Chapter II: Material Synthesis and Characterization

Methods
This chapter deals with the synthesis and characterization methods adopted to prepare pristine and manganese doped nanoparticles of cadmium selenide (CdSe) and cadmium oxide (CdO). Chemical method was chosen to prepare the nanoparticles. Transmission electron microscopy (TEM) was used to take images of the samples. Energy dispersive X-ray spectroscopy was used for elemental analysis. Morphological study was done by X-ray diffraction (XRD). Oxidation states of elements were tested by electron paramagnetic resonance (EPR) spectroscopy and X-ray photoelectron spectroscopy (XPS). Fourier transform infrared (FTIR) spectroscopy was also done to observe the bonds formed.

2.1 Synthesis of pristine and manganese doped CdSe nanoparticles

2.1.1 Preparation of pristine CdSe nanoparticles by one pot synthesis method using water as solvent

CdSe nanoparticles were synthesized using a novel one pot synthesis method [1]. In all other methods a neutral environment is required, but in this case, as SeO$_2$ is used, neutral environment is not required. The precursor consisted of 2 mmol CdCl$_2$.5H$_2$O and 1mmol SeO$_2$. First 2 mmol CdCl$_2$.H$_2$O was added in double distilled water. After stirring the solution for a few minutes, 0.5 ml TGA was added and pH was adjusted to 11 by adding 0.1 molL$^{-1}$ of NaOH. After several minutes 1 mmol SeO$_2$ and 0.1 g NaBH$_4$ was added. SeO$_2$ was reduced using NaBH$_4$. Thioglycolic acid (C$_2$H$_4$O$_2$S, TGA) was used as capping agent. TGA contains a thiol and a carboxylic acid. It forms complex with metal ions. Synthesis method is slightly modified by incorporating size selective precipitation using Acetone to obtain powder samples with uniform size distribution. pH of the solution was kept at 11. The solution was refluxed at 100 °C for 3 hrs to control the size of the CdSe nanoparticles. As the nuclei grow, Van der Waals interactions can cause rapid coalescence of the nuclei and thus forming larger nanoparticles. Ligands such as TGA which are chemically bonded to both the solvent and nanoparticle resist Van der Waals forces. To determine the influence of pH on the properties, nanoparticles were synthesized with different pH levels.
2.1.2 Preparation of manganese doped CdSe nanoparticles

For doping in 1 %, 2.5 % and 5 % molar ratios, (2-X) mmol of CdCl\(_2\).H\(_2\)O was taken in water and the solution was stirred for a few minutes. Then 0.5 ml TGA was added and pH was adjusted to 11 by adding 0.1 molL\(^{-1}\) of NaOH. After stirring for several minutes 1 mmol SeO\(_2\) and 0.1 g NaBH\(_4\) was added. SeO\(_2\) was reduced using NaBH\(_4\). Thioglycolic acid (C\(_2\)H\(_4\)O\(_2\)S, TGA) was used as capping agent. X mmol of manganese acetate after dissolving in 10 ml of water was then added into the precursor solution drop wise. Powder samples were obtained by using size selective precipitation. The solution was refluxed at 100 °C for 3 hrs to control the size of the CdSe nanoparticles.

2.2 Synthesis of pristine and manganese doped CdO nanoparticles

2.2.1 Preparation of pristine CdO nanoparticles:

CdO nanoparticles were prepared by a simple and cost effective sol-gel method [2]. cadmium acetate 6.6 gm (0.5 M) was dissolved in 100 ml of distilled water. Ammonia solution was added to the above solution with constant stirring until pH became 8. White precipitate was obtained which was allowed to settle for 12 hours and then centrifuged and washed 3 times by distilled water. Washed precipitate was dried at 80 °C and ground. Resulting white powder was calcined at 400 °C, 600 °C and 800 °C. To see the differences in the properties of the nanoparticles when annealed in air and vacuum, two parts of the as prepared samples were taken and again dried them in both air and vacuum conditions at 150 °C in 760 mm Hg vacuum pressure.

2.2.2 Preparation of manganese doped CdO nanoparticles

Manganese doped CdO nanoparticle samples were prepared in 1 %, 2.5 % and 5 % molar ratios. First, cadmium acetate 6.6 gm (0.5 M) was dissolved in 100ml of distilled water. Then aqueous Mn acetate was added to the solution drop wise. Ammonia solution was then added to the above solution with constant stirring until pH became 8. White precipitate was obtained which was allowed to settle for 12 hours and then centrifuged
and washed 3 times by distilled water. Washed precipitate was dried at 80 °C and ground. Resulting white powder was calcined at 400 °C.

### 2.3 Transmission electron microscopy (TEM), Selected area electron diffraction (SAED/SAD) and Energy dispersive X-Ray (EDX) studies

To get the image, particle size and/or grain size of the synthesized nanoparticles, Transmission electron microscopy was used. TEM images the transmission of a focused beam of electrons through a sample, forming an image in a way analogous to a light microscope [3]. The image formation is shown by the ray diagram in Figure 2.1 [4]. However, because electrons are used rather than light to illuminate the sample, TEM imaging has significantly higher resolution (by a factor of about 1000) than light-based imaging techniques. At smaller magnifications, TEM image contrast is due to absorption of electrons in the material, due to thickness and composition of the material. At higher magnifications complex wave interactions modulate the intensity of the image. TEM consist of an emission source (electron gun) which may be tungsten filament or a lanthanum hexaboride (LaB₆) source. By connecting this gun to a higher voltage source, the gun will begin to emit electrons. Coupling of magnetic field and electrostatic field in opposite directions allows for the shift in the beam path. Magnetic field allows for the

![Figure 2.1: Ray diagram of TEM (Ref 4)](image-url)
formation of magnetic lens of variable focusing power and electrostatic field can cause the electrons to be deflected through a constant angle. The lenses of the TEM allow for the beam convergence as a variable parameter, giving the ability to modify the amount of current passing through the lenses. Typically, a TEM consists of three stages of lenses; the condenser lens forming the primary beam, the objective lens focusing the electron beam that comes through the sample and the projector lens expanding the beam onto the phosphor screen or other imaging device. Here, TEM images were taken by High resolution transmission electron microscope (HR-TEM/JEM-2100, 200 KV, JEOL).

The selected area diaphragm is used to select only one part of the imaged sample. This mode of TEM, called selected area electron diffraction (SAED) mode, permits to obtain the symmetry of the lattice and calculate its interplanar spacing.

![Principle of EDX](image)

**Figure 2.2: Principle of EDX (Ref 6)**

Energy-dispersive X-ray spectroscopy (EDX) is an analytical technique to investigate the elemental characterization of a sample [5]. It relies on the investigation of an interaction of some source of X-ray excitation and a sample. The fundamental principle of EDX is that each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum. The emission of characteristic X-rays from a specimen is triggered when a high-energy beam of charged particles such as electrons or protons (PIXE), or a beam of X-rays, is focused onto the sample. The incident beam may excite an electron in an inner
shell, ejecting it from the shell while creating an electron hole where the electron was previously. An electron from an outer, higher-energy shell then fills the hole. The difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray which is depicted in Figure 2.2 [6]. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energy of an X-ray is characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the sample to be measured.

2.3.1 TEM, SAED and EDX study of pristine and manganese doped CdSe nanoparticles

TEM images of pristine CdSe nanoparticles are shown in Figure 2.3 (A). The statistical analysis (Figure 2.3 (B)) of the images depicts that the average particle size is 5 nm. EDX and SAED pattern of the pristine nanoparticles are also shown in Figure 2.4 (A and B). EDX (JEOL, JSM-6390LV, INCAx-sight) detector confirms that the sample contains cadmium and selenium without any oxygen and weight percentage of cadmium and selenium are 63.71 % and 31.61 % respectively. SAED confirms the polycrystalline nature of the sample and crystallite planes are also marked in the same. The interplanar spacing for one 5 nm particle is calculated to be 0.35 nm.

![Figure 2.3](image)

**Figure 2.3:** (A) HR-TEM, (B) EDX and (C) particle size calculation of CdSe nanoparticles
Figure 2.5 (A) shows HR-TEM images of the 1% manganese doped samples. Statistical analysis shows that the average particle size is 5 nm and there is a small size variation of 5-13 nm in the sample. SAED pattern of the crystalline areas of Figure 2.5 (A) shows bright circular rings indicating high crystallinity in the sample. EDX shown in Figure 2.5 (C) confirms presence of manganese in the sample.

Figure 2.5: (A) HR-TEM, (B) particle size calculation, (C) EDX of Mn doped CdSe nanoparticles

2.3.2 TEM, SAED and EDX study of pristine and manganese doped CdO nanoparticles

Size of a single CdO nanoparticle synthesized at 400 °C is around 25 nm as depicted in high-resolution image shown in Figure 2.6 (a). Crystal planes can be seen in HR-TEM. Selected area electron diffraction (SAED, Figure 2.6 (c)), was also taken to confirm crystalline nature. Presence of cadmium and oxygen are confirmed by EDX taken by
JEOL, JSM-6390LV, INCAx-sight EDX detector as shown in Figure 2.6 (b). Weight percentage of Oxygen present is 63.37 and cadmium is 31.63.

**Figure 2.6:** (A) HR-TEM image, (B) EDX and (C) SAED of CdO nanoparticles

The unproportional ratio between cadmium and oxygen found from EDX may be due to the defects present in the system. Also since EDX is a surface sensitive tool and can determine dopant concentration upto a few layers from surface, so obtained weight ratio indicates presence of cadmium and oxygen only a few nanometer depth from the surface of CdO.

**Figure 2.7:** (A) HR-TEM, (B) SAED and (C) EDX of Mn doped CdO nanoparticles
HR-TEM images of manganese doped CdO nanoparticles are shown in Figure 2.7 where particle agglomeration was seen. This is because surfactants are not used for preparation of the CdO nanoparticles. EDX (Figure 2.7 (C)) confirms the presence of manganese.

2.4 X-Ray diffraction studies

XRD is very useful to study morphological properties of the nanoparticles. In an XRD measurement, a crystal is mounted on a goniometer and is gradually rotated while being bombarded with X-rays. This produces a diffraction pattern of regularly spaced spots known as reflections. The two dimensional images taken at different rotations are converted into a three-dimensional model of the density of electrons within the crystal using the mathematical method of Fourier transforms, combined with chemical data known for the sample. Poor resolution or even errors may result if the crystals are too small, or not uniform enough in their internal structure [7]. Earlier Scherrer formula was used to determine crystalline size from the XRD plot which is given by, $D=0.9\lambda/\beta\cos\theta$, where $\beta$=FWHM, $\lambda=1.54$ Å, $2\theta$=peak position, $D=$ Crystallite size [8]. From Scherrer formula it is always difficult to separate size and strain broadening present in XRD peaks. Williamson-Hall (W-H) method is used to separate these two effects by equation, $\beta\cos\theta=(k\lambda/D) + \eta\sin\theta$, where $\eta$ is the strain, the value of D represents the size of the crystallites, constant $k$ typically close to 1 [9]. From $\beta\cos\theta$ versus $\sin\theta$ graph as shown in Figure 2.8 (B), a straight line with slope $\eta$ was obtained. Slope $\eta$ gives strain generated in the nanoparticles. Crystallite size (D) can also be determined from this method.

Morphological properties were studied by XRD. XRD pattern was collected by using Bruker D8 focus AXS X-ray diffractometer with CuK$\alpha$ radiation ($\lambda=1.5405$ Å). The XRD pattern and W-H plot for CdSe nanoparticles are shown in the Figure 2.8. Grain size for the CdSe nanoparticles having zinc blende crystalline was found to be 5 nm. D-spacing for the same was found to be 0.35 nm which was also found from HR-TEM of CdSe nanoparticles (Figure 2.5 (A)).
Figure 2.8: XRD and W-H plot of CdSe nanoparticles

Figure 2.9: XRD and W-H plot for CdO nanoparticles

Figure 2.9 is the XRD and W-H plot for Monteponite CdO with a cubic structure which was matched with the XRD data of our samples (JCPDS#050640). Often crystallite size matches with grain size but it may be different from particle size in the nano range. From HR-TEM, particle size of CdO nanoparticle is found to be 25 nm but crystallite size from W-H plot is found to be 24 nm.

2.5 Fourier Transform Infrared (FTIR) Spectroscopy

Infrared spectroscopy is the spectroscopy that deals with the infrared region of the electromagnetic spectrum. It covers a range of techniques, mostly based on absorption
spectroscopy. IR spectroscopy can be used to identify and study chemicals and chemical bonds. Fourier transform infrared (FTIR) spectrometer uses IR spectroscopy technique to analyze samples. The term Fourier transform infrared spectroscopy originates from the fact that a Fourier transform is required to convert the raw data into the actual spectrum. The theory is based on the fact that molecules absorb specific frequencies that are characteristic of their structure. These absorptions are resonant frequencies i.e. the frequency of the absorbed radiation matches the transition energy of the bond or group that vibrates. In this technique, a beam containing many frequencies of light are allowed to fall on the sample at once, and measures how much of that beam is absorbed by the sample [10].

Figure 2.10: FTIR spectra of CdSe nanoparticles before and after dispersion in water

Figure 2.11: FTIR spectroscopy of CdO nanoparticles
Fourier transform infrared spectroscopy is performed by Nicolet Impact I-140. FTIR of the samples before and after dispersion in water are shown in the Figure 2.10. At 1388 cm\(^{-1}\), CH\(_3\) bending vibration can be seen. At 1591 cm\(^{-1}\), there is a CO vibration peak. At 3426 cm\(^{-1}\), an OH vibration peak was found. FTIR spectra confirm absence of -SH group in CdSe sample by the lack of vibration peak at around 2576 cm\(^{-1}\). This is due to the formation of covalent bonds between thiols and Cd\(^{2+}\) ions on the surface of CdSe nanoparticles [11,12]. FTIR spectroscopy of CdO nanoparticles is shown in Figure 2.11 where OH vibrations at around 3439 cm\(^{-1}\)are seen.

2.6 X-ray photoelectron spectroscopy study

XPS is one of the most powerful techniques which can give accurate qualitative elemental analysis (except Hydrogen and Helium) and quantitative composition and at the same time chemical state (binding and oxidation). XPS can get information from the top 10 nm surface [13]. XPS is based on the photoelectric effect discovered by Hertz in 1887 in which interaction of an X-ray photon with sufficient energy with a solid eject an electron from the surface. Since the energy levels are quantized, the photoelectrons have a kinetic energy distribution consisting of discrete peaks associated to the electron levels of the photoionized atom. The emitted electrons have a kinetic energy given by: 

\[
E_K = h\nu - E_B - \phi,
\]

where \(E_K\) is the kinetic energy of the photoelectrons; \(h\nu\), the incident photon energy; \(E_B\), the electron binding energy; and \(\phi\), the work function. \(E_B\) can be obtained by measuring \(E_K\). The identification of the elements present on the surface is done directly by the binding energies of the core photoelectrons [14]. A typical XPS spectrum is a plot of the number of electrons detected (sometimes per unit time) versus the binding energy of the electrons detected.
XPS of CdO nanoparticles are shown in the Figure 2.12. Cd 3d and O 1s binding energies are shown in the Figure. Cd 3d features consists of two main 3d_{5/2} and 3d_{3/2} spin-orbit components at 406 eV and 413 eV which agree well with the 6.74 eV spin-orbit energy splitting between Cd 3d_{5/2} and Cd 3d_{3/2} states [15,16]. Deconvolution of Cd 3d_{5/2} peak renders two peaks with binding energies of 405 eV and 407 eV which can be related to Cd(OH)\(_2\) and CdO respectively. Similarly, Deconvolution of Cd 3d_{3/2} peak gives two peaks at 412 eV and 414 eV at an energy difference of around (≈) 7 eV corresponding to their Cd 3d_{5/2} peaks. Moreover two peaks are found for O1s at 531 eV and 533 eV which are due to related CdO systems and are due to presence of hydroxyl species on the surface.

2.7 Electron paramagnetic resonance spectroscopy

EPR spectroscopy is used at the microscopic level to get information about the oxidation state, lattice defects, color centres, site occupancy and magnetic phases in the host semiconductor lattice. EPR can reveal the subtle changes occurring in the crystal environment surrounding the paramagnetic impurity such as Mn\(^{2+}\). In presence of an external magnetic field, unpaired electron spins absorb microwave radiation. EPR measures the transition frequency between different electron spin states. The energy difference between an electron spin state \(m_s = \frac{1}{2}\) and \(m_s = -\frac{1}{2}\) in a reasonably strong
magnetic field of 1 Tesla is $\Delta E = 1.86 \times 10^{-23}$ J. In the presence of an external magnetic field, the electron's magnetic moment aligns itself either parallel ($\frac{1}{2}$) or antiparallel ($-\frac{1}{2}$) to the field, each alignment having a specific energy due to the Zeeman effect, $E = m_s g_e \mu_B B_0$ where $g_e$ is the electron's so-called $g$-factor, $\mu_B$ is the Bohr magneton. Therefore, the separation between the lower and the upper state is $\Delta E = g_e \mu_B B_0$ for unpaired free electrons. This equation implies that the splitting of the energy levels is directly proportional to the magnetic field's strength. An unpaired electron can move between the two energy levels by either absorbing or emitting a photon of energy $h\nu$ such that the resonance condition, $\Delta E = h\nu$, is obeyed. This leads to the fundamental equation of EPR spectroscopy, $h\nu = g_e \mu_B B_0$ [17]. When incident external magnetic field was varied, the gap between $+1/2$ and $-1/2$ widens and at one point it matches with the $\Delta E$ of the microwave. At this point the unpaired electrons can move between their two spin states. Since, there typically are more electrons in the lower state due to MB distributions, there is a net absorption that is monitored and converted into a spectrum [18].

![Figure 2.13: EPR spectroscopy of CdO nanoparticles](image)

EPR spectroscopy [EPR, ESR-JEOL, Japan, model: ES - FA200 ESR Spectrometer with X and Q band, Standard Frequency (X band) - 8.75-9.65 GHz, Sensitivity - $7 \times 10^9$ spins/0.1mT, Resolution - 2.35(micro) T or better] is used at the microscopic level to get information about the oxidation state, lattice defects, color centres, site occupancy and magnetic phases in CdO nanoparticles as shown in Figure 2.13. Bulk CdO is a general non-stoichiometric n-type semiconductor. When it is in nano size range its
properties change from the bulk. Non-stoichiometric CdO nanoparticles show asymmetric EPR signal. Both bulk and nano CdO crystallizes in the NaCl-type structure. The distance between cadmium and oxygen (Cd-O) is 2.34 Å. The CdO contains Cd nuclei with natural abundance. Apart from the isotopes with even masses, there are the two odd isotopes $^{111}\text{Cd}$ (12.75%; I=1/2; $\mu=0.592\mu_N$) and $^{113}\text{Cd}$ (12.26 %; I=1/2; $\mu=0.619\mu_N$). It is assumed that the paramagnetic center is a Cd$^+$ ion (2S$_{1/2}$ ground state) on the site of a Cd$^{2+}$ ion. The unpaired electron is localized not only at the central Cd$^+$ ion, but reaches far into the crystal [19]. Therefore, on the basis of other already reported results, signals with $g=2.046686$ and $g=2.202907$ were assigned to conduction band electrons, and to Cd$^+$ ions on the site of Cd$^{2+}$. Cd$^+$ ions arise from polaronic self-trapping of electrons introduced by oxygen deficiency at Cd sites to generate localized 5s$^1$ states [20]. Already reported results show that Cd$^+$ states were not involved in the conduction band. Same kind of behavior has been previously elucidated for other systems i.e. SnO$_2$, TiO$_2$. In these systems self-trapped electronic states are observed close to the conduction band edge rather than in the middle of the band gap. At liquid Helium temperature, EPR spectrum gives rise to hyperfine and superhyperfine lines for the peak of localized electrons [21-23]. The presence of nuclear moments in cadmium isotopes can contribute local magnetic fields at the electron in addition to the main applied field. Since the possible orientations of a nuclear moment are $2I + 1$, where I is the nuclear spin quantum number, the absorption spectrum for the electron will consist of $2I + 1$ lines. So, $^{111}\text{Cd}$ and $^{113}\text{Cd}$ should give rise to hyperfine lines. But the other peak due to conduction electrons disappears at liquid Helium temperature. Single electrons can produce localized lattice distortions in ionic solids because of their electrostatic interaction with neighboring ions. As the electron moves through the lattice, this lattice distortion moves with the electron. This results in what is known as polaron. When the distortion is sufficiently strong, the electron may be trapped at a particular lattice site. EPR peaks observed in present experiments are due to localized Cd 5s$^1$ states.
Chapter II

References:


