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RESEARCH ARTICLE

Synthesis and Optical Characterization of CdS and CdS:Mn Nanoparticles

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ABSTRACT

The present paper reports the effect of Mn doping on the structural and optical properties of CdS nanoparticles. The samples have been prepared using wet chemical precipitation method. The so-prepared samples were structurally characterized using XRD, EDXA and TEM. Structural characterization confirms the formation of nanoparticles within the samples. UV-Vis spectrophotometer was used to record the absorption spectra for determination of energy band gap. Photoluminescence emission spectra of both the samples excited at 300 nm have been recorded at room temperature (300 K) to observe the possible radiative recombination in the presence of manganese ions in CdS matrix. The PL emission spectra of CdS:Mn sample shows peak centred at 584 nm and is attributed to forbidden transition $^4T_1$ to $^6A_1$ level.

Key words: *CdS:Mn, nanoparticles, band gap, photoluminescence*

INTRODUCTION

Semiconductor nanoparticles have been studied extensively due to their widespread industrial and technical applications. Among these semiconducting nanoparticles, cadmium sulphide (CdS) is an interesting direct band gap material and has found applications in high-frequency lasers, opto-electronic devices and many other photovoltaic devices (Bhargava, *et al*., 1994; Peng, 2001; Rathore, *et al*.,2010; Rathore, *et al*., 2009). The properties of CdS nanoparticles were found to improve on doping it with suitable transition metal ions. The effect of doping also provided the basic information on impurity statesin quantum dots and to examine their potential applications. It is well known that the quantum confinement effect modifies the electronic structure of nanocrystals when their diameter is comparable toor smaller than the diameter of the bulk exciton (Chen, *et al*., 2000; Norris, *et al*., 2001; Soo, *et al*., 1994). Several studies have reported effect of doping of transition metal ions on properties of CdS nanoparticles.

R. Lozada-Morales et al (Lozada-Morales, *et al*.,2013) studied the influence of internal stress on the optical properties of CdS:Cu nanoparticles and found that two effects i.e. the quantum confinement and the internal stress are responsible for change in E_g values. G. Giribabu *et al*., (Giribabu, *et al.,* 2013), studied the structural, optical and magnetic properties of Co doped CdS nanoparticles and found redshift of absorption edge and band gap narrowing can be attributed to increase in the carrier concentration by the inclusion of cobalt ions and creation of defect levels in the band gap (Hasanzadeh and Shayesteh, 2010) studied the photoluminescence properties of Cu doped CdS nanoparticles.

In the present paper, effect of Mn doping in CdS matrix has been studied. For this, pure CdS and Mn doped CdS sample has been prepared and energy band gap and photoluminescence characteristics has been studied for both the samples.

EXPERIMENTAL DETAILS

CdS nanoparticles were prepared using the method discussed in authors previous paper (Rathore, *et al*., 2008). For preparation of Mn doped CdS nanoparticles, 50 ml of 0.9M solution of

$CdSO_4$, 50 ml of 1M solution of Na_2S and 50 ml of 0.1M solution of $MnSO_4$were dropped simultaneously into 200 ml of distilled water containing 50 ml of 0.1M solution of EDTA and were stirred using a magnetic stirrer. The precipitate was then separated, dried and crushed to fine powder with the help of mortar and pestle. EDTA was used to stabilize the particle against aggregation which may lead to an increase in the particle size. The percentage of Mn was kept at4wt % by adding 4wt% of metal sulphate ($MnSO_4$) to $CdSO_4$ for preparation of different compositions of CdS:Mn nanoparticles. The precipitate was then separated, dried and crushed to fine powder with the help of mortar and pestle.

X-ray diffraction pattern of the samples were recorded on Bragg- Brentanno geometry on Panalytical X'pert Pro differactometer in 2θrange of 15-80° with Cu Kα radiation source (λ= 1.5406 Å). TEM measurements were carried out on Hitachi transmission electron microscope. The EDXA measurements were performed on FEI Quanta 200F SEM fitted with an EDXA. Absorption spectra were recorded on Ocean Optics USB 2000 Spectrophotometer in the wavelength range 200-850 nm. JOBIN YVON (HORIBA) Fluoromax-3 equipped with photomultiplier tube and a Xenon lamp was used to record the PL emission spectra of the powder sample.

RESULT AND DISCUSSION

Fig. 1 show the XRD pattern of pure CdS and CdS:Mn sample. It is observed that XRD peaks are considerably broadened due to finite size of these particles. It is also noticed that three diffraction peaks appearing for both the samples at 2θ values of about 26.55, 44.03 and 52.08 correspond to the (111) , (220) and (311) planes of cubic phase of CdS. The XRD data was refined by removing the broadening due to instrumental and non-uniform strain present in the lattice. This refined data has further been used to determine the particle size of these nanoparticles using Debye Scherrer formula-

$$D= 0.9 \ \lambda / \beta \cos \theta \qquad .....(i)$$

Where, D is the average particle size perpendicular to the reflecting planes, λ is the X-ray wavelength, β is the full width at half maximum (FWHM), and θ is the diffraction angle.

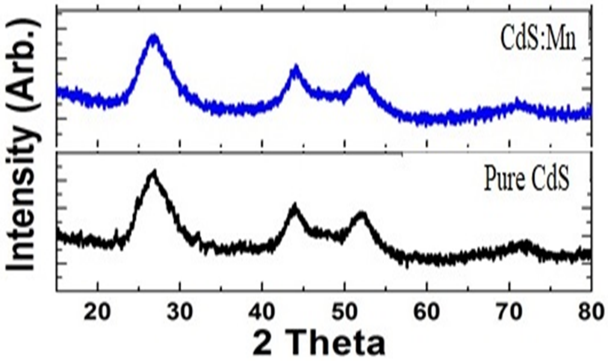

Fig. 1: XRD pattern of pure CdS and CdS:Mn nanoparticles

The particle size determination has also been carried out using TEM measurements. Fig. 2 show the TEM images of pure CdS and CdS:Mn sample. From Fig. 2, it is observed that both the samples have their sizes in the nano regime. The particle size of both the samples obtained from XRD and TEM measurements are given in Table 1.

From Table 1, it is observed that the particle size obtained from TEM is slightly larger than that estimated through XRD results. The slight discrepancy is due to the intrinsic defects like twining and dislocations present in the lattice of these samples

EDXA has been employed to confirm the Mn doping in all the so-prepared samples of CdS:Mn nanoparticles. Fig.3 shows the EDXA of both the samples under study. The EDXA of CdS:Mn sample depict the successful doping of manganese in the lattice of CdS nanoparticles.

The band gap of the samples has been determined using absorption spectra recorded in wavelength range 200-700nm. The relation between the absorption coefficient (α) and the incident photon energy ($h\nu$) can be written as (Patidar, *et al.*, 2008):

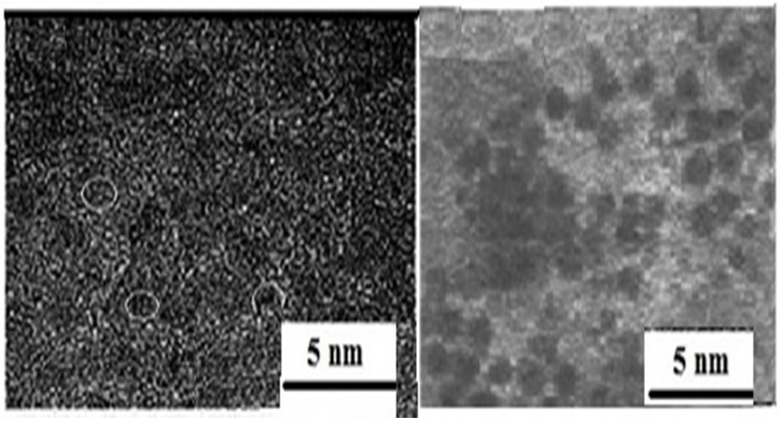

Fig. 2: TEM images of pure CdS and CdS:Mn sample

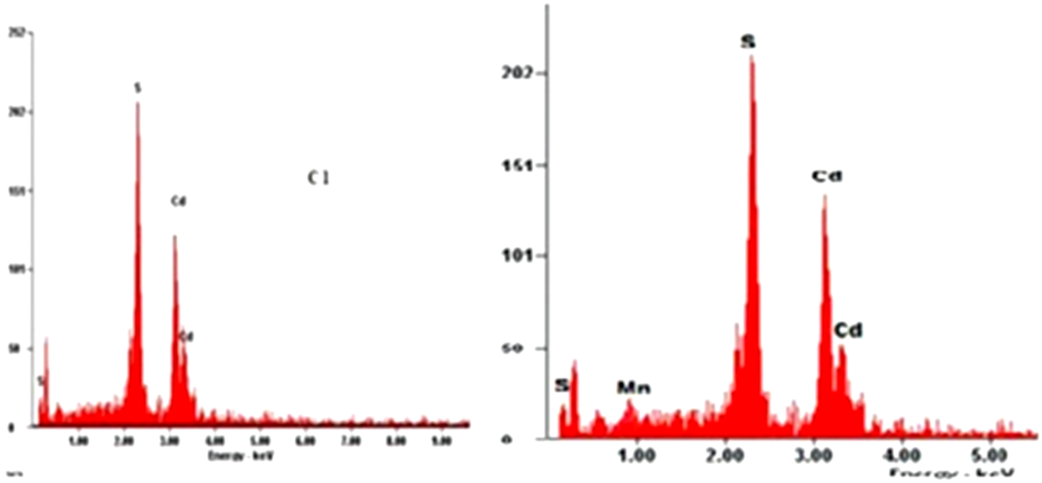

Fig. 3: EDXA of pure CdS and CdS:Mn sample

From Table 1, it is observed that the particle size obtained from TEM is slightly larger than that estimated through XRD results. The slight discrepancy is due to the intrinsic defects like twining and dislocations present in the lattice of these samples.

$$(\alpha h\nu) = A\,(h\nu - E_g)^n \qquad \text{....(ii)}$$

Where, A is a constant and E_g is the band gap of the material and exponent n depends on the type of transition. The present samples show direct transition, therefore n=1/2 was taken for band gap calculation. Fig. 4 shows the plot of $(\alpha h\nu)^2$ versus $h\nu$ for pure CdS and CdS:Mn sample. The extrapolation of the straight line to $(\alpha h\nu)^2 = 0$ axis gives the value of the energy band gap. Table 1 shows the values of band gap obtained for both the samples.

It is observed that band gap increases on doping of Mn in CdS matrix. This increment in the band gap is the outcome of the quantum confinement effect produced due to increased nucleation rate due to doping of Mn in CdS matrix. The increase in band gap on doping with metal ions is similar to that reported earlier (Jayanthi, *et al.*, 2007; Sang, *et al.*, 2002).

Photoluminescence emission spectra of pure CdS and CdS:Mn sample excited at 300 nm have been recorded at room temperature (300 K) to observe the possible radiative recombination in the presence of manganese ions in CdS matrix. Fig.5show the emission spectra of pure CdS and CdS:Mn nanoparticles.

From Fig. 5, it is observed that pure CdS sample shows a peak centered at 545 nm. The broad emission centered at 545 nm is attributed to carrier recombination at surface states. It could be due to either sulphur vacancies or cadmium vacancies depending on the availability of the cations or anions (Mandal, *et al.,* 2008) .This broad emission centered at 545 nm is due to cadmium vacancies at the surface of pure CdS sample. The surface states due to Cd vacancies can act as hole trap states (Ferrer and Salvador, 1989. Hence, the broad emission at ~ 545 nm is attributed to relaxation of carriers from the excitonic to the surface trap states. The broad surface state emission indicate that the surface state also have a finite distribution due to the size variation of nanoparticles.

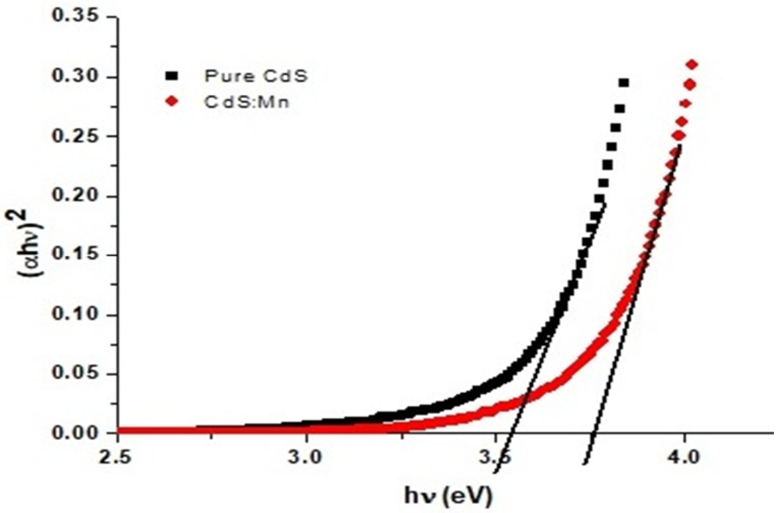

Fig. 4: Plot of $(\alpha h\nu)^2$ versus hν for pure CdS and CdS:Mn sample

Table 1: Values of particle size obtained using XRD and TEM, energy band gap (E_g) for pure CdS and CdS:Mn sample

Sample	**Particle size (XRD)**	**Particle size (TEM)**	**E_g(eV)**
Pure CdS	2 nm	3 nm	3.53
CdS:Mn	1.8 nm	4 nm	3.76

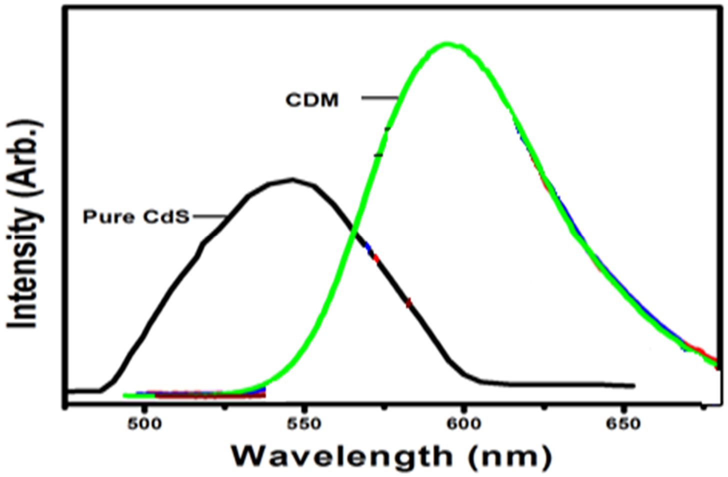

Fig. 5: pure CdS sample shows a peak centered at 545 nm.

For Mn- doped CdS nanoparticles, the PL peak observed at 584 nm was interpreted as due to an indirect excitation, i.e an excitation into the excited state of the host matrix CdS, followed by energy transfer from the host to the Mn^{2+} ions and its subsequent de-excitation leading to luminescence. When Mn doping is done, it occupies the tetrahedral cationic site with T_d symmetry and the electron may be captured by the Mn^{+2} ion in the $^4T_1$ level, from where it decays rediatively to the A_1 level. Mn doping actually reduces the non-radiative recombination and radiative transition takes place between Mn^4T_1 to$^6A_1$ level (Bube, 1960).

CONCLUSIONS

The present paper reports the optical properties of pure CdS and Mn doped CdS nanoparticles. XRD and TEM studied suggest that samples are nano-crystalline in nature. The band gap of the Mn doped CdS sample was found to be higher than pure CdS. This increase is the outcome of quantum confinement effect originated from smaller size of nanoparticles. The PL emission spectra of CdS:Mn samples shows peak centred at 584 nm and is interpreted as due to an indirect excitation, i.e an excitation into the excited state of the host matrix CdS, followed by energy transfer from the host to the Mn^{2+} ions and its subsequent de-excitation leading to luminescence.

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