Chapter 1

Synthesis and opto-physical characterization of CdTe quantum dots
1.1. **INTRODUCTION**

1.1.1. Opto-physical properties of QDs

In recent years, smart nanomaterials such as QDs have gained a lot of interest because of their unique spectral properties (Bruchez et al., 1998; Aoyagi and Kudo, 2005). A brief description on QDs has been given in the literature review (Literature review, Section 4). QDs exhibit size dependent opto-physical and electronic properties due to inherent quantum confinement effects of excited electrons and their corresponding holes called excitons (Alivisatos, 1996). As a result, QDs behave differently in contrast to their bulk counterparts. Quantum confinement effect is a phenomenon of widening of bandgap energy as the size of the material shrunken to nano scale. Due to this quantum confinement effect the movement of electrons in QDs are confined in all three spatial dimensions and hence are called as zero dimensional semiconductor materials (Hornyak et al., 2008). QDs exhibit discrete conduction bands resulting in emission of light due to radiative relaxation when an excited electron returns to the valence band. When an electron absorbs energy from an electromagnetic wave, it reaches an excited state and tends to return to its ground state by releasing absorbed energy. This process of relaxation of an electron from excited state to its ground state is termed as fluorescence (Wiedemann, 1888; Valeur and Berberan-Santos, 2011). Another feature of quantum confinement effect in QDs is the energy band gap which is the distance between valence band and conduction band. The band gap in QDs is size dependent and is inversely proportional wherein band gap of the material increases as the size of the QD decreases. This size dependent property of band gap in QDs allows engineering the QD size to
restrict emission frequencies. Thus, emission wavelength in QDs shifts towards higher wavelength as the size of the particle increases (Prasad, 2004). In fact, gradual increase in the molar extinction coefficient towards shorter wavelengths is an important feature for biological applications allowing simultaneous excitation of multicolor QDs with a single wavelength.

QDs exhibit a typical Gaussian fluorescence curve indicating polydispersity of the material. Hence, Gaussian curves with smaller Full Width at Half Maximum (FWHM) suggests samples with narrower QD size distributions (Galian et al., 2009). Therefore, fluorescence in QDs may be designed based on applications by engineering their crystal size during synthesis. Moreover, absorption spectral analysis may provide an insight into band structure, band gap and in turn on the quantum confinement effects in QDs. Although intrinsic energy states are determined by the material used, band gap energy is significantly directed by size dependent quantum confinement in QDs. Therefore, it is possible to synthesize QDs of the same material to emit at different wavelengths by restricting their sizes.

Surface passivation or capping is a critical factor to be addressed for having photostability in QDs. In general, phosphenes (Manna et al., 2000) and mercaptans (Rogach et al., 2007) are the most widely used capping ligands. Alongside, an issue of hydrophilic or hydrophobic nature of the capping material has to be considered while selecting an appropriate ligand in order to have biocompatible QDs for biosensing applications.
1.1.2. Synthesis of QDs

QDs can be synthesized either by chemical methods or by physical methods. Typical chemical method of synthesis includes conversion of precursors to achieve nanoparticle growth through nucleation process. This occurs by the combination of solute atoms or molecules to reach a critical size. During the course, parameters such as temperature, stabilizers, precursor’s concentration and ratios of anionic to cationic species along with nature of the solvent are critically monitored to synthesize QDs of desired size, shape and composition. Hydrothermal synthesis process (Yang et al., 2008), sol-gel process (Lin et al., 2005), microemulsion process (Darbandi et al., 2005), hot-solution decomposition process (Murray et al., 1993) and microwave synthesis process (Qian et al., 2005) are some of the common synthesis procedures to name just a few by this approach.

In contrary to above, physical methods of QDs synthesis generally begins with formation of layers in an atom-by-atom addition and elemental growth. Molecular beam epitaxy (MBE), Physical vapor deposition (PVD) and Chemical vapor deposition (CVD) are some of the important methods in this category. MBE uses deposition of overlayers for elemental growth on a heated substrate under ultra-high vacuum (Jiao et al., 2006), PVD is done by forming elemental layers through condensation of vapors produced by thermal evaporation or sputtering (Burda et al., 2005) and in CVD QDs are self-assembled on a thin film (Lobo et al., 1998).
1.1.3. Aqueous synthesis of QDs

Synthesis of QDs with biocompatibility is the primary requirement for any biosensing applications. In this direction, aqueous method of synthesis has gained much attention in recent years and remains the best approach aimed at biosensing techniques. Surface coating ligands employed in aqueous phase synthesis render biocompatibility to QDs that enable them to be directly conjugated with biomolecules. Therefore, researchers have focused their attention on coating characteristics to obtain QDs with high quantum yield, narrow size distribution and better fluorescence. Out of several existing methods of synthesis (Samina et al., 2006; Hines and Guyot-Sionnest, 1996; Rosetti and Brus, 1982), currently non-aqueous and aqueous phase synthesis strategies are being commonly adopted to synthesize QDs with high quality. Non-aqueous phase method results in hydrophobic QDs (Murray et al., 1993; Qu and Peng, 2002) due to the pyrolysis of organometallic precursors in organic solvents at high temperature. These QDs need post synthesis surface modification with hydrophilic surface ligands to attain biocompatibility which often result in decreased fluorescence (Bruchez et al., 1998; Mattoussi et al., 2000). Alternatively, QD synthesis in aqueous phase is a direct approach to produce water-soluble QDs without the need for further modification (Yang et al., 2008). Hence, organic capping materials with thiol moieties are being frequently used for surface attachment where terminal polar head group facilitate hydrophilic interactions and bioconjugation to other molecules (Bruchez et al., 1998; Gerion et al., 2001; Mattoussi et al., 2000). Although hydrothermal method has been used for the synthesis of a variety of QD nanoparticles (Gaponik et al., 2002; Gao et al.,
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1998; Zhong et al., 2006) such as CdS, CdSe, CdTe, ZnS, ZnSe and HgTe, focus has been given on synthesis and application of CdTe QD in our work.

Thus, engineering the size and opto-physical characterization of QDs are very much essential for their applications in biosensing and bioanalytical methods. In this chapter, a facile route for the synthesis of CdTe QD using water-soluble thiols as stabilizing agents at a low temperature (100 °C) has been discussed. Further, studies on engineering the morphology and structure of CdTe QD by adjusting precursor and ligand compositions have also discussed in detail.

1.2. EXPERIMENTAL

1.2.1. Materials

Cadmium acetate dihydrate [Cd(CH$_3$COO)$_2$.2H$_2$O], Tellurium powder, Sodium borohydride (NaBH$_4$), 3-Mercaptobutanoic acid (MPA), Propionic acid (PA), 2-Mercaptoethylamine hydrochloride (MEA), 2-Mercaptoethanol (ME), Potassium bromide (KBr), Rhodamine-6G were procured from Sigma-Aldrich India Pvt. Ltd. Bangalore, India. Dialysis membranes having 6-8 kDa molecular weight cut off was procured from Spectra/Por, USA. Amicon bioseparation filters were procured from Millipore (India) Pvt. Ltd., Bangalore, India. All reagents used were of analytical grade and acquired from standard suppliers.

1.2.2. Instruments

The instruments used were UV-Vis Spectrophotometer (UV-1601, Shimadzu, Japan), Spectrofluorophotometer (RF-5301 PC, Shimadzu,
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Japan), Atomic Force Microscopy (AFM, Molecular Imaging, USA), Transmission Electron Microscopy (TEM, Jeol 2100, USA), 400-mesh carbon grid from Pacific Grid Technology (San Francisco, CA 94111, USA). X-ray diffraction (XRD) was carried out using Desktop X-ray diffractometer (Rigaku, Miniflex-II). Fourier Transform Infrared Spectrometer (FT-IR, Nicolet 5700, Thermo Electron India PVT. Ltd. Pune, India).

1.2.3. Synthesis and functionalization of colloidal CdTe QDs

CdTe QDs were synthesized according to Eychmuller and Rogach, (2000), Li et al. (2007). In brief, 0.02 M of Cd(CH\textsubscript{3}COO)	extsubscript{2}.2H\textsubscript{2}O was dissolved in 25 mL of argon saturated double distilled water. The solution was reacted with 0.05 M of MPA to obtain a molar ratio of 1:2.5 between Cd\textsuperscript{2+} and MPA respectively followed by bubbling argon gas for 30 minutes and preserved till further use.

1.2.4. Synthesis of sodium hydrogen telluride (NaHTe)

NaHTe was produced in argon saturated aqueous solution by reducing 0.01 M Te powder in presence of 0.03 M NaBH\textsubscript{4}. The reaction mixture was incubated for 120 minutes at room temperature.

1.2.5. Growth of CdTe nanoparticles

Finally, NaHTe produced was added dropwise to argon saturated Cd-MPA mixture followed by adjusting the pH to 11 ± 0.5 using 1N NaOH. The molar ratio of Cd\textsuperscript{2+}:MPA:HTe\textsuperscript{-} was fixed at 1:2.5:0.5 for initial experiment. Further, the resulting mixture was subjected to refluxing at 99 ± 1 °C for 150
minutes separately under continuous argon flow to control the size of the CdTe nanoparticles (Fig 1.1). CdTe nanoparticles produced were precipitated using absolute ethanol and further, centrifuged at 8000 RPM repeatedly for 3 times to obtain the crystals.

**Fig. 1.1** Setup for quantum dot synthesis

(a) Magnetic stirrer with heating coil, (b) Oil bath, (c) Sample injection port, (d) Water condenser, (e) Water outlet, (f) Water inlet, (g) Argon cylinder

Both absorption (Fig. 1.2) and fluorescence (Fig. 1.3) spectra were recorded for CdTe QDs. CdTe QDs were excited at 350 nm and FWHM was monitored.
**Fig. 1.2** Absorption spectra of CdTe QDs. (1) CdTe$_{516}$, (2) CdTe$_{523}$, (3) CdTe$_{557}$, (4) CdTe$_{576}$ and (5) CdTe$_{601}$

**Fig. 1.3** Fluorescence spectra of CdTe QDs. (1) CdTe$_{516}$, (2) CdTe$_{523}$, (3) CdTe$_{557}$, (4) CdTe$_{576}$ and (5) CdTe$_{601}$
1.2.6. Studies on reaction time on nanoparticles growth

The reaction mixture having molar ratio of \( \text{Cd}^{2+} : \text{MPA} : \text{HTe}^- \) fixed at 1:2.5:0.5 was subjected to prolonged refluxing with the above mentioned reaction conditions. Te powder was reduced at room temperature as mentioned previously. Sample was drawn at regular intervals of 30 minutes from 0 hrs to 6 hrs. Both absorption and fluorescence spectral changes were recorded for each sample. FWHM with respect to reaction time was monitored.

1.2.7. Studies on effect of ligand concentration

CdTe QDs were synthesized at different molar ratios of precursors to probe the effect of capping material (MPA, MEA, PA and ME) on nanoparticle growth. Initially, molar concentration of MPA was varied (0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08 M) in presence of 0.02 M of \( \text{Cd(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O} \) and 0.01 M of Te. The effective molar ratio of \( \text{Cd}^{2+} : \text{MPA} : \text{HTe}^- \) were 1:1:0.5, 1:1.5:0.5, 1:2:0.5, 1:2.5:0.5, 1:3:0.5, 1:3.5:0.5 and 1:4:0.5. Te was reduced at room temperature in presence of 0.03 M \( \text{NaBH}_4 \) by incubating for 120 minutes. Further, the reaction mixtures were subjected to refluxing for 120 minutes at 99 ± 1 °C separately under continuous argon flow. Further, MEA, ME and PA were also tested as capping materials with the above mentioned reaction conditions. The molar ratio of \( \text{Cd}^{2+} : \text{R} : \text{HTe}^- \) was fixed at 1:2.5:0.5 where ‘R’ is the respective capping material.
1.2.8. Effect of pH on QD synthesis

CdTe QDs were synthesized at various pH to probe the influence of hydrogen ion concentration on nanoparticle growth. The molar ratio of Cd\(^{2+}\):MPA:HTe\(^{-}\) was fixed at 1:2.5:0.5 and pH of the reaction mixtures were adjusted to 4.0, 5.5, 6.5, 7.0, 8.0, 9.0, 10.0, 11.5, 12.0 ± 0.2 in separate experiments prior to refluxing. The refluxing conditions remained same as mentioned in previous section. Finally, CdTe nanoparticles of various sizes having emission maximum at 516 nm, 523 nm, 557 nm, 576 nm and 601 nm were synthesized at different refluxing conditions by adjusting pH to 9 ± 0.2 in separate experiments. CdTe nanoparticles produced were precipitated with absolute ethanol as mentioned earlier. Photo-absorption and fluorescence spectra were recorded.

1.2.9. Photophysical characterization of QDs by absorption and fluorescence profiles

Absorption spectra were taken for CdTe nanoparticles of various sizes (516 nm, 523 nm, 557 nm, 576 nm and 601 nm) and respective first absorption peak was recorded. Sizes of QDs were determined according to equation 1.1 given by Donega and Koole, (2009).

\[
E_{\text{(CdTe)}} = E_{g}(\infty) + \frac{1}{ad^2+bd+c} 
\]  
(1.1)

Where \(E_{\text{(CdTe)}}\) and \(E_{g}(\infty)\) are the band gap energies (electron Volt, eV) for CdTe synthesized and bulk respectively. \(a, b\) and \(c\) are constants (0.137, 0 and 0.206 respectively) for CdTe QDs and \(d\) is the diameter of QD in nm.
Size of QDs was also determined by equation 1.2 given by Kayanuma, (1986 and 1988), equation 1.3 given by Yu et al. (2003) and Pu et al. (2006)

\[ \Delta E = E - E_g + R_y = \left( \frac{\hbar^2 \pi^2}{2 \mu r^2} \right) - \left( 1.786 \frac{e^2}{\varepsilon_{CdTe}} \right) + 0.752 R_y \]  

(1.2)

\[ d = (9.8127 \times 10^{-7}) \lambda^3 - (1.7147 \times 10^{-3}) \lambda^2 + 1.0064 \lambda - 194.84 \]  

(1.3)

where \( \lambda \) is the wavelength of the first excitonic absorption peak in nm, \( E_g = 1.606 \) eV is the band gap energy (in eV) for CdTe bulk and \( E \) is the band gap energy of CdTe synthesized, \( h \) is reduced plank’s constant, \( \mu = 0.0774 m_0 \) is the reduced mass of an electron mass \( m^* = 0.096 m_0 \) and a hole mass \( m^*_h = 0.4 m_0 \), \( m_0 \) is electron mass, \( r \) is the radius of the dot, \( e \) is the charge of an electron, \( \varepsilon_{CdTe} = 7.1 \) is the dielectric constant and \( R_y = 10 \) meV is the exciton Rydberg energy (Masumoto and Sonobe, 1997). The band gap energy of CdTe QDs was calculated using absorption spectra. Molar extinction coefficient (\( \varepsilon \)) for all the QDs was calculated according to Yu et al. (2003) and Pu et al. (2006) as given below:

\[ \varepsilon = 3450 \left( E_g \right) \left( d \right)^{2.4} \]  

(1.4)

Fluorescence spectra were taken for all QDs exciting at their respective first excitonic peak (Fig. 1.3). FWHM and effective Stokes shift were recorded. Fluorescence efficiency (quantum yield, QY) of QDs was determined by comparative method according to Williams et al. (1983). For this Rhodamine 6G was employed as standard considering its QY as 95% in absolute ethanol at room temperature (Crosby and Demas, 1971; Kubin and Fletcher, 1982). Gradient absorption was taken in the range 0, 0.02, 0.04, 0.06, 0.08 and 0.10 for both standard and QD having identical optical density at the respective excitation wavelength (\( \lambda_{ex} \) 528 nm for Rhodamine 6G and \( \lambda_{ex} \) 452 nm, 469 nm,
501 nm, 509 nm and 547 nm for CdTe$_{516}$, CdTe$_{523}$, CdTe$_{557}$, CdTe$_{576}$ and CdTe$_{601}$ respectively). A graph of integrated fluorescence against absorption was plotted (n=5) to determine the gradient ‘m’ for both standard (Fig. 1.4) and QD (Fig. 1.5) separately.

**Fig. 1.4** Standard graph of Rhodamine 6G integrated fluorescence

**Fig. 1.5** Standard graph of QDs integrated fluorescence
Further, fluorescence QY ($\Phi$) of QDs were calculated according to the following equation:

$$\Phi_X = \Phi_{ST} \left( \frac{\text{Grad}_X}{\text{Grad}_{ST}} \right) \left( \frac{\eta^2_X}{\eta^2_{ST}} \right)$$  \hspace{1cm} (1.5)

In this equation, the subscripts ST and X denote standard and QD respectively, \text{Grad} was the gradient obtained from the plot and $\eta$ was the refractive index of the solvent used, methanol for Rhodamine 6G and water for QDs at their excitonic wavelengths according to El-Kashef, (2000); Daimon and Masumura, (2007) respectively (Table 1.1).

Table 1.1 Oppto-physical properties of CdTe QDs

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>CdTe QDs ($\lambda_{em}$ in nm)</th>
<th>First excitonic peak (nm)</th>
<th>Band Gap (eV)</th>
<th>Particle Size $^a$ (nm)</th>
<th>Molar extinction coefficient $^b$ $(\varepsilon/M \text{cm}) \times 10^4$</th>
<th>Stokes shift (nm)</th>
<th>FWHM (nm)</th>
<th>QY (%) $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>516</td>
<td>452</td>
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<td>6.2716</td>
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<td>2.64</td>
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<td>54</td>
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<td>11.4198</td>
<td>54</td>
<td>80</td>
<td>22.234</td>
</tr>
</tbody>
</table>

$^a$ is calculated according to Donega and Koole, (2009), $^b$ is calculated according to Pu et al. (2006) and Yu et al. (2003), $^c$ is calculated according to Williams et al. (1983) using Rhodamine 6G as standard considering its QY as 95% in absolute ethanol at room temperature
1.2.10. TEM, AFM and XRD studies

Morphology of CdTe\textsubscript{557} was studied using TEM AFM and XRD. TEM was carried out by placing a drop of colloidal solution dried on a 400-mesh carbon copper grid at an acceleration voltage at 200 kV. An AFM picture was taken in tapping mode on a molecular imaging system. AFM picture was scanned over an area of 5 x 5 µm on a mica slide spread with CdTe\textsubscript{557} using a cantilever of 4-8 µm thickness and a typical length of 125-225 µm at a resonant frequency of 190-300 kHz. Powder X-Ray diffraction (XRD) was measured on the dried powder sprinkled over glass slide in a Rigaku Miniflex X-ray diffractometer using rotating anode coupled with Cu-K\textalpha line (λ= 1.54 Å) operating at 30 kV output voltage. The 2θ scanning range was from -3° to +145°. The diffractograms were recorded between angles 6° and 80°.

1.2.11. Disposal of QDs

CdTe QDs were disposed after experiments by treating them in 10% potassium dichromate solution prepared in concentrated sulfuric acid as a general technique proposed by International Agency for Research on Cancer (IARC) for carcinogens. The solutions were kept for 2 days before draining them in running water (Montesano et al., 1979).
1.3. RESULTS AND DISCUSSION

1.3.1. Synthesis and functionalization of colloidal CdTe QDs

1.3.1.1. Growth of CdTe QD nanoparticles

CdTe QDs were synthesized in aqueous phase according to a general procedure of reacting transition metal with thiol-based stabilizer in presence of a chalcogen source. Generally nanoparticle growth depends on molar concentrations of precursors, capping material, pH and temperature of the medium. Initially at high temperature, the chemical transformation of precursors into monomers results in supersaturation. This in turn results in nanoparticle growth with the nucleation process followed by slower growth on the existing nuclei. Temperature being a critical factor allows rearrangement and annealing of atoms. During this process called “focusing”, initially all monomers will turn into smaller particles. As the monomer concentration drops below the critical concentration for nucleation, materials can only be added to the existing nuclei. At this distinct growth stage of “Ostwald ripening” smaller nanoparticles undergo dissolution and atoms are re-deposited on larger particles called as “defocusing” resulting in increase in the average nanoparticle size over time (Ge et al., 2008).

Since QDs are synthesized from organometallic precursors, they have no intrinsic aqueous solubility. The native coordinating organic ligands (capping agents) on the surface of QDs must either be exchanged or functionalized with a ligand that can impart both solubility and potential bioconjugation sites (Sapsford, et al., 2006). Ligands those form a capping layer on the surface of the QDs must be biocompatible as biomolecules and most of biological reactions except reactions involving lipids are highly
hydrophilic in nature. Therefore, MPA was used to stabilize the QD that impart biocompatibility and necessary functional carboxylic group for bioconjugation in aqueous medium. Initial Cadmium-thiol complex formation can be explained from the following equations. Sodium borohydride being a strong reductant reduces Te (equation 1.6).

\[
2\text{Te} + 4\text{NaBH}_4 + 7\text{H}_2\text{O} \rightarrow 2\text{NaHTe} + \text{Na}_2\text{B}_4\text{O}_7 + 14\text{H}_2\uparrow \quad (1.6)
\]

\[
\text{R-SH} + \text{OH}^- \rightarrow \text{SR}^- + \text{H}_2\text{O} \quad (1.7)
\]

\[
\text{Cd}^{2+} + 2\text{SR}^- \rightarrow \text{Cd(SR)}_2 \quad (1.8)
\]

\[
\text{Cd(SR)}_2 + \text{HTe}^- \rightarrow \text{CdTe} + \text{SR}^- \quad (1.9)
\]

During nanoparticle growth, thiolated ligands (R-SH) reversibly adsorb on to the surfaces of nanoparticles forming a capping layer. This stabilizes the nanoparticle size mediating their growth. Cd\(^{2+}\) ion reacts with thiolate ion (equation 1.7) to form a complex (equation 1.8), which strongly depends on the pH of the solution. The complex formation is more favorable at basic pH and is insoluble in acidic conditions as complexes may exist in a polymer state as reported by Gao et al. (1998). Thus, cadmium-thiol complex at high pH values further reacts with reduced tellurium ion promoting the growth rate of CdTe nanoparticles (equation 1.9) (Zou et al., 2008).

1.3.1.2. Coordination chemistry

Generally surface atoms which are decisive in the creation of highly luminescent nanoparticle bears all structural defects as they differ from the core atoms in coordination number and charge state. Therefore, capping agents containing hetero-atoms with the lone pair of electron are added to
stabilize the nanoparticles preventing them from aggregation. On the other hand, presence of an excess of uncoordinated Te atoms with free valencies diminishes luminescence. There are two possibilities of coordination for MPA with Cd\(^{2+}\). MPA forms complex with Cd\(^{2+}\) either by losing their -COOH proton or -SH proton binding to the same Cd\(^{2+}\) atom or two adjacent atoms (Zhang et al., 2006). MPA forms 6-membered planar ring if both S and one of the oxygen of the carboxylate bind to the same Cd\(^{2+}\) atom. On the other hand, it may form 8-membered ring if it coordinates with two adjacent Cd\(^{2+}\) atoms. Acar et al. (2009) has reported that thermodynamically most stable form is MPA coordinating with two adjacent Cd\(^{2+}\) atoms. However, thiol coordinated QDs possessing free -COOH functional group is the most preferred state aiming at bioconjugation studies.

1.3.1.3. Characterization of functionalized CdTe\(_{557}\)

CdTe\(_{557}\) was analyzed by FTIR spectroscopy equipped with KBr detector and KBr beam splitter. The FTIR spectrum showed an intense characteristic broad band at 3385 cm\(^{-1}\) corresponding to -OH stretching vibration, strong stretching vibration at 1566.4 cm\(^{-1}\) and medium stretching vibration for carboxyl group at 1404.6 cm\(^{-1}\). Disappearance of characteristic absorptions for -SH thiols, generally found at 2550-2600 cm\(^{-1}\), infers thiol coordinated CdTe QD formation. This confirms free carboxylic functional moiety in CdTe QD and coordination from thiol moiety of MPA. This also infers that –OH group is not involved in the coordination and is free to render biocompatibility to CdTe QD (Fig. 1.6).
Fig. 1.6 FTIR spectrum revealing thiol coordinated CdTe$_{557}$ nanoparticle having free -COOH moiety

A typical XRD pattern for the MPA-coated CdTe$_{557}$ was shown in Fig. 1.7. The powder XRD profile shows characteristic broad peaks of Zinc blende cubic CdTe due to small size of the nanoparticles (Zou et al., 2008). The reflections could be indexed to the (111), (220) and (311) planes of Zinc blende cubic CdTe (Chen and Yan, 2009; Duan et al., 2009).

Fig. 1.7 Typical XRD pattern of MPA-coated CdTe$_{557}$
Masumoto and Sonobe, (1997) reported that due to valence band degeneracy, Zinc-blende CdTe QD has got complicated excited quantized levels as the conduction band is made of the $s$ orbital of Cd and valence band is made of the $p$ orbital of Te. Temperature being a critical factor during nanoparticle growth determines the crystalline structure formation and thus, synthesis at low temperature always favors Zinc blende structure (Jose et al., 2004). However, it appears that bulk CdTe is known only in the Zinc blende form under ambient conditions possessing tetrahedral coordination of every atom (Ratcliffe et al., 2006).

1.3.2. Optical characterization of CdTe QDs

Photo-absorption and fluorescence studies revealed the synthesis of CdTe QDs. CdTe QDs with different emission peaks were synthesized under conditions of varying pH, different ratios of precursors and at different reaction time. Photo-absorption and fluorescence properties of these CdTe QDs revealed the effects of above parameters on their surface modification and crystal growth. Photo-absorption spectrum of QDs appeared as a series of overlapping peaks revealing the multiple energy states in these particles that allow the possibility of excitation at shorter wavelengths (Fig. 1.2).

1.3.2.1. Studies on surface stabilizing ligand (capping agents) on QD synthesis

Growth of QD may be controlled by tailoring the ratio of the concentration of precursors to that of stabilizing ligands. Generally high stabilizer concentration initially favors the formation of small nuclei and thus
smaller particles. Fig. 1.8 and 1.9 show the absorption and fluorescence spectra of CdTe QDs synthesized at different molar ratio of MPA respectively. Presence of first excitonic peak at lower wavelength indicates quantum confinement effect in these particles.

**Fig. 1.8** Effect of capping agent (MPA) concentration on photo-absorption spectra of CdTe QDs. (1) 0.07 M, (2) 0.08 M, (3) 0.04M, (4) 0.06 M, (5) 0.05 M, (6) 0.03 M and (7) 0.02 M

**Fig. 1.9** Effect of capping agent (MPA) concentration on fluorescence spectra of CdTe QDs. (1) 0.02 M, (2) 0.03 M, (3) 0.04M, (4) 0.05 M, (5) 0.06 M and (6) 0.07 M
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It was observed that effective molar ratios of 1:2:0.5, 1:2.5:0.5 and 1:3:0.5 (Cd²⁺:MPA:HTe⁻) resulted in CdTe QDs with better fluorescence quantum yield. Fluorescence was stronger for QD synthesized at 1:2.5:0.5 followed by 1:2:0.5, 1:3:0.5 respectively and weaker with gradual increase in the concentration of MPA. This could be due to an unfavorable environment created by surface crowding for surface construction and passivization. On the other hand, molar ratio of Cd²⁺:MPA below 1:2 fails to synthesize QDs. Reason could be surface defects resulting in non radiative couplings, as lower concentrations of MPA were not sufficient for proper surface coverage (Acar et al., 2009). In case of MEA, better fluorescence was obtained with effective molar ratios of 1:1.5:0.5 followed by 1:1:0.5. However, QDs synthesized with ME resulted in poor fluorescence and with PA there was no detectable fluorescence (Fig. 1.10).

![Graph showing effect of capping agent concentration on fluorescence intensity](image.png)

**Fig. 1.10** Effect of capping agent concentration on fluorescence intensity (RFU) of CdTe QDs
1.3.2.2. **Influence of reaction time on QD synthesis**

Temperature is one of the critical parameter during QD synthesis as it influences the reaction rate. QD size increases with increasing reaction time at high temperature due to increase in the rate of addition of precursors (Cadmium and Tellurium ions) into the existing nuclei. In general, temperature determines the critical size for the stable primary particles (Acar et al., 2009). Therefore, temperature must be high enough to allow the rearrangement and annealing of atoms during surface modification of primary particles. Further, time of refluxing allows QDs growth based on Ostwald ripening that reflects on photoluminescent properties of QD. Fig. 1.11 and Fig. 1.12 shows the evolutional fluorescence peak position of CdTe QDs synthesized at 100 °C at different refluxing period.

![Fluorescence spectra and homogeneity of CdTe QDs](image)

**Fig. 1.11** Effect of reaction time on fluorescence spectra and homogeneity of CdTe QDs
Fig. 1.12 Effect of reaction time on fluorescence intensity and FWHM of CdTe QD

There was a shift in the emission peak towards longer wavelength with prolonged refluxing period. Initial emission peak was observed at 522 nm after 15 minutes of refluxing that shifted to 633 nm after 360 minutes. Initially, there was a gradual increase in the luminescence intensity up to 120 minutes of refluxing that started decreasing slowly with continuous refluxing (Fig. 1.11). Moreover, FWHM that determines the homogeneity of QD growth was narrow up to 90 minutes and increased gradually with refluxing time (Table 1.2).
Table 1.2 Effect of refluxing time on CdTe QD growth and its optical properties

<table>
<thead>
<tr>
<th>Refluxing time (in minutes)</th>
<th>$\lambda_{ex}$</th>
<th>$\lambda_{em}$</th>
<th>RFU</th>
<th>FWHM (nm)</th>
<th>Stokes shift (nm)</th>
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It was observed that there was a visible change in the emission color of CdTe QDs (Fig. 1.13) that was ascribed to the electronic structure of nanoparticle resulting in a direct correlation between crystal size and band gap energy. It was reported by Acar et al. (2009) that surface adsorption-desorption might cause surface defects in nanoparticle resulting in
nonradiative combination of electron and the hole. Initial increase in the fluorescence could be due to generation of particles with small size resulting in increased electron transfer rates with better surface coordination (Acar et al., 2009; Li et al. (2007).

Fig. 1.13 Effect of reaction time on CdTe QD growth resulting in shift in coloration and emission wavelength towards red end of electromagnetic spectrum

However, desorption of MPA from QD surface might have left uncoordinated sites associated with Te atoms that has resulted in dangling bond, which act as hole traps. Thus, due to these surface defects CdTe QD emission was red shifted resulting in increased FWHM and loss of QY (Byrne et al., 2006). Stokes shift is also an important characteristic feature while determining the optical properties of QDs. Stokes shift in QDs generally depends on the thickness of surface capping material and quantum confinement effect that influences the absorption and the emission
wavelengths. Stokes shift is an additional observation due to frequency shifts during phonon emission that couples the fluorescence and absorption spectral profiles. Prolonged reaction time resulted in increased Stokes shift suggesting efficient electron-phonon coupling (Ipatova et al., 2001).

1.3.2.3. **Effect of pH on QD synthesis**

Nanoparticle growth also depends on pH values of the reaction medium as it influences the nucleation and stability of primary particles. Fig. 1.14 and Fig. 1.15 displayed the impact of pH on the photoabsorption and fluorescence properties of MPA capped CdTe QDs respectively. Cadmium ions react with MPA to form a complex whose solubility and stability depends on pH of the reaction medium. Initially, Cd\(^{2+}\)-MPA complex formed a white precipitate that was insoluble at lower pH. The complex found soluble above pH 4.0 but growth of CdTe QD was observed in presence of sodium hydrogen telluride only above pH 5.5. Fluorescence also strongly depends on the pH value of the reaction medium due to the possibility of structural changes on the surface. First excitonic peak and fluorescence was observed for CdTe QDs synthesized above pH 5.5 ± 0.2 with MPA. Intense excitonic peak and fluorescence was observed for QDs synthesized at pH 9 ± 0.2.
Fig. 1.14 Effect of pH on photo-absorption spectra of MPA capped CdTe QDs

Fig. 15 Effect of pH on fluorescence spectra of MPA capped CdTe QDs. 
(1) pH 5.5, (2) pH 6.5, (3) pH 7, (4) pH 8, (5) pH 9 (6) pH 10, (7) pH 11.5 and (8) pH 12
The wavelength at which both excitonic peak and fluorescence observed were almost narrower up to pH 9 ± 0.2 and shifted towards longer wavelength gradually after pH 9 ± 0.2. CdTe QDs synthesized at pH 11.5 ± 0.2 also showed intense fluorescence but QDs synthesized at pH 9 ± 0.2 were found to be more homogenous as FWHM was lesser compared to QDs synthesized at pH 11.5 ± 0.2 (Fig. 1.16 and Fig. 1.17).

**Fig. 1.16** Effect of pH on absorption at first excitonic peak of MPA capped CdTe QDs

**Fig. 1.17** Effect of pH on homogeneity (FWHM) of MPA capped CdTe QDs
Since QD was synthesized at basic pH coordination bond can occur only through thiol moiety as carboxylic acid do not ionize to carboxylate ion at basic pH due to its low pK values (Gao et al., 1998). It was reported that the coordination between the carboxyl groups and cadmium ions can effectively improve the photoluminescence (PL) efficiency of the CdTe nanoparticles by diminishing the nonradiative channel for electron-hole recombination (Zhang et al., 2003). However, coordination between the carboxyl groups and cadmium ions are not favorable for bioconjugation applications. Hence, to retain free carboxylic acid functional moiety necessary for bioconjugation applications CdTe QD has been synthesized at basic pH. The concentration of the cadmium-thiol complexes dramatically decreases as the pH of the solution decreases from a neutral to acidic range releasing free thiols and cadmium ions. Thus, excess MPA together with cadmium ions will form a shell around the surface of CdTe particles at acidic pH. Thus, increase in FWHM and diminished fluorescence suggests the influence of pH on nanoparticle surface.

Studies conducted with other capping agents such as MEA and ME exhibited difference in their optimum pH for QD synthesis. In case of MEA, maximum fluorescence yield was observed in the range of pH 5-6. However, stability of MEA capped QDs was not as good as MPA capped QDs which was in accordance with the earlier report by Gaponik et al. (2002). Whereas, fluorescence yield of ME capped QDs was poor (Fig. 1.10). Each type of capping agents has its own advantages and disadvantages, however considering the future bioconjugation work MPA was chosen as an ideal capping agent.
1.3.3. Size characterization of CdTe QDs by absorption and fluorescence profiles

The average particle size of CdTe QDs was determined from the absorption spectral 1s-1s electronic transition (Table 1.1). Size of each CdTe QD was calculated based on the empirical relation between size (diameter in nm) and respective band gap energy in eV given by Donega and Koole, (2009). Here energy of the wavelength (in eV) at first excitonic peak which is the lowest excited energy state or band edge absorption of respective CdTe QDs was considered as band gap energy. Size was also calculated based on the relation between band gap energy of CdTe bulk, CdTe synthesized, size in radius, reduced mass of electron/hole and exciton Rydberg energy, which accounts for spatial correlation between the excited electron and hole according to equation 2 given by Kayanuma, (1986 and 1988). Donega and Koole, (2009) have reported that equation 2 fails to quantitatively describe the size dependence because the effective Coulomb interaction and the self-polarisation energies are not properly evaluated. However, equation adequately describes the transition energy shifts in the strong confinement regime. Yu et al. (2003) has reported another polynomial relation between wavelength of the first excitonic peak (in nm) and size (diameter in nm) of CdTe QD that was also used to calculate the size of QDs synthesized. With respect to the above there was a shift in the first excitonic peak and fluorescence towards higher wavelength with decrease in band gap energy suggesting quantum confinement effect. More the band gap, higher will be the energy required for electrons to cross the energy barrier to attain excited conduction band region. Therefore, band edge absorption will be at lower
wavelength and particles will be smaller. On the other hand, smaller the band gap lesser will be the energy requirement for electrons and band edge absorption will be at higher wavelength suggesting bigger particles. This is because larger the QD size, energy levels will be more and are more closely spaced allowing the QD to absorb photons containing less energy. The particle size of CdTe QD synthesized were inversely proportional with band gap energy (Table 1.1). Thus, shift in the photo-absorption and fluorescence peak were correlated to the size of the material. This in turn depends on the band gap energy, which is determined by the quantum confinement contribution of the synthesized particle (Donega and Koole, 2009).

AFM and TEM revealed morphological characteristics and surface topological information of the CdTe surface structure. The height variation plot across wide-area AFM image showed even-sized particles (Fig. 1.18). 

![Atomic force micrograph of CdTe]
TEM has further confirmed the size and distribution of CdTe$_{557}$ and CdTe$_{601}$ that was calculated by mathematical equations based on observations of optical characteristics (Table 1.1). Both QDs appeared as spherical crystalline particles with a narrow size range of 3 ± 0.2 nm and well dispersed in aqueous medium without any aggregation (Fig. 1.19).

**Fig. 1.19** Transmission electron micrograph showing CdTe$_{557}$ (a & c), CdTe$_{601}$ (b) appeared as spherical crystalline particles with a narrow size range of 3 ± 0.2 nm and well dispersed in aqueous medium

### 1.3.4. FWHM and QY of CdTe QDs

FWHM that determines the homogeneity and purity of CdTe QDs synthesized was in the range of 45 nm to 80 nm. Fluorescence efficiency (QY) was also calculated in comparison with Rhodamine 6G. CdTe$_{557}$ whose band gap was 2.47 eV had a calculated QY of 33.046% and FWHM of 60 nm.
Therefore, CdTe\textsubscript{557} was selected for further work on bioconjugation studies. Although, FWHM for CdTe QDs emitting at 516 nm and 576 nm were in the expected range their QY were significantly low. However, QY of CdTe\textsubscript{523} (25.078\%) and CdTe\textsubscript{601} was satisfactory (22.234\%) but FWHM of CdTe\textsubscript{601} was considerably higher (80 nm). The average size of CdTe\textsubscript{601} was 3.06 nm as calculated (Table 1.1).

1.4. CONCLUSIONS

In brief, aqueous route of synthesis provided biocompatibility for QDs aimed at biosensing applications. CdTe QDs were synthesized at an effective molar concentration of 1:2.5:0.5 respectively for Cd\textsuperscript{2+}:MPA:HTe\textsuperscript{-} at pH 9 ± 0.2. CdTe\textsubscript{557} which was approximately 2.61 nm in size having band gap of 2.47 eV unveiled fluorescence quantum yield (QY) up to 33\% with a narrow spectral distribution. The powder X-ray diffraction profile elucidated characteristic broad peaks of zinc blende cubic CdTe nanoparticles with 2.5-3 nm average crystallite size having regular spherical morphology as revealed by transmission electron microscopy (TEM). Infrared spectroscopy confirmed disappearance of characteristic absorptions for -SH thiols inferring thiol coordinated CdTe\textsubscript{557} nanoparticles. Systematic investigations on photo-absorption and fluorescence studies revealed the effects of varying pH, molar ratios of precursors, nature of the surface ligands, temperature and reaction time playing a critical role on surface modification and crystal growth of CdTe QDs with diverse size having better luminescent properties. Thus, engineering the size and opto-physical characterizations of QDs are very much essential for their applications in biosensing and bioanalytical methods.
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Chapter 1


Synthesis and opto-physical characterization of CdTe quantum dots

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Chapter 1


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