Chapter III: Effect of pH and Dopant on Cadmium Selenide Nanoparticles
3.1 Effect of pH on structural and optical properties of CdSe nanoparticles

Optical properties of cadmium selenide (CdSe) nanoparticles prepared by a novel one pot synthesis method described in page section 2.2.1 of chapter II were investigated by varying pH of the precursor. Four different pH were taken for the solution. It is found that luminescence intensity of CdSe nanoparticles change with pH and it is highest for pH 11. Also it is found that for pH 11, band gap is maximum. High-resolution transmission electron microscope (HR-TEM) image of the CdSe nanoparticles is shown in Figure 2.3 and 2.4 of chapter II. These particles crystallize in zinc blende crystalline structure. Only first [111] peak was prominent. It has been observed that [111] peak is broadened. Comparison of the XRD pattern is shown in Figure 3.1.

![Figure 3.1: XRD of the synthesized nanoparticles](image)

Crystallite size of the nanoparticles prepared in pH 11 is calculated by Williamson-Hall method as shown in Figure 3.2 which is found to be 4 nm. W-H plot could not be plotted for all other particles as XRD pattern is not clear. Later, it is explained that CdSe nanoparticles were in crystalline form when they are prepared in a certain pH. Otherwise, it may also possible that at pH 8, 9 and 10, these nanoparticles are so small that XRD pattern is not well defined for them.
UV-Vis absorption spectra of the CdSe nanoparticles prepared in pH 8, 9, 10, 11 were taken as shown in Figure 3.3. From absorbance spectra band gap of the nanoparticles can be derived by using Tauc’s plot [1-3]. For direct band gap semiconductors, band gap is determined from the plot of square of the product of absorption co-efficient and photon energy along y-axis and photon energy along x-axis. This plot is a curve which should have a section of straight line. If this straight line portion is extended to the x-axis, the x-intercept of this line gives the optical band gap.

Figure 3.3: UV-Visible absorption spectra
Tauc’s plots for calculating band gap of the nanoparticles are shown in the Figure 3.4 bellow. Band gaps are 1.71 eV, 1.73 eV, 1.76 eV and 1.77 eV for pH 8, 9, 10 and 11 respectively.

**Figure 3.4:** Tauc’s plot of the CdSe samples at different pH

![Tauc's plots](image1)

**Figure 3.5:** PL spectra of CdSe nanoparticles prepared in different pH

![PL spectra](image2)
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PL spectra of the nanoparticles are shown in the above Figure 3.5. When a system of molecules absorbs energy it goes to an excited state. One way of relaxation is to emit photons. Here this case, it was found that emission of the nanoparticles prepared in pH 11 is at around 550 nm. At pH 11, CdSe nanostructures showed maximum luminescence. For other pH luminescence intensity decreases. For pH 8, it is lowest. So, it may be possible that luminescence intensity highly depends upon pH. CdSe nanoparticles are coated with organic capping agent Thioglycolic acid (TGA). Thioglycolic acid (TGA) is an organic compound with the formula HSCH$_2$CO$_2$H. TGA is often called Mercaptoacetic acid (MAA). It contains both a thiol (mercaptan) and a carboxylic acid. It is a clear liquid with a strong unpleasant odor. Its IUPAC name is 2-Sulfanylacetic acid.

In our case, some of the TGA molecules may depart from the CdSe nanoparticles into the solvent until a dynamic equilibrium is established between the adsorbing and desorbing of TGA from the NPs surfaces. At pH 11, a dynamic equilibrium is finally established and so the luminescence intensity is highest and also from XRD it is confirmed that at pH 11 CdSe nanoparticles took crystalline nature [5]. This argument is further confirmed from the Fourier transform infra-red spectra results shown in Figure 3.6.

![Figure 3.6: FTIR spectra of the CdSe nanoparticles prepared in pH 8, 9, 10 & 11](image-url)
FTIR spectra confirm presence of -SH group in CdSe nanoparticles which were prepared in pH 8. For pH 9, 10 and 11, –SH vibrational peak which should be at around 2576 cm\(^{-1}\), was absent [4]. This is due to the formation of covalent bonds between thiols and Cd\(^{2+}\) ions of the surface of CdSe nanoparticles.

Optical and structural properties of the nanoparticles were investigated by varying pH of the solution. Crystallite size of the nanoparticles prepared in pH 11 was found to be 4 nm. XRD pattern for all other pH were not clear. It may be possible that due to small size of the particles XRD for pH 8, 9, 10 were not clear. Band gap of the nanoparticles were calculated and it was found that band gap increase with increase in pH which may be due to increase in particle size of the nanoparticles with pH. In intermediate pH levels (pH=11), chemical interaction between thiolate group of TGA and the surface of Cd\(^{2+}\) is same as that between thiolate groups and H\(^+\) ions in water [5]. Lowering pH enhances the number of H\(^+\) concentration which promotes increase in the number of free thiols and uncoated nanoparticles and aggregated nanoparticles. And so photoluminescence intensity for lower pH (8, 9, 10) is low. At pH 11, a dynamic equilibrium is established and so the luminescence intensity is highest.

3.2 Effect of dopant on structural and optical properties of CdSe nanoparticles

Synthesis of manganese doped CdSe nanoparticles are described in section 2.2.2 of chapter II. High resolution transmission electron microscopy pictures are shown in Figure 2.5 of chapter II. Synthesized particles are precipitated as powder and diffuse reflectance spectra were taken which is shown in Figure 3.7. From diffuse reflectance spectra band gap was calculated by using Kubelka-Munk function, \(F(R) = (1-R)^2/2R\) and is shown in Figure 3.8. Where R is the reflectance in percentage, \(h\) is the Planck’s constant, \(v\) is the frequency of incident light. For a semiconductor sample \([F(R).h^2] vs Energy (hv)\) in electron volt plot gives Tauc’s plot.
Figure 3.7: Diffuse reflectance spectra of pristine and doped CdSe nanoparticles

Figure 3.8: Band gap calculation of pristine and doped CdSe nanoparticles
Since Mn$^{2+}$ has no spin allowed ligand field transitions, only the transitions for CdSe were observed in the F(R) versus energy curves for all the doping concentrations. Band gap of the nanoparticles decrease for 1 % and 2.5 % doping concentrations. But for doping concentration 5 %, band gap of the nanoparticles again increased than that for pristine ones. The table for band gaps is shown below:

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe</td>
<td>2</td>
</tr>
<tr>
<td>1 % Mn CdSe</td>
<td>1.90</td>
</tr>
<tr>
<td>2.5 % Mn CdSe</td>
<td>1.89</td>
</tr>
<tr>
<td>5 % Mn CdSe</td>
<td>2.02</td>
</tr>
</tbody>
</table>

XRD pattern is shown in Figure 3.9. First peak is shown in inset. Displacement of the peaks can be clearly seen towards higher angle. This shift in the position of first peak of XRD pattern confirmed that manganese ions replaced cadmium ions from their positions and occupied the corresponding positions in the lattice. First peak of XRD shifts towards higher angle indicating lattice contraction. However, peaks are broadened due to small crystal dimensions [6]. And lattice contraction is maximum for 1 % doping concentration. Crystallite size and strain in the nanoparticles are calculated by Williamson-Hall plot shown in Figure 3.10. With increase in the doping concentration to 1 %, 2.5 % and 5 %, negative strain started to decrease and lattice constants gradually increased. Here lattice constant is calculated for all the peaks in XRD and then an average is taken. Ionic radius of manganese (Mn$^{2+}$) is 70 pm and that of cadmium (Cd$^{2+}$) is 99 pm. When a manganese ion replaces a cadmium ion lattice strain is generated in the crystal and lattice contracts. For 1 % and 2.5 % manganese doping it can be seen that crystallite size decreased and lattice constant also decreased. Lattice contraction is highest for 1 % doping. The reason for increase in crystallite size for 5 % doping may be is that for this amount of Mn$^{2+}$ a
phenomenon called self purification occurs in CdSe nanocrystals [7]. For this reason Mn$^{2+}$ ions were not properly incorporated inside the crystal and so lattice contraction is least. Table for crystallite size, strain and lattice constant is shown in table 3.2.

![Figure 3.9: XRD pattern of pristine and doped CdSe nanoparticles](image)

**Figure 3.9:** XRD pattern of pristine and doped CdSe nanoparticles

![Figure 3.10: Williamson-Hall plot for pristine and doped CdSe nanoparticles](image)

**Figure 3.10:** Williamson-Hall plot for pristine and doped CdSe nanoparticles
PL spectra of the pristine and Mn doped CdSe nanoparticles are shown in Figure 3.11. Luminescence of manganese doped CdSe at 620 nm is not due to band to band transition that is not due to the electron transition from conduction band also called lowest unoccupied molecular orbital composed of selenium (Se) 4P to the valence band i.e. highest occupied molecular orbital composed of cadmium (Cd) 5S. This luminescence is attributed to the defects present in the system that is selenium vacancies. In case of CdSe nanoparticles if the size of the nanoparticles is higher than 3.3 nm then Mn$^{2+}$ transition is absent in the luminescence spectra because in that case Mn$^{2+}$ states are present above the excitonic levels. It can be seen from the luminescence spectra that luminescence peak for dopant concentration 5 % is not quenched and shows more intense peak than the other two concentrations. It has already found that only when the dopants are not properly incorporated inside the host material, the luminescence shows intense peak [8].

**TABLE 3.2:** Comparison table of crystallite size and strain for doped and undoped samples

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Crystallite size nm</th>
<th>Strain×10$^{-3}$</th>
<th>Lattice constant, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>a</td>
</tr>
<tr>
<td>CdSe</td>
<td>4</td>
<td>0.151</td>
<td>8.66</td>
</tr>
<tr>
<td>1% Mn CdSe</td>
<td>2.6</td>
<td>-5.5549</td>
<td>4.5</td>
</tr>
<tr>
<td>2.5% Mn CdSe</td>
<td>3</td>
<td>-0.1985</td>
<td>5.54</td>
</tr>
<tr>
<td>5% Mn CdSe</td>
<td>6</td>
<td>-0.05173</td>
<td>8.87</td>
</tr>
</tbody>
</table>

The local electronic structures of Mn ions in such II-VI semiconductor crystals are generally described well by ligand field theory. Mn$^{2+}$ has five 3d electrons. The ground state is split into six Zeeman components ($\pm1/2$, $\pm3/2$, $\pm5/2$) as shown in Figure 3.12.
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[9,10]. The $^{4}T_{1} \rightarrow ^{6}A_{1}$ ligand field transition is responsible for the characteristic luminescence of Mn$^{2+}$ ions in doped II-VI crystals. But in our case of CdSe nanoparticles, Mn$^{2+}$ PL emission is not seen. Mn-doped II–VI semiconductor nanocrystals are organized into three distinct categories according to the nature of their lowest energy excited state, which determines their resulting photophysical properties [11-17].

**Figure 3.11:** Photoluminescence spectra of pristine and doped CdSe nanoparticle

**Figure 3.12:** Schematic diagram of the splitting excited states of 3d$^5$ level for a Mn$^{2+}$ ion in presence of a tetrahedral crystal field (Ref 7)
In scenario I, Mn$^{2+}$ ligand-field excited states are lowest in energy and within the band gap (e.g., Mn$^{2+}$ doped ZnS, CdS, and ZnSe etc). In scenario II, Mn$^{2+}$ photoionization excited states are lowest in energy and within the gap (e.g., Mn$^{2+}$ doped ZnO). In scenario III: semiconductor excitonic excited states are lowest in energy (Mn$^{2+}$ excited states are outside the gap, e.g., Mn doped CdSe) as shown in Figure 3.13. Mn doped CdSe QDs differ from all other doped semiconductor nanocrystals in that they are the first that have allowed tuning of the semiconductor band gap energy across the dopant excited state levels. In PL spectra of Mn doped CdSe QDs, the characteristic Mn$^{2+}$ $^4T_1$ emission is observed when the bandgap energy is greater than the Mn$^{2+}$ $^4T_1$ excited state energy as shown in Figure 3.14. With decrease in nanocrystal diameter dopants are excluded from the nanocrystal bellow critical nuclei and hence for smaller size undoped nanocrystals are found. Energy of the excitonic transition depends strongly on particle size, but the energy of the localized Mn$^{2+}$ transition does not. The nature of the emissive state changes at d=3.3 nm, marking the cross-over between scenarios I and III. Although scenarios I and III both also exist among bulk DMSs, these Mn doped CdSe QDs are unique in that they allow tuning from one scenario to the other quite readily, simply by changing the nanocrystal diameter. Although only vacancy related emission is observed in Mn doped CdSe QDs in the present case, the properties of this luminescence are still fundamentally altered by the presence of the Mn$^{2+}$ ions.

Figure 3.13: Scenarios of PL emission in different nanoparticles (Ref 8)
Figure 3.14: PL emission in Mn doped CdSe dependent upon size of the nanocrystal (Ref 8)

So, it was seen that Mn doped CdSe nanoparticles with diameter higher than 3.3 nm do not show pseudo-tetrahedral Mn$^{2+}$ ($^{6}T_{1} \rightarrow ^{6}A_{1}$) transitions. But it is observed that presence of Mn dopant leads to decrease in luminescence intensity. The reason behind partial quenching of photoluminescence intensity is may be due to the shrinking distance between the dopant-dopant or presence of deep Mn$^{3+}$ neutral state that facilitates nonradiative recombination of band-edge electrons and holes [18-20]. Since, any Mn$^{3+}$ related phase was not found in XRD pattern, so shrinkage in Mn-Mn distance should be the reason for partial quenching of PL intensity.

Raman spectra of pristine and doped CdSe nanoparticles were also studied by Renishaw Invia Raman spectrometer. Figure 3.15 shows the Raman spectra of pristine and Mn doped CdSe samples. Raman spectroscopy is a non-destructive method for studying vibrational and electronic states of a confined system. The Raman effect arises when an intense monochromatic radiation undergo inelastic scattering on passing through a sample containing molecules and result in the change in molecular polarizability on vibration. When a sample is irradiated with incident light of frequency $v_0$, the scattered light is shifted by frequency $v(v_0+v)$. Raman scattering light undergoing a frequency shift ($v_0-v$) (longer wavelength) are known as Stoke’s light and scattered light with frequency shift ($v_0+v$) (shorter wavelength) are called Anti-Stoke’s light. The frequency shift is attributed to transfer of energy due to lattice vibrations, molecular vibrations and rotations of molecules and electronic transitions. Raman studies on nanoparticles revealed that whenever a system goes from bulk to nano a wavenumber shift and
broadening of Raman peaks is observed. Since CdSe nanoparticles are spherical in shape so on the basis of Heisenberg uncertainty principal, $\Delta x \Delta p \geq \frac{h^2}{4}$ it can be said that with decrease in grain size, the phonon position is confined in the particle size $\Delta x$ and the phonon momentum distribution $\Delta p$ will increase. Here, $h = h/2\pi$, $h$ is the Planck’s constant. The broadening of the phonon momentum leads to a broadening of scattered phonon momentum according to the law of conservation of momentum. And this may lead to shift of the Raman lines [21]. In the present case, longitudinal optical phonon (LO) is observed near 280 cm$^{-1}$. That is Raman spectra of CdSe nanoparticles are blue shifted than their bulk counterpart due to phonon confinement as explained above. For bulk CdSe LO phonon mode is observed at 210 cm$^{-1}$. Position of the peaks slightly changed due to doping. Deviation in the spectra due to doping is also seen in the intensity of the spectra. This is because now the manganese ions have replaced some of the cadmium ions and lattice contraction occurred.

![Figure 3.15: Raman spectra of Mn doped CdSe nanoparticles](image)

Figure 3.15: Raman spectra of Mn doped CdSe nanoparticles
3.3 Origin of ferromagnetism in Doped CdSe nanoparticles

To investigate oxidation state of the dopant and to know whether dopant ions are incorporated inside the nanocrystal or not EPR spectroscopy was done. EPR spectroscopy gives local electronic structure of dopant ion in the host crystal. Traces of Mn$^{2+}$ doped in II-VI bulk semiconductors result in numbers of isolated tetrahedrally co-ordinated Mn$^{2+}$ ions. From Figure 3.16, it was seen that EPR spectra of 2.5 % and 5 % doping is well defined. EPR spectroscopy of 1 % doping is actually composed of two spectra with a hyperfine structure with six lines and a broad spectrum.

The smaller Mn$^{2+}$ ion is expected to distort the CdSe lattice by replacing Cd$^{2+}$. The EPR data suggest that the Mn site is trigonally or tetragonally distorted which leads to the observation of forbidden EPR transitions. These transitions are attributed to a stronger spin-orbit term arising from symmetry breaking and are assigned to $-\frac{1}{2} \rightarrow \frac{1}{2}$ /spin-spin interactions [23, 24]. Six line pattern is from the Mn nucleus ($J=5/2$) and corresponds to the transition of $M_s=\pm1$ and $M_I=0$ where $M_s$ and $M_I$ are electron spin and nuclear spin quantum numbers, respectively. The Mn-Mn interaction which inversely related to the hyperfine interactions becomes stronger as more and more Mn ions are introduced into CdSe nanoparticles. A broadening effect is seen with increase in Mn concentration. This broadening effect with increase in Mn concentration is due to Mn-Mn interaction.

Magnetic hysteresis (M-H) loops at room temperature for all the three doping concentrations of manganese in CdSe nanoparticles are shown in Figure 3.17 and zoomed.
image is shown in Figure 3.18. Magnetic properties are analyzed in a superconducting quantum interference device (SQUID) (Quantum Design MPMS SQUID VSM Evercool system, USA). Squid is based on Josephson effect to measure small variations in magnetic flux. Squid is a ring of superconductor cut short by one or more Josephson junctions [25]. The superconducting magnetic coil produces the magnetic field. The sample is moved through the pick-up coils by means of a hydraulic system. Magnetic moment of sample induces a magnetic flux change in the pick-up coils into the SQUID [26].

![M-H curves for Mn doped CdSe nanoparticles](image.png)

**Figure 3.17:** M-H curves for Mn doped CdSe nanoparticles

The origin of ferromagnetism in II-VI (CdSe, CdTe etc) doped semiconductors comes from the spin exchange interaction between the Mn-ions mediated by the carriers (conduction-band electrons or valence-band holes), in particular through the sp-d exchange interaction [27]. In spite of the fact that Mn differs from the group-II cations by the 3d⁵ shell which is only half-filled, Mn can contribute its 4s² electrons to the s-p³ bonding. Therefore, Mn can substitute the group-II elements in wurtzite or zinc blende structures. Following Hund’s rule, these five d-electrons have parallel spins that adding another electron with opposite spin to the manganese (Mn) atom needs a considerably
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large energy. As a result, the $3d^5$ orbit is stable and the Mn-atom resembles a group-II element. In the II-VI doped semiconductors, the Mn-ion is isoelectronic which means that no additional electric field is created and the number of carriers is conserved. Besides, the polarity of the elements in II-VI group is strong. This makes them attractive for interesting optical properties. The magnetic interaction in II-VI doped semiconductors is dominated by antiferromagnetic exchange between the Mn spins, which results in paramagnetic, spin glass, and ultimately long-range antiferromagnetic behavior. Incorporated Mn doped CdSe [28] nanoparticles are expected to be good candidates to achieve suitable nanoscaled ferromagnetism [29,30].

Coercivity and saturation magnetization were found to be 196, 69, 67 Oe and 0.010, 0.013, 0.017 emu/g were for 1 %, 2.5 % and 5 % doping concentration respectively. The coercivity decreases with increase in doping concentration. The saturation magnetization (Ms) values of the three samples were found to increase with increasing doping but Ms per dopant decreases with increase in doping concentration.

Figure 3.18: Zoomed image of M-H curves of Mn doped CdSe nanoparticles

Ferromagnetism ordering may arise due to many possible reasons. One origin is small secondary phases of manganese such as ferromagnetic Mn$_3$O$_4$. But in XRD confirms absence of any secondary oxide phases as shown in Figure 3.9 and EDX also confirms absence of oxygen and other magnetic impurities as described in chapter II Figure 2.5. Another origin may be carrier mediated ferromagnetic Ruderman-Kittel-Kasuya-Yosida
(RKKY) mechanism of spin-spin exchange interaction. But with such low doping RKKY interaction is not possible. Low carrier densities of II-VI doped semiconductor nanoparticles are usually paramagnetic but neighbor Mn-Mn pairs are antiferromagnetically coupled or even blocked owing to short range superexchange interactions but RTFM is found in the present case. In addition to superexchange coupling, strong spin dependent coupling (sp-d) exchange interaction between the band of host semiconductor (sp-state) and magnetic moments (d-state) exists in Mn doped CdSe nanoparticles [31]. The antiferromagnetic coupling in these nanoparticles can be overcompensated by ferromagnetic interactions mediated by holes. In the presence of band carriers, the RKKY mechanism of spin-spin exchange interaction operates. But RKKY interaction is possible only if there are sufficient carriers in the system. But CdSe do not have sufficient carriers with such low doping. So, there may be an alternative F-centre mediated exchange mechanism responsible for this system. An F-centre is a selenium vacancy with a trapped electron. Presence of selenium vacancy is also confirmed from PL spectra. This trapped electron occupies an extensive orbital state that overlaps with the d shells of some nearby transition metal atoms. The radius of this trapped electron orbital is predictable to be of the order of $a_0$, where $a_0$ is the Bohr radius [32]. This pair is called bound magnetic polaron (BMP). The BMP will align in a parallel arrangement with the surrounding individual dopant ion spins by sp-d exchange interaction. This implies that the electronic states of the carriers are delocalized and extended, and when the concentration exceeds a certain value, ferromagnetism may be expected.

3.4 Conclusion

Novel findings of the chapter III is summarized in the following points:

1. pH dependent properties are seen in CdSe nanoparticles. At pH 11, CdSe nanoparticles show highest luminescence. In TGA capped CdSe nanoparticles, some of the TGA molecules may depart from the CdSe nanoparticles into the solvent until a dynamic equilibrium is established between desorption and
absorption. At pH 11, this equilibrium is established between the adsorbing and desorbing of TGA from the NPs surfaces.

2. XRD confirms successful substitutional doping and absence of any oxide phases of manganese. Shifting of the first XRD peak towards higher angle indicating lattice contraction due to replacement of larger Cd$^{2+}$ ions by manganese.

3. Mn$^{2+}$ doping in CdSe nanoparticles leads to partial quenching of PL intensity for 1% and 2.5% dopant concentration due to shrinking distance between Mn-Mn. But for 5% luminescence intensity increases due to improper incorporation of dopants inside host.

4. In EPR spectroscopy, hyperfine splitting was seen in 1% Mn doped CdSe nanoparticles. EPR spectra confirm presence Mn$^{2+}$ in CdSe nanoparticles.

5. Room temperature ferromagnetism is found in Mn doped CdSe which is ascribed to bound magnetic polaron mediated sp-d exchange interactions.

References:


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