUTIONS

The samples were characterized by SEM, from which the geometry of impurity doped CdS nanoparticles was predicted. The XRD pattern indicated the growth of the nanoparticles. The blue shift in the absorption spectra and the calculation of particles size by the measurement of absorption edge from two theoretical models indicates the reduction in the particles size with the increase in the molar concentration of the capping agents. The studies have revealed that the capping agent restricts the growth of crystals and by increasing its concentration, the crystals can be obtained. PL spectra of manganese CdS samples having different crystalline size were studied. The intensity of peak A decrease with increasing crystalline size, in contrast to the B peak. The strong wave photoluminescence of chemically synthesized CdS nanoparticles function overlap between the host and impurity along with the enhanced oscillator strength in nanocrystallites is responsible for the enhancement of the A peak intensities. The intensity of peak B should also decrease with increasing crystalline size, which is opposite to that observed experimentally.

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