CHAPTER 3

PREPARATION AND CHARACTERIZATION OF CdS NANOPARTICLES

3.1 INTRODUCTION

Among the semiconductors, CdS is one of the most important wide band gap semiconductors, which has been extensively studied due to its ability to tune emission in the visible region simply by changing their size and shape (Bhattacharjee et al 2002; Zhang 1997). Traditional synthesis approaches of nanomaterials such as solvothermal and hydrothermal methods have been widely applied to improve the crystallinity of nanosized particles, wires and rods. For the past few years, various methods have been developed for the morphology control of semiconductor nanoparticles (Graham et al 2011; Xie and Shang 2007; Zhai et al 2009). For example, a well-controlled synthetic scheme to prepare CdSe nanoparticles with different morphology by thermal decomposition of organometallic precursors in a hot mixture of binary surfactants had been developed by Peng et al (2000). Moreover, they demonstrated that the control of the growth kinetics of the II-VI semiconductor CdSe can be used to vary the shapes of the resulting particles from a nearly spherical morphology to a rod-like one, with aspect ratios as large as ten to one.

The development of a general approach to the rational synthesis of crystalline nanowires of arbitrary composition, the intrinsic properties of 1D systems and the atomic structure and electronic properties of nanotubes were
discussed by Hu et al (1999). By the combined control of the monomer concentration, surfactant ratio, injection volume, reaction temperature and reaction time, the shape could be varied from hexagon, rod, arrow, tetra pod, to multi-armed rod. This can be achieved by selecting the appropriate reactant, capping agent, precursor concentration and solvent (Mthethwa et al 2009; Qinqing et al 2005; Vosmeyer et al 1994). It has been reported that the crystal structure of the fabricated nanoparticles also depends on the solvent agent. However, studies on the comparative role of different solvent agents in the formation, stability, size distribution and crystal structure of the CdS nanoparticles do not seem to have been fully addressed so far. Such studies, therefore, would be a worthwhile challenge in the production of nanoparticles with certain size and structure.

In this chapter, we present a controllable and rapid approach to synthesis of CdS nanoparticles by using a new single source molecular precursor. High yield CdS nanorods and nanoparticles with controlled diameters and high quality optical properties were prepared and the size and shape of nanoparticles thus obtained can be easily varied by different modes of heating process. The synthesis of CdS nanoparticles was achieved by thermal decomposition of cadmium (II) pyrrolidine dithiocarbamate (Cd(pdtc)$_2$) complex with added long chain amines under conventional heating and microwave irradiation. The complex Cd(pdtc)$_2$ is very easy to prepare and air stable for very long periods. Long chain amines (Hexadecylamine (HDA), Octadecylamine (ODA) and Dodecylamine (DDA)) provide more stable capping environment of the CdS nanoparticles. The effect of polar solvents (dimethylformamide (DMF), ethylene glycol (EG)) on the decomposition of the complex under microwave and conventional heating were observed. The effect of precursor concentrations in the preparation of nanoparticles was also analyzed. The formation of CdS nanoparticles with different shape and size prepared by both thermal decomposition and
microwave irradiation and their structural and optical characterizations are presented in this chapter.

3.2 SYNTHESIS OF Cd(pdtc)$_2$ COMPLEX

The chemicals used were of analytical grade and were received from commercial sources. In a typical synthesis procedure, the aqueous solution (1 mM in 25 ml of deionized water) of tetrahydrated cadmium nitrate (Cd(NO$_3$)$_2$ 4H$_2$O) was added drop by drop into ethanolic solution (2 mM in 100 ml of ethanol) of ammonium pyrrolidine dithiocarbamate (C$_5$H$_9$NS$_2$·NH$_4$) and the mixture was stirred for 2 h at room temperature. The resulting product was filtered, washed with a mixture solution of water and ethanol and dried at room temperature.

3.3 SYNTHESIS OF CdS NANOPARTICLES

The CdS nanoparticles were prepared according to the well established procedure outlined by Jun et al (2001). Thermal decomposition of single source molecular precursor Cd (pdtc)$_2$ with added long chain amines leads to the formation of CdS nanoparticles with different morphologies. Thermal decomposition of Cd(pdtc)$_2$ was carried out by both conventional and microwave heating. In conventional heating, the precursor Cd(pdtc)$_2$ was dissolved in warm solution of amine (e.g., 300 mg dissolved in 2 g of HDA at 70 °C) and the temperature of the reaction mixture was slowly raised to 150 °C. The mixture was maintained at a temperature of 150 °C for 30 minutes. The yellow precipitate CdS was collected by centrifugation and washed with absolute methanol and chloroform and dried in a hot air oven at 50 °C. The resultant nanoparticles were obtained as orange-yellow powders and readily re-dissolved in chloroform for further analysis. The same procedure was repeated for different concentrations (50, 100, 200 mg) of Cd(pdtc)$_2$ complex with 2 g of HDA under conventional heating process.
In microwave heating, same equimolar quantity of Cd(pdtc)$_2$ and amine were taken in a 100 ml beaker and placed at the center of the microwave oven and was irradiated with 90% power (total power of 800 W) for scheduled time. Without the addition of polar solvent, the microwave irradiation failed to decompose the complex Cd(pdtc)$_2$ even heated up to 5 minutes. The addition of 1 ml of DMF to the reaction medium [Cd(pdtc)$_2$ + amine] and heating it for 1 minute with 800 W power microwave resulted spontaneous formation of CdS nanoparticles. The solution was cooled and washed with absolute methanol and chloroform. Flocculent precipitate was centrifuged and dried in air. Schematic representation of chemical reaction involved in the formation of CdS nanoparticles by thermal decomposition of single source molecular precursor Cd(pdtc)$_2$ is shown in Figure 3.1.

\[
\begin{align*}
\text{N} & \quad \text{C} \\
\text{S} & \quad \text{S} \\
\text{NH}_4^+ & + (\text{Cd(NO}_3)_2 \cdot 4\text{H}_2\text{O} & \rightarrow \text{Cd}^{2+}
\end{align*}
\]

**Figure 3.1** Scheme of synthesis process

### 3.4 EFFECT OF POLAR SOLVENT IN MICROWAVE HEATING

Cd(pdtc)$_2$ does not absorb microwave radiation i.e., the microwave photons cannot induce any chemical bond breaking within the complex and even in the presence of HDA. The polar solvent DMF is widely used for the
synthesis of various metal sulfide and oxide nanoparticles. The solvent DMF having high boiling point and high permanent dipole is an excellent absorber of the microwave irradiation, which can take up the energy from the microwave field and get the polar reaction solution heated up to high temperature instantaneously (Tu and Liu 2000). The polar solvent acting both reaction media and dispersion media can efficiently absorb and stabilize the surface of the particles and produce monodispersed CdS nanoparticles (Feldmann and Metzmacher 2001). It is understood that the addition of DMF to the reaction medium affects the axial growth of CdS and also it disturbs the self-assembly of cylindrical shape fatty amines. Thus it is clear from this reaction the addition of catalytic amount of polar solvents could generate the heating, which is turn decomposing of the metal complexes. The formation of nanocrystalline CdS using Cd(pdtc)$_2$ complexes in both conventional and microwave heating under identical experimental conditions were tested. The substitution of HDA with polar solvent DMF did not generate any noticeable changes in conventional heating process.

3.5 CHARACTERIZATION STUDIES OF Cd(pdtc)$_2$ COMPLEX

Fourier Transform Infrared spectroscopy studies of the Cd(pdtc)$_2$ complex was performed using Perkin Elmer Spectrum1 FT-IR instrument. Thermo gravimetric analysis of the precursor Cd(pdtc)$_2$ was carried out with a Perkin-Elmer TGA in nitrogen atmosphere with a heating rate of 10°C/min.

3.5.1 Fourier Transform of Infrared Spectral Analysis

FT-IR measurements have been made in the wave number range 400 to 2000 cm$^{-1}$. The most significant bands recorded in the FT-IR of the complex and precursor is reported in Figure 3.2. For cadmium pyrrolidine dithiocarbamate compounds (a), three main regions of IR are of interest. First, the 1580–1450 cm$^{-1}$ region, which is primarily associated with the stretching
vibration of C–N group of N–CSS moiety; second, the 1060–940 cm\(^{-1}\) region, which is associated with \(\nu(\text{CSS})\) vibrations; third, the 417–420 cm\(^{-1}\) region associated with \(\nu(\text{M–S})\) vibrations (Brown et al 1976; Dawood et al 2009). The Cd(pdtc)_2 spectrum has bands at 1452, 1158 and 935 cm\(^{-1}\) which could be assigned to the vibrational modes of (C–N), (N–CSS) and (C=S) respectively. The metal-sulfur stretching frequency occurring at 416 cm\(^{-1}\) supported the formation of the complex.

![FT-IR spectra](image)

**Figure 3.2** The FT-IR spectra of (a) precursor (Apdtc) and (b) Cd(pdtc)_2 complex

### 3.5.2 Thermal Analysis of Cd(pdtc)_2

The thermal behaviour of the synthesized complex (Cd(pdtc)_2) has been studied by thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) under nitrogen atmosphere. The TGA and DTA traces of the
Cd(pdtc)\textsubscript{2} are shown in Figure 3.3. It shows that the complex is stable up to 130 °C and the first decomposition curve was observed at temperature ranging from 130-260 °C with about 5% weight loss. Its TGA curve revealed the occurrence of an initial mass loss that cannot be attributed to the loss of residual solvent and it does not present stoichiometric correlation with a decomposition process. The (pdtc) intermediate is stable in the 260-312 °C temperature interval and the subsequent decomposition process ends at 366 °C with major weight loss is about 60%. The sudden sublimation of the residues leads to rapid decomposition and the TGA curve goes straight which illustrates the presence of only CdS. There is sharp endothermic transition, started at 312 °C, corresponds to the decomposition of the legends (pdtc) from the complex and it reaches the maximum at 366 °C. This information is used to set the temperature range for decomposition of metal complex.

Figure 3.3  TGA and DTA plot for the decomposition of Cd(pdtc)\textsubscript{2} complex
3.6 CHARACTERIZATION STUDIES OF CdS NANOPARTICLES

Fourier Transform Infrared spectroscopy studies of the prepared CdS nanoparticles were performed using Perkin Elmer Spectrum1 FT-IR instrument. The obtained CdS nanoparticles were confirmed by powder X-ray diffraction (PANanalytical X’Pert PRO with CuKα radiation, 2θ ranging from 20° to 80° in steps of 0.017°/second). The energy dispersive X-ray spectrum (EDX), elemental mapping and the morphological analysis were conducted by scanning electron microscope (SEM, Hitachi S-4700). High Resolution Transmission Electron Microscopy (HRTEM) observation and the corresponding selected area electron diffraction were performed on a JEOL JEM-3010 electron microscope at accelerating voltage of 300 kV. UV-Visible spectra were obtained from Perkin-Elmer Lambda 35 UV-Visible spectrophotometer. Steady state fluorescence spectra were recorded at room temperature with a spectrofluorometer (FluoMax2) using 400 nm as the excitation wavelength.

3.6.1 Fourier Transform of Infrared Spectral Analysis

The FT-IR spectra of HDA and the as synthesized CdS nanoparticle from conventional heating were recorded and are shown in Figure 3.4. CdS particles showed two stretching bands, asymmetric and symmetric; around 2920.2 cm⁻¹ and 2852.6 cm⁻¹ are associated with C–H stretching. It can be seen that in CdS, the C–N vibration peak (1465 cm⁻¹) and C–H peak (1570 cm⁻¹) of HDA are observed, whereas the N–H asymmetric stretch peak (3100–3300 cm⁻¹) is slightly weaker and broader due to the amine ligands bound to the nanoparticles surfaces. This observation demonstrates that the nanoparticles were stabilized by HDA. Similar phenomena have been observed in HDA-capped semiconductors (Cai et al 2008). The nanoparticles
could be easily redispersed in various organic solvents such as chloroform and toluene.

Figure 3.4  FT-IR spectra of (a) HDA and (b) CdS nanoparticles

3.6.2  Powder X-ray Diffraction Studies

Figure 3.5 shows the XRD patterns of HDA capped CdS nano powders obtained from Cd(pdtc)$_2$ with different concentrations under conventional heating process. The XRD pattern of samples (a), (b), (c) and (d), prepared using different concentrations of complex 50, 100, 200 and 300 mg, respectively, clearly shows the hexagonal (wurtzite type) CdS crystal structure. This is evident from the prominent peaks (Figure 3.5 (d)) at scattering angles ($2\theta$) of 24.8, 26.5, 28.1, 36.6, 43.6, 47.8 and 51.8, which could be indexed to (100), (002), (101), (102), (110), (103) and (112) planes, respectively. On the other hand the XRD pattern of samples (a), (b) and (c)
indicates the hexagonal CdS crystal structure with additional peak at scattering angle 23.7°. This could be due to the non decomposed species of complex present in the samples. The calculated lattice parameter values of wurtzite hexagonal structure in sample (d) were $a=4.14$ Å and $c=6.719$ Å, which are in agreement with the reported values such as $a=4.15$ Å and $c=6.750$ Å (JCPDS 41-1049). However, in sample (d), the relative intensity of the peaks corresponding to the planes (100), (002) and (101) are varied from the literature values, indicating the distortion of the crystal structure due to the formation of nanorods.

![XRD patterns](image)

**Figure 3.5** The XRD patterns of obtained CdS nanoparticles with different concentrations of complex Cd(pdte)$_2$ in conventional heating process, (a) 50 mg, (b) 100 mg, (c) 200 mg and (d) 300 mg
The diffraction patterns (Figure 3.6) of CdS nanoparticles, synthesized by thermolysis of complexes (300 mg in conventional heating) in presence of different amines, such as HDA, ODA and DDA. Figures 3.6 (a), (b) and (c) show the XRD patterns of the CdS samples prepared using ODA, DDA and HDA, respectively. The peaks present in these three patterns can be indexed to hexagonal phase of CdS. However, the pattern in Figure 3.6 (a) and (b) shows the additional peaks that indicate the presence of complexes in the samples. This could be attributed to the partial-decomposition of the complexes in the case of DDA and ODA.

![XRD patterns](image)

**Figure 3.6** The XRD patterns of obtained CdS nanoparticles with different capping agents in conventional heating process, (a) ODA, (b) DDA and (c) HDA
Figure 3.7 shows XRD patterns of CdS nanoparticles, prepared by thermolysis of cadmium complex in microwave irradiation with different solvents. The sample (b) synthesized using DMF can be indexed as two CdS crystal phases. By examining the whole pattern it may be attributed that these nano powders contain a mixture of hexagonal (wurtzite) and cubic (sphalerite) structures. The broad peak centered at 2θ of 26.08° should be seen as an overlapped peak involving the planes of wurtzite and sphalerite structures of CdS. The diffraction peaks could be identified and found to the reflections from the lattice planes of disordered close-packed structure of CdS (Vorokh and Rempel 2007).

![XRD patterns of CdS nanoparticles with different solvents in microwave irradiation](image)

**Figure 3.7** The XRD patterns of obtained CdS nanoparticles with different solvents in microwave irradiation, (a) EG and (b) DMF

The diffraction pattern of sample (a) obtained using EG indicates the crystal structure is assigned to hexagonal phase with some impurity peaks.
The broadening of the peak shape in Figure 3.7 indicates the sizes of the CdS particles are in nanometer scale. The mean crystallite diameter of CdS nanoparticle (~5 nm) was estimated by application of Scherrer equation. From the above powder XRD observations, the ratio of amine and the complex, 2 g and 300 mg, is highly efficient to synthesize good quality nanocrystalline CdS with HDA and DMF. Figure 3.8 shows the diffraction pattern of CdS nanoparticles prepared by conventional heating process with the addition of polar solvents EG and DMF. The hexagonal CdS structure is identified and the corresponding reflections of planes (101), (002), (101), (110), (103) and (112) are clearly seen in both cases. But when compared with the diffraction peaks for bulk CdS, all the characteristic peaks are broadened, which is in agreement with the nature of the nanocrystalline CdS. The strong diffraction peaks in Figure 3.8(b) indicate that the as-obtained CdS nanostructures are well crystalline in nature.

Figure 3.8  The XRD patterns of obtained CdS nanoparticles with different solvents in conventional heating, (a) EG and (b) DMF
3.6.3 Transmission Electron Microscopic Studies

Figure 3.9 and 3.10 show HRTEM micrographs of two different CdS nanoparticles. CdS nanoparticles obtained from microwave irradiation (Figure 3.9) shows monodispersed spherical particles with an average size of 5 nm in diameter whereas CdS nanorods were produced under conventional heating (Figure 3.10).

Figure 3.9 (a)-(d) HRTEM micrographs of CdS nanoparticles synthesized by Microwave irradiation of Cd(pdtc)$_2$ complex
The morphology of the CdS varies from longer rods to spherical particles, which shows the shape evolution of CdS nanoparticles that arises from different kind of heating process.

Figure 3.10  (a)-(d) HRTEM micrographs of CdS nanorods synthesized by conventional heating of Cd(pdtc)$_2$ complex. The spherical particle, marked in (c), is obtained along with nanorods

The morphology of CdS nanoparticles, synthesized by conventional heating process with the addition of polar solvents DMF and EG were also investigated using HRTEM. The typical TEM images of CdS in Figure
3.11(a) and (b) corresponding to DMF and EG, shows the formation of nanorods. It is found that the axial growth in conventional heating was not affected by the addition of polar solvents in CdS nanoparticles. Figure 3.11 (a) shows the nanorods having an average diameter of 5 nm and a length of 20 nm. In the case of EG, the CdS nanoparticles are very thin and narrow rods and are shown in Figure 3.11(b) at the magnification of 50 nm. From this observation, the conventional heating process is suitable for the synthesis of rod-like CdS nanostructure whereas microwave heating produces a good quality of monodispersed spherical nanoparticles with an average size about 5 nm.

3.6.4 Selected Area Electron Diffraction Studies

The selected area electron diffraction patterns in Figure 3.12(a) and 3.12(b) reveal that the CdS nanostructures are in crystalline phase. The diffracted rings of SAED patterns could be assigned the corresponding planes of hexagonal phase. The calculated values of the ‘d’ spacing 3.59 Å, 2.37 Å, 2.12 Å and 3.63 Å, 2.45 Å, 2.03 Å for the planes (100), (102) and (110) is observed in both heating process. The lattice spacing of nanoparticles are measured at different places in higher magnification inset images (Figure 3.9c and 3.10d), which shows the corresponding planes of hexagonal structure of CdS. The patterns support the existence of crystalline structure and reveal the ‘d’ spacing of 3.34 Å and 3.33 Å, which are assigned for the lattice plane (002) of hexagonal phase.

The calculated value of average particles size from XRD of sample (b) in MWI is about 5 nm, which makes good agreement with HRTEM results. Similarly, the average size of nanorods calculated from TEM images is approximately 3 nm in width and 15 nm in length. The micrograph shows the nanorods appear to be the mixture of spherical nanoparticles.
Figure 3.11 HRTEM micrographs of CdS nanorods synthesized by conventional heating with (a) DMF and (b) EG

Figure 3.12 The electron diffraction pattern of CdS nanoparticle synthesized by (a) Microwave Irradiation and (b) Conventional heating
TEM images indicate that the single source precursor method could allow crystalline materials to be readily prepared under the certain experimental conditions.

3.6.5 Scanning Electron Microscopic Studies

The SEM image for the CdS nanoparticles synthesized by thermal decomposition of Cd(pdtc)$_2$ under microwave heating and the corresponding EDX spectra with elemental mapping are shown in Figure 3.13.

Figure 3.13 SEM image and EDX spectrum of CdS nanoparticles prepared under Microwave irradiation shown in (a) and (b), the elemental mapping of CdS shown in (c) and (d)
It is noted that the Cd and S are uniformly distributed along the size and shapes of nanoparticles, while the Cd and S elements were found on the same spot corresponding to their position in nanoparticles regime. The composition of the product was studied by energy dispersive X-ray analysis and is depicted in Figure 3.13(b). The atomic ratio of sulfur is relatively higher than cadmium, which indicates that the vacancy of Cd\(^+\) or some sulfur dangling bonds were present in the sample.

3.6.6 Optical Properties of CdS Nanoparticles

The optical properties of the prepared samples were analyzed by UV-Visible absorption and Fluorescence emission spectroscopy techniques. UV-Vis absorption spectra were observed to investigate the size of CdS nanoparticles prepared under different conditions.

Figure 3.14 The absorption spectra of CdS nanoparticles dissolved in chloroform with different concentration of the complex precursor in conventional heating process.
CdS is a typical direct band gap semiconductor, when the sizes of CdS nanoparticles become smaller than the exciton radius, quantum size effect leads to size-dependent increase of band gap and corresponding blue-shift in absorption onset. Figures 3.14, 3.15 and 3.16 show the room-temperature UV-Vis absorption spectrum for the CdS nanocrystal samples prepared in chloroform. Figure 3.14 shows absorption spectra of the CdS nanoparticles at different precursor concentrations.

![Absorption Spectra](image)

**Figure 3.15** The absorption spectra of CdS nanoparticles prepared with the addition of polar solvents DMF and EG in conventional heating process.

As shown in Figure 3.14, the CdS particles obtained at a precursor concentration of 300 mg exhibited an absorption edge of 490 nm, which is considerably blue-shifted relative to absorption onset of bulk CdS. With increasing concentration of precursor from 50 to 300 mg, the absorption edge
of the obtained CdS nanoparticles decreased gradually from 501 to 490 nm, suggesting that smaller CdS nanoparticles were produced at a higher precursor concentration. The absorption spectra of CdS nanoparticles, prepared using two different solvents are shown in Figure 3.15. It can be seen that the absorption peak or absorption edge is shifted toward blue region, from EG to DMF. This blue shift in the absorption edge is a consequence of the enhancement of band gap of the semiconductor nanoparticles with reduction of their sizes.

UV–Visible absorption spectra for CdS nanoparticles prepared from different heating process are shown in Figure 3.16. An absorption edge was observed at 485 nm in sample (a) and 490 nm in sample (b) for CdS nanoparticles synthesized by MWI and conventional heating process respectively.

![Absorption Spectra](image)

**Figure 3.16** The absorption spectra of CdS nanoparticles dissolved in chloroform with different conditions (a) CdS prepared by Microwave irradiation (b) Conventional heating process. Inset figure shows the peak position at 485 nm.
The observed spectral features for the nanoparticles (485 nm; 2.57 eV) and the nanorods (490 nm; 2.55 eV) are significantly sharper and blue shifted to a greater extent relative to the corresponding bulk semiconductor (515 nm; 2.42 eV). A sharp excitonic feature appeared at 450 nm in sample (a) could be the indication for the formation of monodispersed CdS nanoparticles. The shape of the spectrum in sample (b) is indicative of a slightly less monodisperse sample than the one obtained by MWI. The observed band gap for the nanophase CdS is higher than that of bulk, which is due to nanometer-sized particles. The calculated values of particle size from XRD and UV are given in Table 3.1.

Table 3.1 Calculated values of crystal size for CdS nanoparticles

<table>
<thead>
<tr>
<th>Compound</th>
<th>Energy Gap (eV)</th>
<th>Particle size from $E_g$ (nm)</th>
<th>Particle size from XRD (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS (CH)</td>
<td>2.55</td>
<td>6.9</td>
<td>7.5</td>
</tr>
<tr>
<td>CdS (MWI)</td>
<td>2.57</td>
<td>5.1</td>
<td>5.4</td>
</tr>
</tbody>
</table>

A fluorescence spectrum of CdS nanoparticles dissolved in chloroform was recorded at excitation wavelength of 400 nm in room temperature and the resulting spectra are shown in Figure 3.17. The observed fluorescence peaks at 465 nm; 585 nm in sample (a) (MWI with DMF) and 470 nm; 603 nm in sample (b) (conventional heating) are commonly attributed to the excitonic (or) band edge emission and surface trapped emission. The sample (a) shows blue shift than sample (b) and the fluorescence emission shift to lower wavelength with changing in particle size and shape is well known. Due to quantum confinement effect, the
fluorescence peak position of band edge emission of the nanostructure is strongly size dependent and usually in the wavelength range of 420 to 500 nm for CdS. The broad emission band around 500 to 800 nm is ascribed to the transition from trap state arising from surface atoms to the ground state (Bawendi et al 1992).

Figure 3.17 The Fluorescence emission spectra of CdS nanoparticles from Microwave irradiation and Conventional heating process

On the other hand the surface defect emission is caused by surface state vacancies and/or sulfur dangling bonds. The fluorescence spectrum of CdS nanoparticles shows a strong and broad deep trap emission near 585 and 603 nm indicates a relatively high density of trap state with broad distribution of energy. In earlier studies CdS nanocrystallites formed by several techniques have a broad emission in this range and indicated as the recombination of trapped charge carriers at the surface defect (Mandal et al 2009).
These surface defects have been attributed to Cd and S vacancies and also the broad emission is caused by donor-acceptor pairs, which indicates the donor state may be shallow in nature. The surface states due to Cd vacancies in CdS nanoparticles were reported to act as hole trap states (Chestnoy et al 1986). Thus, the broad emission centred at ~585 nm is attributed to the relaxation of carriers from the excitonic states to the surface acceptor states. This is in good agreement with the result of EDX spectrum, which shows the excess amount of sulfur present in the system.

3.7 DISCUSSION

Several complexes of Cd with sulfur-containing ligands have been used as precursors to synthesize CdS nanoparticles. Dithiocarbamate complexes have been well-studied (Jun et al 2001; Memon et al 2006) and Nair et al (2001, 2002 and 2003) have reported the use of Cd complexes of ethylxanthate, thiohydrocarbazide and alkyl-substituted thiourea as precursors for synthesize the CdS nanoparticles with monodispersed spherical particles. Recently, Pradhan et al (2003) synthesized the high quality metal sulfide nanoparticles using alkyl xanthate. In principle, these complexes may be of interest for thermal formation of nanoparticles; however, the Cd-pyrrolidine dithiocarbamate is a new interesting molecular precursor for the preparation of CdS nanoparticles with high yield and we anticipate the nanoparticle with different size and shape by controlling the heating process. The yield of the nanoparticles is approximately 80% i.e., 300 mg of complex gives us nearly 220 mg of nanoparticles.

According to the literature, many researchers reported the different architectural size and shape of nanoparticles obtained from MWI (Tang et al 2003; Panda et al 2006). In our case the monodispersed spherical nanoparticles were obtained in MWI, whereas the rod-like structure in conventional heating. Moreover, the yield of the nanoparticles in conventional
heating is relatively higher than that of MWI. We tried different long chain amines such as HDA, DDA and ODA as a capping agent of the nanoparticles. In our observation, the capping environment of the nanoparticles with HDA has an improved property. Some researchers have developed their synthesis method for nanoparticles with good stability using long chain amines. In structural aspect of CdS nanoparticles, the powder XRD shows the wurtzite hexagonal phase CdS is formed in all cases and the HRTEM images reveal that the spherical and rod like structure of nanoparticles. Absorption edge of rod-like nanoparticle show a slight red shift compare with the spherical particles. In both cases of heating, the emission behaviour shows the broad peak at longer wavelength, which is attributed to the defect state or trapped emission.

From these observations, the precursor concentration 300 mg and the capping agent HDA are highly suitable for the preparation of good quality of CdS nanoparticles by thermolysis of organometallic complexes. In microwave synthesis, the usage of DMF as a polar solvent gives better results than EG. Further synthesizes have been carried out with 300 mg as the concentration of metal complex, HDA as a capping agent and DMF as a solvent for the case of doped CdS nanoparticles.