Chapter 4

Templated synthesis of CdSe quantum dots in cationic and anionic surfactant based microemulsions: Tuning of photoluminescence and their morphology

4.1. Introduction

The application areas of microemulsions in the contemporary life have increased during the past decades.\(^2\), \(^5\), \(^{12}\), \(^{13}\), \(^{22}\) One such important area is the controlled synthesis of nanomaterials.\(^5\), \(^{14}\), \(^{22}\) There are a wide range of techniques based on physical\(^{147}\), \(^{233}\), \(^{234}\) and chemical methods,\(^{148-162}\) which have been developed for the preparation of nanomaterials. Among all the chemical methods, the microemulsion based synthetic technique is one of the most versatile and reproducible one, that allows control over the size and yield of nanoparticles with a narrow size distribution.\(^{235}\) Essentially, the water droplets inside the microemulsion act as a nanoreactor and provide a suitable environment for controlled nucleation and growth. The size of the core of these media can also be controlled by changing the water to surfactant ratio i.e. \(W_0\) values.

The synthesis of semiconductor nanoparticles and QDs has received extensive research interest in the recent years due to their morphology dependent optical and electronic properties.\(^{130}\), \(^{236}\) Owing to these promising functions and properties, colloidal
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Semiconductor nanocrystals have found numerous potential applications in optoelectronics, catalysis, sensing, and bio-labeling. As discussed in the introduction, CdSe, a group II–VI semiconductor, has medium band gap energy ($E_g = 1.75 \text{ eV}$), thereby providing a sort of model system to study the effect of morphology and surface composition on the optoelectronic properties of similar compounds. This is one of the important aspects in the synthesis/growth of the semiconductor nanomaterials vis-à-vis their applications.

After acquainting with the CTAB w/o microemulsions, the same system (CTAB/1-butanol/water/cyclohexane) was employed as a reaction media for the synthesis of CdSe QDs via normal as well as radiation chemical route. It is to be mentioned here that significant number of reports are available in the literature regarding the synthesis of CdSe nanostructures in anionic surfactant (mainly AOT) based w/o microemulsions. On the contrary, there are very few studies on the application of CTAB microemulsions for the templated synthesis of CdSe nanoparticles. This part of the present thesis is focused on two main objectives. The first one was to probe the role of the intrinsic structural dynamics of CTAB microemulsions at various $W_0$ values in influencing the morphology and the associated photoluminescent behavior of the CdSe QDs. The second objective was to investigate the effect of the fundamental differences in the structural and dynamical aspects of the AOT and CTAB microemulsions in directing the morphology, and the photophysical behavior of the QDs. Furthermore, the inherent features of the employed techniques on the optical properties of CdSe nanoparticles were also examined.
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Based on these objectives, the work carried out in this part of the thesis has been divided and described under two sections i.e. (i) Normal and (ii) Radiation chemical routes for the controlled synthesis of CdSe QDs in the host matrices of the w/o microemulsions.

4.2. Normal chemical route for the synthesis of CdSe QDs in CTAB based quaternary w/o microemulsions

4.2.1. Materials and Methods

High purity chemicals, cyclohexane, n-butanol (spectroscopic grade), cadmium sulphate (CdSO₄), sodium sulphite (Na₂SO₃) and selenium (Se) powder were obtained from Sigma-Aldrich and used without any further purification. CTAB, was purchased from Sigma-Aldrich, was re-crystallized twice from ethanol.¹¹ The stock solution of the Cadmium precursor i.e. ammoniated cadmium sulfate (Cd[NH₃]SO₄) with a concentration of 200 mM was prepared as follows.⁴⁰ 1.04 g of CdSO₄ was taken in a 25 ml flask and dissolved in 15 ml of nanopure water. Subsequently, 25% ammonia solution was added to it with the appearance of a milky white color till the solution turned colorless and transparent. The total volume of the solution was made to 25 ml with nanopure water.

This particular stock solution of Cd precursor was utilized to prepare different concentrations and can be called as solution A. The stock precursor solution for Se i.e. sodium selenosulphate (Na₂SeSO₃) was prepared by refluxing the solution containing 1g Se powder and 10 g Na₂SO₃ in 50 ml nanopure water at 70°C for 7 hours.⁴⁰ This solution can be called as B.
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After preparing the stock solutions of precursors (A & B) with different concentrations (50, 100 and 150 mM), the synthesis of the CdSe QDs was carried out by the following procedure. 0.1 M CTAB was added to cyclohexane and 1-butanol was added to this solution to achieve a 1-butanol/CTAB ratio of 5:1. Different volumes of aqueous solution containing equimolar precursors of Cd and Se i.e. solution A and B, respectively, were added to this system to obtain $W_0$ values of 20, 30 and 40. For example, preparing a 10 ml microemulsion of $W_0 = 20$, requires 360 $\mu$l of aqueous solution containing a mixture of solution A and B. Similarly, for preparing microemulsions (of 10 ml volume) with $W_0$ values of 30 and 40 requires aqueous solution of volume 540 and 720 $\mu$l, respectively. Subsequently, the as prepared microemulsions containing the precursor solutions inside the water pool were continuously stirred for about 1-2 hrs at room temperature. Since, microemulsions are dynamic in nature, inter-droplet collisions lead to the reaction between the precursors. The colorless microemulsion transformed into greenish yellow or light orange color after stirring, depending on the experimental parameters, and this sol was used for further studies. Scheme 4.1 shows the diagrammatic representation of the synthesis of CdSe QDs inside the CTAB w/o microemulsions.
4.2.2. Results and Discussion

4.2.2.1. Growth of CdSe nanoparticles in microemulsion and TEM microscopy

The microemulsions ($W_0 = 30$) containing the precursor solutions turned greenish yellow color after stirring for about 2 hrs at room temperature. The camera-ready pictures of the sols prepared in microemulsions are shown in the Fig.4.1.

**Fig.4.1.** Camera-ready pictures of CdSe sols prepared in microemulsions with $W_0 = 30$ and [stock precursor] = 50, 100, 150 mM, a) after 2 hrs, b) after 24 hrs and c) after a week from the time of mixing of the individual precursor solutions.
It was observed that the color of the sols were different for different concentration of precursors. It has been previously reported by our group that the mixture of the as employed precursors lead to the formation of CdSe.\textsuperscript{239} Nonetheless, it can be anticipated here that the CdSe nanoparticles would be formed inside the water pool of the microemulsions, as the precursors are in the aqueous phase.\textsuperscript{240, 241} The HRTEM images recorded from a freshly prepared CdSe nanoparticle sol in microemulsion of $W_0 = 20$ with [precursor] = 50 mM is shown in Fig.4.2a and b. The image in the inset of Fig.4.2b clearly shows the lattice fringes of CdSe nanoparticles, while the SAED pattern indicates their polycrystalline nature. Fig.4.2c shows the TEM image of CdSe nanoparticles sampled from the same sol after a time period of 1 week.

\textbf{Fig.4.2.} HRTEM images (a) and (b) of CdSe nanoparticles sampled from freshly prepared sol (microemulsion of $W_0 = 20$ and [stock precursor] = 50 mM) and TEM image (c) of nanoparticles sampled from the same sol after a time period of 1 week. Inset of image (b) depicts the SAED pattern and the lattice fringes of the nanoparticles.

It can be observed from the image Fig.4.2c that with aging, the CdSe QDs in the microemulsions exist in rather associated form instead of completely separated from each other, which could be due to the dynamic nature of the microemulsions.\textsuperscript{13}
4.2.2.2. UV-visible absorption spectroscopic study

The room temperature optical absorption spectra of the sols were recorded after 24 hrs of preparation and are shown in Fig.4.3.

Fig.4.3. Optical absorption spectra of CdSe nanoparticles synthesized at RT (a) in microemulsions of $W_0 = 20, 30, 40$ and a fixed [stock precursor] = 50 mM; (b) in microemulsions of $W_0 = 20$ and [stock precursor] = 50, 100, 150 mM.

It is a well established fact that the dimensions of the water pools are directly proportional to the $W_0$ values.$^{235, 238}$ Contrary to this, no significant shift in the excitonic peak position with the increase in the $W_0$ values of microemulsions for a fixed precursor concentration was observed (Fig.4.3a). However, a red shift can be noticed in the excitonic peak position with the increase in precursor concentration for a fixed $W_0$ value (Fig.4.3b). The band gap ($E_g$) values (listed in Table 4.1) were determined from the Tauc plot of $(\alpha' h\nu)^2$ vs. $h\nu$, as CdSe is a direct band gap semiconductor. The symbol ‘$\alpha$’ represents the term, ‘$\alpha c$’ where ‘$\alpha$’ is the absorption coefficient and ‘c’ is the concentration of the CdSe QDs. The values of ‘$\alpha$’ were determined from the absorbance
values, by using the relation, \( \alpha c = \frac{(2.303A)}{l} \), where A is the absorbance value and ‘l’ is the optical path length (10 mm). The term ‘\( hv \)’ represents the photon energy. The average size of the nanoparticles was determined from these \( E_g \) values using equation (4.1), which is the representation of the modified effective mass approximation model, as proposed by Brus (discussed in the introduction).\(^{242}\) Since, the excitonic peak is widely blue shifted from the bulk band gap value of CdSe (1.75 eV implies \( \lambda = 714 \) nm), which is an indication of strong confinement, the coulomb interaction between the electron and hole can be neglected.\(^{243}\) The average sizes of the primary nanoparticles estimated using modified Brus equation (4.1) have been listed in Table 4.1:

\[
E_g = E_g(0) + \frac{\alpha}{d^2}
\]  

where, \( \alpha = 3.7 \) eV nm\(^2\), \( E_g(0) = 1.75 \) eV, \( d = \) particle size (nm) and \( E_g = \) band gap value in eV. It can be seen that the size of initially formed CdSe nanoparticles are 2 to 3 nm in diameter within the water pool of the microemulsion. Furthermore, the variation of the size of the primary CdSe nanoparticles with the \( W_0 \) values is very less (Table 4.1).

However, contradictory results are present in the literature regarding the ability to control the particle size by varying the water pool size in CTAB microemulsions. Zhang \textit{et al.}\(^{244}\) prepared nanoparticles of size ranging from 4 to 8 nm with increasing \( W_0 \) values from 5.01 to 24.45 thus, indicating that the w/o microemulsion droplet can be utilized as a nanoreactor to restrict the growth of nanoparticles. On the other hand, Agastiano \textit{et al.}\(^{241}\) and others\(^{245}\) have shown that the size of the nanoparticles seems to be poorly correlated with the aqueous droplet dimension (i.e. \( W_0 \) values) in the quaternary microemulsion. Moreover, the dynamic nature of the CTAB microemulsions and the inefficient capping
by the surfactant are the probable reasons for the association of the nanoparticles with each other. The TEM images of the nanoparticles sampled from the freshly prepared sol (shown in Fig.4.2a & b) and that from a week old sol (shown in Fig.4.2c) clearly support the above statement.

Table 4.1 The band gap values (eV) and the size of the CdSe nanoparticles (nm) (shown in parentheses) synthesized at room temperature as determined from the optical absorption measurements.

<table>
<thead>
<tr>
<th>$W_0$ (mM)</th>
<th>20 (nm)</th>
<th>30 (nm)</th>
<th>40 (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>2.78 (1.8)</td>
<td>2.62 (2.0)</td>
<td>2.46 (2.2)</td>
</tr>
<tr>
<td>100</td>
<td>2.46 (2.2)</td>
<td>2.38 (2.3)</td>
<td>2.35 (2.4)</td>
</tr>
<tr>
<td>150</td>
<td>2.35 (2.4)</td>
<td>2.27 (2.5)</td>
<td>2.16 (2.8)</td>
</tr>
</tbody>
</table>

4.2.2.3. Photoluminescence (PL) study

4.2.2.3.1. Photo-excitation wavelength dependent photoluminescence

The steady-state PL spectra from the as prepared CdSe sols were recorded at room temperature. The excitation wavelength dependence PL spectra of one of the CdSe sols prepared in the microemulsion with $W_0 = 20$ and [stock precursor] = 100 mM, is shown in Fig.4.4. It can be seen that the nanoparticles exhibit two distinct PL bands, one with the peak position at 500 nm and the other with the peak position at 580 nm. The PL band with the peak at 500 nm gets converted to another band with the peak at 580 nm upon increasing the excitation wavelength from 380 to 480 nm, under identical conditions. This clearly indicates that with decrease in the excitation photon energy, the red shifted PL band dominates.
Fig. 4.4. Excitation wavelength dependent PL spectra along with the absorption spectrum of CdSe nanoparticles synthesized in microemulsion with $W_0 = 20$ and [stock precursor] = 100 mM. The arrows at the absorption spectrum indicate the excitation wavelengths for the PL spectra.

The present observation could not be correlated to the size distribution of the CdSe nanoparticles, as the average size of the primary nanoparticles was about 3 nm without much variation (see Fig. 4.2a). It is to be mentioned here that, this observation is quite different from the earlier study reported by Chandrasekharan et al.,$^{237b}$ where the emission maximum shifts from 490 to 610 nm upon increasing the $W_0$ value of the AOT microemulsion with a drastic reduction in the emission intensity at 490 nm. The PL band with the peak at 500 nm was assigned to the band gap PL (BG-PL) due to its close proximity from the excitonic absorption peak. The PL band with the peak at 580 nm can be attributed to the trap state PL (TS-PL) due to the large Stokes shift between the exciton absorption and the PL peak position. Based on these observations, a model for the photo-
excitation and the de-excitation processes occurring in these nanoparticles has been proposed, as shown in Scheme 4.2. When the energy of the excitation photon (a) is more than the band gap energy (E_g), then BG-PL dominates. When it is less than that of the E_g value i.e. (c), TS-PL predominates. However, for the excitation photon energy (b) close to the E_g value, both BG-PL as well as TS-PL appears with different proportions. Also, the overall PL intensity for this excitation photon energy was found to be higher.

**Scheme 4.2:** Diagrammatic representation of the photo-excitations and PL occurring in as synthesized CdSe nanoparticles in w/o CTAB microemulsions.

Thus, the tuning of the magnitude of either of the bands is possible in these nanoparticles. As it is shown in the Scheme 4.2, the BG-PL is obtained through the photo-excitation channels ‘a’ and ‘b’, whereas the TS-PL is obtained through the photo-excitation channels ‘b’ and ‘c’. The PL quantum efficiency (PLQE) of the CdSe nanoparticles was determined by using the standard reference, quinine sulfate (Φ = 0.55) dissolved in 0.5 M sulfuric acid and was found to be ~ 18%.
4.2.2.3.2. Precursor concentration dependent photoluminescence

The PL from the as synthesized CdSe nanoparticles in microemulsions with different \( W_0 \) values and precursors concentration was also recorded at room temperature. Fig.4.5 shows the PL spectra (\( \lambda_{\text{ex}} = 420 \text{ nm} \) and normalized at the TS-PL peak position of 580 nm) measured from the CdSe sols synthesized in microemulsions with a fixed \( W_0 = 20 \) and different [stock precursor] = 50, 100 and 150 mM.

![Fig.4.5. Room temperature PL spectra of CdSe nanoparticles synthesized in microemulsions with \( W_0 = 20 \) and [stock precursor] = 50, 100 and 150 mM normalized at the TS-PL peak position of 580 nm.](image)

It was observed that the magnitude of the BG-PL band does not change much with increasing the concentration from 50 to 100 mM but at 150 mM, we can see a drastic decrease in the band gap emission peak (at 500 nm), while the magnitude of the TS-PL increases with the increase in the precursor concentrations. This variation in the intensities of band gap and trap state emission peaks with the increase in the precursor
concentration could be attributed to the increase in the number of unsaturated selenium vacancies on the surface of CdSe nanoparticles. Although, equimolar precursors of cadmium and selenium were used, but due to the highly dynamic nature\(^{13}\) of microemulsions, it is possible that selenium rich surfaces reside on the CdSe nanoparticles, as here the capping agent is CTAB which is a cationic surfactant. Further support for this argument lies in the broad emission spectra (Fig.4.5), which usually originates due to the selenium vacancies.\(^{237b, 246}\) Thus, the magnitude of the PL bands could be tuned by controlling the concentration of the precursors used for the synthesis of nanoparticles.

### 4.2.2.3.3 Water pool size dependent photoluminescence

In another set of experiments, the CdSe sols were synthesized in microemulsions with different \(W_0 = 20, 30\) and 40 and a fixed \([\text{stock precursor}] = 50\ \text{mM}\). The PL spectra measured from these sols at room temperature with the excitation wavelength at 420 nm, normalized at the TS-PL peak position of 580 nm are shown in the Fig.4.6. It was observed that both the BG-PL and TS-PL bands were clearly visible in case of \(W_0 = 20\). However, for the other two \(W_0\) values, either of one is only prominent. BG-PL was more prominent for \(W_0 = 30\) whereas, TS-PL was more predominant in case of \(W_0 = 40\). The exact reason for this particular behavior is not clear.
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Fig. 4.6. Room temperature PL spectra of CdSe nanoparticles synthesized in microemulsions with $W_0 = 20, 30, 40$ and [stock precursor] = 50 mM normalized at the TS-PL peak position of 580 nm.

However, as seen from Table 4.1, the size of the CdSe nanoparticles poorly correlates with the dimensions of the water pool (i.e. $W_0$ values) in CTAB microemulsions. Therefore, the observed trend in the PL properties of CdSe nanoparticles with the $W_0$ values could probably be attributed to the variation in the shape of the nanoparticles.\textsuperscript{236b, 247} It is well established that the shape of water droplets in the CTAB microemulsions turns from spherical to cylindrical at very low water content.\textsuperscript{237a, 248} Essentially, the hydrophilic groups of surfactant molecules reassemble in order to maximize their contact with water, resulting into the formation of cylindrical droplets. As the water content increases, the preference for the cylindrical shape decreases. This is due to an increased hydrophilicity in the system, which favors the presence of relatively smaller sized water droplets separately instead of staying together. Therefore, the shape of water droplets
changes with the volume ratio of oil to water. Nevertheless, the same phenomenon has been envisaged during the synthesis of CdSe nanoparticles in CTAB based microemulsions via electron beam radiation, where the shape of nanoparticles changed from rods-to-cubes-to-spheres, on increasing the \( W_0 \) values from 10 to 40.\(^{41}\) Thus, the two PL peaks (Fig. 4.6) exhibited by CdSe nanoparticles synthesized in the CTAB microemulsion with \( W_0 = 20 \) may be due to their anisotropic shape.

Cantele \textit{et al.}\(^{249}\) on the basis of their calculation on semiconductor ellipsoidal QDs explained that the decrease in the degree of symmetry as well as the anisotropy effect can rupture the degeneracy leading to the splitting of the excited states of cylindrical or ellipsoidal shapes. In the present case, with the change in the \( W_0 \) value from 20 to 30, the BG-PL becomes more prominent. The most probable reason behind this could be the decrease in the shape anisotropy. The other contributing factor could be the better optimization of the parameters (such as water content and the surfactant-nanoparticles interactions) in terms of droplet shape and effective capping, which are resulting in predominantly band gap originated emission. While, in case of \( W_0 = 40 \), the TS-PL was found to be the major contributor in the emission spectra of nanoparticles (Fig. 4.6). At such high \( W_0 \) values, the interfacial film rigidity decreases and so, the intermicellar collisions would be more in that case, resulting in higher mass transfer between the droplets. At this stage, it can be anticipated that the surfactant may not be able to effectively cap the nanoparticles thereby, leading to the enhancement in the trap states as well as increase in the size polydispersity of the nanoparticles. Hence, the combination of these factors could be assigned for the broad emission observed for nanoparticles.
synthesized in microemulsion with $W_0 = 40$. Similar observations were obtained for the other concentrations of the precursors.

4.3. Radiation chemical route for the synthesis of CdSe QDs in microemulsions: A rapid and one step templated approach

In this methodology, CdSe QDs were synthesized inside the water pool of AOT based w/o microemulsions via electron beam irradiation technique (high dose rate). This hybrid approach possesses inherent advantageous features of radiation induced technique (discussed in Chapter-1) and is relatively new for the controlled synthesis of semiconductor nanomaterials. The interplay of different experimental parameters such as precursor concentration, absorbed dose and $W_0$ values of microemulsions were found to have interesting consequences on the morphology, PL, surface composition and carrier recombination dynamics of as grown QDs. Besides, the fundamental roles of the chemical nature of water pool and the interfacial fluidity of AOT microemulsions in influencing the photophysical properties of QDs were investigated by carrying out the similar study in CTAB based microemulsions.

4.3.1. Materials and Methods

AOT was obtained from Sigma-Aldrich. Other chemicals used were same as in the first part and are described in section 4.2.1. The precursors employed for the synthesis of CdSe QDs are same in the present methodology as employed in the earlier one i.e. $\text{Cd}([\text{NH}_3]_2\text{SO}_4$ and $\text{Na}_2\text{SeSO}_3$. However, the procedure for the preparation of their stock solutions in this particular case is slightly different in the sense that tert-butanol (1 M) was added to the precursor solutions of cadmium (labeled as solution A) and selenium
(labeled as solution B). The purpose of adding tert-butanol was to scavenge the OH radicals generated in the water pool of the microemulsion during the irradiation of the sample solutions. For preparing the microemulsion, 0.1 M AOT was added to hexane followed by the addition of aqueous solutions containing equimolar precursors of Cd and Se i.e. Solution A and B, respectively. Different volumes of required aqueous solutions were added to this system to obtain microemulsions with various $W_0$ values. The procedure for preparing CTAB based microemulsions have been explained earlier in section 4.2.1.

Various experimental parameters such as precursor concentration effect, $W_0$ value of the microemulsions (AOT and CTAB) and radiation dose were varied and their effect on the morphology and the photophysical properties of the as synthesized QDs were investigated. The microemulsions containing the precursors were freshly prepared and de-aerated by purging with N$_2$ just before the electron beam irradiation (7 MeV, FWHM = 2 μs, from LINAC) in each case. The absorbed dose per pulse was kept at 140 Gy and the samples were irradiated with repetitive electron pulses at 12 Hz.

The colorless microemulsion solutions immediately transformed into light green/orange color after the irradiation, depending on the experimental parameters, which indicated the formation of CdSe QDs and this sol was used for carrying out the optical studies. It is to be noted that the microemulsions are highly complex and dynamic systems, so all the optical measurements reported herein were carried out after 15 minutes and within 1-2 hours of the irradiation to facilitate better consistency and reliability in the results of various set of experiments. For carrying out other characterization studies (i.e.
SEM, XRD), the QDs were extracted from the microemulsion by breaking its structure on adding 5-10 drops of ethanol. Subsequently, the solution became turbid and was centrifuged to 9000 rpm. The precipitates were collected and washed for at least 3 times with nanopure water and ethanol.

4.3.2. Results and Discussion

4.3.2.1. Characterization and formation mechanism

Fig. 4.7A shows the typical XRD patterns of as synthesized CdSe QDs (in AOT microemulsions), immediately and at a time interval of 24 hours after electron beam irradiation. The spectrum recorded immediately after the irradiation shows a broad and noisy spectrum, which makes it difficult to identify the phase of the QDs. However, diffraction peaks consistent with the hexagonal structure (JCPDS file no. 08-0459) of CdSe could be seen in the XRD spectrum recorded at time duration of 24 hours after the irradiation. The lattice planes corresponding to the respective peaks have been marked in the spectrum.

HRTEM image showing the lattice fringes of as grown QDs have been shown in Fig.4.7B. The interplanar distance was found to be 0.25 nm, which matches well with the standard value of the interplanar distance of 0.255 nm for (102) plane of the hexagonal phase of CdSe. Furthermore, the appearance of rings in the SAED pattern (inset of image B) clearly indicates the polycrystalline nature of the as grown QDs.
Fig. 4.7. (A) XRD patterns of CdSe QDs (synthesized in AOT microemulsions) immediately (a) and 24 hours (b) after the irradiation; (B) HRTEM image of the QDs showing the lattice fringe pattern with the interplanar distance of 0.25 nm. Inset of image (B) depicts the SAED pattern of the corresponding QDs.

The plausible mechanism for the formation of the QDs in the host matrix of AOT microemulsions has been discussed as follows. The water pool of the microemulsion acts as a nanoreactor, comprising of Cd and Se precursors. It is to be noted that the formation of CdSe QDs took place only when the microemulsions containing the precursors were irradiated with the electron beam. Essentially, radiation-induced synthesis of nanomaterials in the aqueous phase is mainly preceded by the radiolysis of water.\(^3\)\(^-\)\(^5\) It is well known that the radiolysis of water generates three major primary radical species such as \(e_{\text{aq}}^-\) (aquated electron), \(\text{OH}^+\) and \(\text{H}^+\). Amongst these, \(e_{\text{aq}}^-\) and \(\text{H}^+\) are reducing, while \(\text{OH}^+\) is oxidizing in nature. Since, the \(\text{H}^+\) and \(\text{OH}^+\) are scavenged by adding tert-butanol (\(\text{CH}_3(\text{CH}_3)_2\text{COH}\)) to the aqueous phase therefore, the \(e_{\text{aq}}^-\) with a high redox potential (\(E_{\text{red}} = -2.9\) V) reduces the precursor ions thereby, resulting in the formation of nanoparticles.
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The radiolytic synthesis of CdSe nanoparticles in pure aqueous solutions has been previously reported by our group.\(^5\) The probable radiolytic reactions taking place during the formation of CdSe nanoparticles are mentioned below.

\[
\text{H}_2\text{O} \xrightarrow{\gamma} e_{aq}^-, \text{OH}^-, \text{H}^+, \text{H}_3\text{O}^+, \text{H}_2, \text{H}_2\text{O}_2 \tag{4.2}
\]

The radiolysis of oil phase (hexane in the present case) also generates electrons, which are scavenged by the water pool to form \(e_{aq}^-\).\(^{22,24}\)

\[
\text{OH}^-(\text{H}^+) + \text{CH}_3(\text{CH}_3)_2\text{COH} \rightarrow \cdot\text{CH}_2(\text{CH}_3)_2\text{COH} + \text{H}_2\text{O}(\text{H}_2) \tag{4.3}
\]

\[
e_{aq}^- + [\text{Cd(NH}_3)_4]^2+ \rightarrow \text{Cd}^{2+} \tag{4.4}
\]

\[
e_{aq}^- + [\text{SeSO}_3]^2- \rightarrow [\text{SO}_3]^2- + \text{Se}^- \tag{4.5}
\]

\[
\text{Cd}^{2+} + \text{Se}^- \rightarrow \text{CdSe} \rightarrow (\text{CdSe})_{\text{nanoparticles}} \tag{4.6}
\]

Such reactions taking place in the water pool of the microemulsions eventually lead to the formation of CdSe nanoparticles. Subsequently, the microemulsion itself acts as a shell for stabilizing these nanoparticles.

4.3.2.2. Optical studies

A systematic set of experiments were carried to fix the optimum dose of irradiation for the synthesis and it was observed that an absorbed dose of \(\sim 25\) kGy is sufficient for a complete transformation of precursor reactants into CdSe QDs. However, samples were irradiated with different absorbed doses to investigate its effect on the morphology and optical properties of the QDs.

4.3.2.2.1. Dose effect

While investigating the dose effect, the \(W_0\) value of the microemulsions and the precursor concentration were kept constant at 10 and 20 mM, respectively and the imparted dose
was varied from 10 to 50 kGy. Fig. 4.8a shows the absorption spectra of the sols irradiated at different radiation doses. No absorption was observed in case of unirradiated sols in the region 400-700 nm, which rules out the formation of CdSe QDs, whereas appearance of excitonic peaks can be clearly seen in the absorption spectra of irradiated sols.

**Fig. 4.8.** Absorption spectra (a) and Normalized room temperature PL spectra (b) of CdSe QDs synthesized in w/o AOT microemulsions via electron beam irradiation with variable absorbed doses at fixed precursor concentration (20 mM) and \( W_0 = 10 \). Inset of plot (a): Tauc plot for the determination of band gap values (\( E_g \)). Inset of plot (b): Plot showing the excitation wavelength independent PL spectra of CdSe QDs synthesized at an absorbed dose of 25 kGy.

The blue-shift in the excitonic peak with the increase in the absorbed dose indicates the decrease in the size of QDs. The band gap (\( E_g \)) values (listed in Table 4.2) were determined from the Tauc plot shown in the inset of Fig. 4.8a. The average size of the QDs was estimated from these \( E_g \) values using equation (4.1). Essentially, the droplets of microemulsions are kinetically unstable and involve continuous inter-droplet collisions followed by the mass transfer/or exchange in between them.\(^{4d, 250}\) This dynamic exchange
of material on one hand facilitates the growth process to take place after the nucleation stage induced by the electron beam irradiation; while on the other hand, it may lead to the changes in the particle size at different intervals of time. Nevertheless, the estimated sizes (listed in Table 4.2) unambiguously illustrates the trend in their sizes and band gap energy values, as all the measurements were carried out within the particular time frame (mentioned in the experimental section) to ensure the reproducibility and the reliability of the results. It can be clearly seen from Table 4.2 that the size of the QDs decreases with the increase in the absorbed dose. The observed trend can be explained on the basis that at higher absorbed doses, more number of nucleation centers are formed, which leads to the retardation of growth process. Similar results regarding the effect of dose on the size of the nanoparticles have been reported earlier by various researchers.251,252

The corresponding PL spectra of the CdSe QDs reflecting the effect of absorbed dose has been shown in Fig.4.8b. Interestingly, contrary to the absorption spectra, the as usual blue shift in the peak (with the decrease in the size of the QDs) is not emulated in the PL spectra. Although, there is a slight blue shift in the peak (see emission maxima values provided in Table 4.2) with increasing the absorbed dose from 10 to 25 kGy. But, there is a significant red shift in the peak position of the PL spectra on further increasing the dose to 50 kGy. This clearly indicates that the emission predominantly originates from the defects/trap states, as the surface states-assisted emission is independent (or has poor correlation) of the size of the QDs.253
Table 4.2: Various measurements i.e. band gap values ($E_g$, eV), size ($d$, nm), FWHM (nm), emission maxima ($\lambda_{\text{max}}$, nm), QE ($\eta$, %) and average lifetime ($<\tau>$, ns) values of CdSe QDs synthesized via electron beam irradiation with different combination of $W_0$ values, precursor concentrations and absorbed radiation dose.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Sample</th>
<th>Absorbed dose, kGy</th>
<th>Precursor conc., mM</th>
<th>Band gap value, $E_g$ (eV)</th>
<th>Estimated size, nm</th>
<th>Emission maximum, $\lambda_{\text{max}}$, nm</th>
<th>FWHM, nm</th>
<th>Quantum efficiency, $\eta$</th>
<th>Average lifetime, $&lt;\tau&gt;$, ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$W_0 = 5$, AOT ME</td>
<td>25</td>
<td>20</td>
<td>2.96</td>
<td>1.74</td>
<td>501</td>
<td>145</td>
<td>~ 9 %</td>
<td>44.1 ($\chi^2 = 1.1$)</td>
</tr>
<tr>
<td>2</td>
<td>$W_0 = 10$, AOT ME</td>
<td>10</td>
<td>20</td>
<td>2.32</td>
<td>2.52</td>
<td>548</td>
<td>122</td>
<td>~ 6 %</td>
<td>18.5 ($\chi^2 = 1.2$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>10</td>
<td>2.48</td>
<td>2.23</td>
<td>535</td>
<td>126</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>20</td>
<td>2.36</td>
<td>2.44</td>
<td>542</td>
<td>147</td>
<td>~ 8 %</td>
<td>37.7 ($\chi^2 = 1.1$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>30</td>
<td>2.18</td>
<td>2.89</td>
<td>580</td>
<td>179</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>20</td>
<td>2.54</td>
<td>2.15</td>
<td>569</td>
<td>169</td>
<td>~ 2 %</td>
<td>73.7 ($\chi^2 = 1.2$)</td>
</tr>
<tr>
<td>3</td>
<td>$W_0 = 15$, AOT ME</td>
<td>25</td>
<td>20</td>
<td>2.15</td>
<td>3.00</td>
<td>583</td>
<td>155</td>
<td>~ 4 %</td>
<td>25.6 ($\chi^2 = 1.1$)</td>
</tr>
<tr>
<td>4</td>
<td>$W_0 = 5$, CTAB ME</td>
<td>25</td>
<td>20</td>
<td>2.75</td>
<td>1.91</td>
<td>522</td>
<td>154</td>
<td>~ 0.2 %</td>
<td>2.7 ($\chi^2 = 1.3$)</td>
</tr>
<tr>
<td>5</td>
<td>$W_0 = 10$, CTAB ME</td>
<td>25</td>
<td>20</td>
<td>2.62</td>
<td>2.05</td>
<td>584</td>
<td>192</td>
<td>~ 0.8 %</td>
<td>6.8 ($\chi^2 = 1.2$)</td>
</tr>
<tr>
<td>6</td>
<td>$W_0 = 15$, CTAB ME</td>
<td>25</td>
<td>20</td>
<td>2.58</td>
<td>2.09</td>
<td>573</td>
<td>190</td>
<td>~ 1.1 %</td>
<td>8.2 ($\chi^2 = 1.1$)</td>
</tr>
</tbody>
</table>

Furthermore, it is to be noted here that the PL spectra is quite broad and extends from 450-800 nm region. The FWHM values were determined and have been listed in Table 4.2. In general, such broadening in the PL spectra of QDs can be rationalized by: (i) polydispersity in the size distribution\textsuperscript{254} or (ii) polydispersity in the density and the nature of distribution of trap/defect states leading to various recombination paths for the photogenerated carriers in the QDs.\textsuperscript{253b,255} Even though, the contribution of the first factor...
cannot be completely ruled out, the as grown CdSe QDs exhibits emission spectra with peak shifts independent of the excitation wavelength (shown in the inset of Fig.4.8b). Also, the polydispersity in this particular case was found to be only ~ 15 % (from TEM measurements, discussed later), which further suggests the major role of trap/defect states in the broadening of the PL spectra.

The quantum efficiencies (QEs) of the QDs synthesized with different absorbed doses were calculated and are listed in Table 4.2. As can be observed that the QDs synthesized with the optimum dose of 25 kGy exhibited highest QE of ~ 8 % followed by those synthesized with an absorbed dose of 10 kGy (~ 6%). This decline in the QE could be due to the insufficient amount of absorbed dose employed for the synthesis of QDs. Further, the least QE (~ 2 %) was obtained in case of QDs synthesized with the highest absorbed dose of 50 kGy. This could be due to the enhancement in the participation of non-radiative relaxation processes owing to the rise in density of the trap/defects of the QDs synthesized at higher absorbed doses. Therefore, it is imperative to optimize the absorbed dose for the synthesis of good quality nanomaterials.

The charge carrier dynamics of the QDs synthesized with different absorbed doses was investigated by measuring the time resolved PL decay using TCSPC at room temperature. The excitation and emission wavelengths were fixed at 374 and 550 nm, respectively. The PL decay curves of as synthesized QDs exhibited multi-exponential (tri-exponential) behavior (shown in Fig.4.9), which were analyzed and fitted using equation (4.7):

\[
I(t) = a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2} + a_3 e^{-t/\tau_3}
\]  

[4.7]
where, \( I(t) \) is the time-dependent emission intensity, ‘a’ is the amplitude, and ‘\( \tau \)’ is the lifetime. The average PL lifetime (\( <\tau> \)) values were deduced using equation (4.8) and have been listed in Table 4.2. The corresponding \( \chi^2 \) (represents the goodness of fit) values have been provided within the parentheses.

\[
<\tau> = \frac{\tau_1 a_1 + \tau_2 a_2 + \tau_3 a_3}{a_1 + a_2 + a_3} \tag{4.8}
\]

Such multi-exponential behavior of the CdSe QDs is widely known and has been reported earlier.\(^{256}\) Although, most of these reports attribute such behavior to the diverse recombination paths owing to the varying degree of size, shape, surface defects/energy traps between the individual nanocrystals. However, the origin and the explanation for this multi-exponential behavior still remain unclear and is currently a subject of debate.

**Fig.4.9.** Emission decay curve (\( \lambda_{ex} = 374 \text{ nm} \)) along with the IRF and the best fitted curve for CdSe QDs synthesized via electron beam irradiation with variable absorbed doses at fixed precursor concentration (20 mM), and \( W_0 = 10 \).
Nevertheless, the average lifetime values ($\langle \tau \rangle$) listed in Table 4.2 does provide an assessment about the excitonic dynamics and the nature of distribution of surface/trap states of as-grown CdSe QDs at various absorbed doses. The average lifetime representing the excitonic recombination increases with the enhancement in the radiation dose, which further substantiates the predominant contribution of trap/defect states in the photoluminescent behavior of the QDs (broadening of the PL spectra as well as the decline in the quantum efficiency) at higher absorbed doses. Indeed, this can be realized on deconvoluting the PL spectra of the QDs synthesized at different doses. Fig.4.10 shows the deconvoluted emission spectra at various doses. It can be noticed that at higher absorbed dose (25 kGy), the emission spectra in addition to the band gap emission (peak at 513 nm) comprises of contributions from defect/trap states. The nature of these trap states can be appraised from the appearance of peaks at 569 nm and 638 nm, which are widely shifted from the excitonic peak position and have been assigned to be originated from the shallow and deep trap states, respectively. Similarly, the broadening of the PL spectra obtained at dose of 50 kGy can be attributed to the principal contribution from the trap states.

These observations support the multi-exponential behavior of the QDs as well as the longer PL lifetime decay accompanied by the low quantum yields at higher absorbed doses. Nevertheless, it is being emphasized here that this aspect of the controlled induction of the surface/trap can contribute to the better understanding of the role of trapping sites on the dynamics of charge recombination processes, which eventually governs the efficiency of solar cell devices. 

256d
Fig. 4.10. Deconvoluted PL spectra of CdSe QDs synthesized in w/o AOT microemulsions via electron beam irradiation with an absorbed dose of 10 (a), 25 (b) and 50 kGy (c) at fixed precursor concentration (20 mM) and $W_0 = 10$.

4.3.2.2. Concentration effect

Fig. 4.11a shows the absorption spectra of irradiated sols with different precursor concentrations. The excitonic peak position red shifted with the increase in precursor concentration, which indicates an increase in the size of QDs.
Fig. 4.11. Absorption spectra (a) and Normalized room temperature PL spectra (b) of CdSe QDs synthesized in w/o AOT microemulsions via electron beam irradiation with variable precursor concentrations at fixed absorbed dose (25 kGy) and \( W_0 = 10 \). Inset of plot (a): Tauc plot for the determination of band gap values \( (E_g) \). Inset of plot (b): A representative de-convoluted PL spectrum of CdSe QDs synthesized in microemulsion of \( W_0 = 10 \) @ 25 kGy and precursor concentration = 30 mM.

The band gap \( (E_g) \) values were determined from the Tauc plot (inset of Fig. 4.11a) and the average sizes (listed in Table 4.2) of the QDs were estimated by using equation (4.1). Similar type of experiment (precursor concentration was varied keeping other parameters constant) was performed in our earlier work\(^43\) wherein the CdSe QDs were synthesized in CTAB based w/o microemulsions. It was found that the excitonic peak shift was nominal with an increase in the precursor concentration and the same was correspondingly reflected in the size values of the QDs. Such contrasting observations in the two cases (AOT and CTAB w/o microemulsions) could be explained on the basis of the interfacial rigidity/or fluidity. It has been mentioned earlier (in the introduction) that contrary to the AOT microemulsions, the CTAB microemulsions are more dynamic and flexible in
nature, which lead to the distribution of the primary nanoparticles, thereby minimizing the effect of precursor concentration in the later case.

The PL spectra of the QDs demonstrating the effect of precursor concentration have been shown in Fig.4.11b. It could be seen that the PL peak position shifts to the red side with an increase in the precursor concentration, which is in agreement with the QDs size variation as was indicated by the absorption spectral studies. However, this increase in the average size of the QDs was also accompanied with higher FWHM values (listed in Table 4.2). The peak position was found to be independent of the excitation wavelength. Unlike other synthetic methodologies, large amount of energy is dumped within a small fraction of time in the electron beam irradiation technique (e.g. only a time duration of 15 seconds is required for imparting a dose of 25 kGy). Consequently, it could lead to the formation of large amount of nuclei instantaneously. The small nuclei at this juncture possess high surface energy (involving unsatisfied valencies/or dangling bonds and surface defects) and subsequently leading to aggregation followed by the growth process. Moreover, higher precursor concentrations would be accompanied by correspondingly higher amount of nucleation in the present scenario. Apparently, the growth process would lead to various amounts and types of defects including surface as well as deep trap states. This is indicated by deconvoluting the PL spectrum of QDs (synthesized by employing precursor concentration of 30 mM) shown in the inset of Fig.4.11b. The peak 1 (535 nm) represents band gap emission, while peaks 2 (590 nm) and 3 (667 nm) could be attributed due to the defects involving surface as well as deep trap states. Therefore, the broadening in the PL spectra (with increase in the precursor concentration) could be attributed to the
differences in the density and distribution of trap states accompanied by a possible contribution from the polydispersity in the particle size.

### 4.3.2.2.3. \( W_0 \) effect

It is one of the most important parameters to characterize and manipulate the water pool size as well as the fluidity of the interface of microemulsions (as discussed in Chapter 1). Considering this, the \( W_0 \) values of the microemulsions were varied from 5 to 15, while keeping the precursor concentration and absorbed dose constant at 20 mM and 25 kGy, respectively. Fig.4.12a shows the absorption spectra of the irradiated sols representing the significant red shift in the excitonic peak position (of CdSe QDs) with the subsequent increase in the \( W_0 \) values of the AOT microemulsions. This indicates an increase in the average size of the QDs, which was determined by using the Brus equation (4.1).

**Fig.4.12.** Absorption spectra (a) and Normalized PL spectra (b) of CdSe QDs synthesized in w/o AOT microemulsions via electron beam irradiation with variable \( W_0 \) values at fixed absorbed dose (25 kGy) and precursor concentration (20 mM). Inset of plot (a): Tauc plot for the determination of band gap values \( (E_g) \).
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The band gap ($E_g$) and the average size values of the QDs as determined are listed in Table 4.2. It is to be mentioned here that the QDs synthesized in microemulsion with $W_0 = 5$ were found to be ultrasmall (i.e. $d \sim 1.7$ nm). Moreover, the excitonic peak in this particular case appeared at $\sim 400$ nm, which is very close to the band-edge absorption peak (408 nm) of ultrasmall CdSe nanocrystals reported by Dukes et al.\textsuperscript{253} Generally, ultrasmall nanocrystals are defined as those which are having a diameter of less than 2 nm.\textsuperscript{253, 257} Such nanomaterials have recently become an active area of research as they own very interesting properties (that differ considerably from those of larger nanocrystals) such as quantized (sequential) growth,\textsuperscript{258} size-independent emission spectrum\textsuperscript{253, 257} and white light emission.\textsuperscript{259}

In analogy with the absorption spectral measurements, the PL peak positions also red shifted with the subsequent variation in the $W_0$ values of the microemulsions (see Fig.4.12b). In fact, the observed tunability in the PL spectra can be realized from the periodic variation of $\sim 40$ nm in the maximum peak positions (listed in Table 4.2) with the step wise increase in the $W_0$ values from 5 to 15. This can be clearly visualized from the photos of the CdSe QDs taken in a UV chamber, as shown in Fig.4.13.

Indeed, the as displayed tunability in the photoluminescent behavior of these QDs clearly signifies their potential applications in light emitting devices (especially, white light emitting diodes i.e. WLEDs).
Fig. 4.13. Camera ready picture of vials containing CdSe QDs synthesized in AOT microemulsions with variable $W_0$ values [$W_0 = 5$, Bluish-white color (a); $W_0 = 10$, greenish-yellow color (b); $W_0 = 15$, reddish-orange color (c)] via electron beam irradiation at fixed absorbed dose (25 kGy) and precursor concentration (20 mM).

The nature of the light emitted by as grown QDs under various conditions has been listed in Table 4.3 along with their respective CIE (Commission Internationale d’Eclairage) x, y co-ordinates.

Table 4.3: CIE chromaticity co-ordinates along with the nature of the light emitted by CdSe QDs synthesized in AOT microemulsions via electron beam irradiation under various experimental conditions.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Sample</th>
<th>Absorbed dose, kGy</th>
<th>Precursor conc., mM</th>
<th>CIE x, y co-ordinates</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$W_0 = 5$, AOT ME</td>
<td>25</td>
<td>20</td>
<td>0.20, 0.27</td>
<td>Blue-white light</td>
</tr>
<tr>
<td>2</td>
<td>$W_0 = 10$, AOT ME</td>
<td>25</td>
<td>10</td>
<td>0.25, 0.38</td>
<td>Cyan light</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>20</td>
<td>0.34, 0.44</td>
<td>Green-yellow light</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>30</td>
<td>0.37, 0.46</td>
<td>Yellow-green light</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>20</td>
<td>0.44, 0.49</td>
<td>Yellow-orange light</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>20</td>
<td>0.43, 0.45</td>
<td>Orange-yellow light</td>
</tr>
<tr>
<td>3</td>
<td>$W_0 = 15$, AOT ME</td>
<td>25</td>
<td>20</td>
<td>0.42, 0.46</td>
<td>Yellow light</td>
</tr>
</tbody>
</table>
Chapter 4

The electron beam mediated synthesis of CdSe QDs has been represented in Scheme 4.3 along with the chromaticity diagram illustrating the optical tunability achieved by varying the different experimental parameters.

Scheme 4.3: Diagrammatic representation of the electron beam assisted synthesis of CdSe QDs in the host matrix of AOT microemulsions and the PL tunability displayed by the QDs as shown in the chromaticity diagram at various experimental conditions.

However, the QE of the QDs was found to decrease with the increase in the $W_0$ values, (see Table 4.2) and the highest QE of ~ 9 % was obtained for QDs synthesized in microemulsion with $W_0 = 5$, while it decreases to ~ 4 % in case of microemulsion with $W_0 = 15$. The polydispersity in size distribution was found to be ~ 12 % for $W_0 = 5$, which slightly increased to ~ 15 % and ~ 16 % for higher $W_0$ values of 10 and 15, respectively (size distribution plots shown in the inset of Fig.4.14). Thus, the main reason for the above decline in QE (with increase in the $W_0$ values) has been attributed to the increase in the number of trap/defects states.
Fig. 4.14. TEM images of CdSe QDs synthesized in AOT microemulsions with $W_0 = 5$ at different time intervals: immediately (a) and at time duration of ~ 12 hours (b) after irradiation. Images (c) and (d) represents CdSe QDs synthesized in AOT microemulsions with $W_0 = 10$ and 15, respectively at time duration of ~ 12 hours, after irradiation. Inset in the images (b), (c) and (d) shows the corresponding size distribution plot of the nanoparticles at respective $W_0$ values of microemulsions. The other experimental parameters are: [precursor] = 20 mM, absorbed dose = 25 kGy.

In fact, the increase of defects (at higher $W_0$ values) comprising of energetically distributed trap states (i.e. shallow and deep) could be substantiated from the appearance of several peaks in the deconvoluted PL spectra (shown in Fig. 4.15) at higher wavelength regions.
Fig. 4.15. Deconvoluted PL spectra of CdSe QDs synthesized in w/o AOT microemulsions via electron beam irradiation with variable $W_0$ values i.e. 5 (a), 10 (b), 15 (c) at fixed precursor concentration of 20 mM and absorbed dose of 25 kGy.

Basically, at higher $W_0$ values, the rigidity of the interface decreases, thereby resulting into the increased inter-droplet exchange of material.$^{4d, 250}$ Under such conditions, the augmented amount of trap/defects and the polydispersity in the size distribution of the QDs could be anticipated. This is further evidenced from the increasing trend of the FWHM values (obtained from the PL spectra and have been listed in Table 4.2) for the QDs synthesized in microemulsions with higher $W_0$ values.

However, contrary to the AOT microemulsions, the QDs size (as well as the photoluminescent properties) and the $W_0$ value was poorly correlated in case of CTAB
based quaternary w/o microemulsions, as reported earlier. Similar results were observed by Curri *et al.* and others in which the size of semiconductor nanoparticles could not be correlated well with the aqueous droplet dimension (represented by the \( W_0 \) value) of quaternary microemulsions. Fig. 4.16a clearly shows the marginal changes in the excitonic peak positions with the subsequent increase in the \( W_0 \) values (of CTAB microemulsions), especially above \( W_0 = 5 \). This can be further realized from the band gap energy values (determined from the Tauc plot, shown in the inset of Fig. 4.16a) and the estimated average size (using equation 4.1) of the QDs listed in Table 4.2. Analogous to the absorption behavior, minor shift was observed in the peak positions of the PL spectra (shown in Fig. 4.16b) with variation in the \( W_0 \) values of CTAB microemulsions. These observations clearly reflect the difference in the interfacial rigidities of the two microemulsion systems.

![Fig. 4.16. Absorption spectra (a) and Normalized PL spectra (b) of CdSe QDs synthesized in w/o CTAB microemulsions via electron beam irradiation with variable \( W_0 \) values at fixed absorbed dose (25 kGy) and precursor concentration (20 mM). Inset: Tauc plot for the determination of band gap values (\( E_g \)).](image)
On comparing the same $W_0$ values, the FWHM values (see Table 4.2) determined from the PL spectra of the QDs synthesized in CTAB microemulsions are higher than those in case of AOT microemulsions. Considering the negligible excitonic peak shifts with the increase in the $W_0$ values, the polydispersity in the size distribution cannot be the predominant factor behind the higher FWHM values (obtained in case of CTAB microemulsions), as has also been explained earlier.\textsuperscript{43} However, polydispersity in the density and distribution of the trap/defect states in CdSe QDs synthesized in CTAB microemulsions might be assigned as the main rationale behind the broadening of the PL spectra. Keeping aside the case of $W_0 = 5$, the estimated average size of the QDs grown in CTAB microemulsions was found to be less than the average size of QDs synthesized in AOT microemulsions. Therefore, the amount of surface states would be more in the former case. Further, it was observed that after 24 hours, agglomeration of the QDs (synthesized via electron beam irradiation) takes place in CTAB microemulsions, thereby rendering them less stable. On the other hand, no such phenomenon was noticed in case of CdSe QDs grown in AOT microemulsions. One of the most striking differences between the QDs synthesized in CTAB and AOT microemulsions is their QEs. The QDs synthesized in the former case shows poor QE, as can be seen from Table 4.2. At this stage, it is important to point out the differences in the molecular structures of CTAB and AOT (shown in Chapter 1). The former one is linear and require a cosurfactant to form microemulsions, while later has a branched double-chained structure which facilitates molecules to pack together to form microemulsions without the involvement of any cosurfactant. Taking into account of QEs, it can be anticipated that the nanosized
templating cages present in AOT microemulsions provide better encapsulation for the QDs as compared to those of CTAB based microemulsions. Furthermore, it is to be mentioned that unlike the case of AOT microemulsions, the QE of the QDs grown in CTAB microemulsions increases with increase in the \( W_0 \) values. This indicates towards the difference in compositions (or the chemical nature) of the water pool environments prevailing in the CTAB and the AOT microemulsions. In CTAB microemulsions, the bromide ion (\( \text{Br}^- \)) being the counter ion resides inside the water pool with high molar concentrations, thereby acting as a quencher.\(^{21}\) This is also regarded as heavy ion effect and results in lower quantum yields.\(^1\),\(^{260}\) Therefore, the observed increase in the QEs of the QDs (synthesized in CTAB microemulsions) with the \( W_0 \) values could be explained from the fact that the concentration of bromide ions and their proximity from the QDs would be relatively lower at larger water pool sizes.

Apart from the quantum yields, the heavy atom halides (mostly bromide and iodide) have also been reported to shorten the lifetime of fluorophores.\(^1\) Indeed, a very profound and contrasting influence was observed wherein the average lifetime values, \(<\tau>\) exhibited by the QDs synthesized in case of CTAB microemulsions were found to be at least 3 times lower (considering same \( W_0 \) values) as compared to those grown in AOT microemulsions. To the best of our knowledge, the contrasting influence of cationic and anionic surfactant based microemulsions on the PL lifetime of CdSe QDs has not been reported earlier. Fig.4.17 shows the emission decay curves (\( \lambda_{\text{ex}} = 374 \) nm) for CdSe QDs synthesized in CTAB and AOT microemulsions with variable \( W_0 \) values at fixed precursor concentration (20 mM) and absorbed dose (25 kGy).
Fig. 4.17. Emission decay curve \((\lambda_{ex} = 374 \text{ nm})\) along with the IRF and the best fitted curve for CdSe QDs synthesized via electron beam irradiation in CTAB and AOT microemulsions with variable \(W_0\) values at fixed precursor concentration (20 mM) and absorbed dose (25 kGy).

The PL decay curves exhibited multi-exponential behavior and were analyzed using equation (4.7). The average lifetime values \(<\tau>\) have been listed in Table 4.2. A good correlation between the lifetime and the QE of the QDs was observed. CdSe QDs with high QEs synthesized in either of the microemulsions were found to have higher average PL lifetime values. The QDs synthesized in AOT microemulsions with \(W_0 = 5\) had smallest size, highest QE and longest lifetime of 44.1 ns. Since, the QDs were ultrasmall and the presence of surface states can be realized from the deconvoluted PL spectrum shown in Fig.4.15a. Evidently, the long PL lifetime could be attributed to the surface state assisted recombination process of charge carriers.\(^{261,262}\) However, QDs synthesized
at higher $W_0$ values (of AOT microemulsions) exhibit lower QEs indicating the enhancement in the non-radiative relaxation processes, which further resulted in shorter PL lifetime (as compared to the case of AOT microemulsion with $W_0 = 5$). Apart from this, the PL decay trace recorded at 600 nm showed much slower PL decay ($<\tau> = 74$ ns) as compared to that measured at 550 nm ($<\tau> = 37.7$ ns). Evidently, this shows the higher contribution of surface states in the relaxation dynamics, since the band edge charge carrier recombination rate is faster than that taking place at surface states.\textsuperscript{261, 263}

Nevertheless, the shortest PL lifetime, $<\tau> = 2.7$ ns was observed in case of QDs grown in CTAB microemulsions with $W_0 = 5$. On increasing the $W_0$ values, the PL lifetime was found to increase (Fig.4.17) (see Table 4.2). Similar to the trends of QEs (for the QDs grown in CTAB microemulsions), the PL lifetime behavior can be explained primarily on the basis of the halide ion effect (discussed earlier).

Furthermore, as indicated from the absorption spectra, the variation in the $W_0$ values of AOT microemulsions was found to have substantial influence on the morphology of the CdSe QDs. TEM images recorded at later stages of the growth process revealed the formation of nanorods, as shown in Fig.4.18. The aspect ratio of the rods was determined and has been listed in Table 4.4. It is to be mentioned here that the values presented represents the average aspect ratio of many such rods examined during the TEM measurements. So, the nanorods shown in Fig.4.18 may appear to have different aspect ratios.
Fig. 4.18. TEM images showing CdSe nanorods synthesized in AOT microemulsions with variable $W_0$ values of 5 (a); 10 (b); 15(c) via electron beam irradiation at fixed absorbed dose (25 kGy) and precursor concentration of 20mM. The images were taken at ~ 12 hours after irradiation of the sols.

Nonetheless, the aspect ratio of the nanorods decreases with the increase in the $W_0$ values of AOT microemulsions. The reason for this observation is probably the following. Microemulsions formed of ionic surfactants undergo structural transitions from rod-to-sphere as a function of water content and thus, the water pool size. At lower $W_0$ values (generally for $W_0$ values $\leq 10$), the amount of free water is negligible or very less, which enables the ionic surfactants to re-orient themselves into cylindrical or rod shapes in order to acquire maximum contact with the aqueous polar phase. While, cylindrical (or rod) to spherical shape transition takes place for higher $W_0$ values (generally for $W_0$ values $\geq 10$) as the amount of free water in the water pool increases, which is further accompanied by the subsequent rise in the bulk water characteristics. Similar type of shape tuning from rods-to-cubes-to-spheres has been reported by our group during the synthesis of CdSe QDs in CTAB based microemulsions on increasing the $W_0$ values (from 10 to 40).
Table 4.4: Aspect ratio of CdSe nanorods grown in AOT microemulsions with variable \( W_0 \) values via electron beam irradiation at fixed absorbed dose (25 kGy) and stock precursor concentration of 20 mM.

<table>
<thead>
<tr>
<th>S. No</th>
<th>AOT MEs</th>
<th>Aspect ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( W_0 = 5 )</td>
<td>20 ± 2</td>
</tr>
<tr>
<td>2</td>
<td>( W_0 = 10 )</td>
<td>13 ± 1</td>
</tr>
<tr>
<td>3</td>
<td>( W_0 = 15 )</td>
<td>7 ± 1</td>
</tr>
</tbody>
</table>

Another interesting aspect is the initial formation of quasi-spherical QDs, which self-assemble into nanorods. This was evident from the TEM and SEM images of the QDs recorded at different time intervals. The TEM image shown in Fig.4.14a illustrates the formation of quasi-spherical shaped CdSe QDs (synthesized in AOT microemulsions with \( W_0 = 5 \); [precursor] = 20 mM@ 25 kGy) and was recorded immediately after the electron beam irradiation. The image shown in Fig.4.14b was recorded after ~ 12 hours of irradiation and represents the self-assembling of primary QDs into rod like anisotropic structures. Similar growth mechanism was observed in case of other \( W_0 \) values. Fig.4.19 shows the TEM images at different magnifications and regions of the grid demonstrating the self-assembling of CdSe QDs.
Fig.4.19. TEM images at different magnifications and regions of the grid showing the self-assembling of CdSe QDs (synthesized in AOT microemulsions with $W_0 = 10$, [precursor] = 20 mM @ 25 kGy) into rod shaped structures. The images were recorded at time intervals of ~ 6 hours after the electron beam irradiation.

Some more TEM images of nanorods comprising of CdSe QDs have been provided in Fig.4.14 c & d. Apart from these, SEM images shown in Fig.4.20 further confers the aforementioned transformation of quasi-spherical shaped (or globular shaped, image (a)) CdSe QDs into nanorod-like structures (image (b)).
Fig. 4.20. SEM images showing the transformation of globular shaped (a) CdSe nanoparticles (formed initially after the irradiation) into nanorod like structures (b). The experimental parameters are: \( W_0 = 10 \), [precursor] = 20 mM, absorbed dose = 25 kGy.

4.4. Conclusions

CdSe nanoparticles were synthesized in CTAB based quaternary w/o microemulsions under purely ambient conditions without any external reducing/stabilizing agents. It was observed that the water pool dimensions have poor correlation with the size of the as grown nanoparticles. However, photoluminescent properties of the nanoparticles were found to vary with the \( W_0 \) values of the CTAB microemulsions. This was attributed to the probable variation in the shape of the nanoparticles. The nanoparticles exhibited excitation wavelength dependent PL spectra and the ratio of BG-PL and the TS-PL could be tuned by varying the precursor concentrations and the \( W_0 \) values. On the contrary, the PL properties displayed by CdSe nanoparticles synthesized in CTAB based microemulsions via electron beam irradiation technique were predominantly originated from the trap states. A comparison between the two methodologies (i.e. normal and
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radiation chemical routes) for the synthesis of CdSe nanoparticles in CTAB microemulsions has been shown below.

<table>
<thead>
<tr>
<th>NORMAL chemical route</th>
<th>RADIATION chemical route</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Both BG-PL and TS-PL were observed</td>
<td>1. Predominantly TS-PL was observed</td>
</tr>
<tr>
<td>2. Excitation wavelength dependent PL spectra was obtained</td>
<td>2. Excitation wavelength independent PL spectra was obtained</td>
</tr>
<tr>
<td>3. Slower approach &amp; requires 2-3 hours</td>
<td>3. Very fast; synthesis can be done in seconds</td>
</tr>
</tbody>
</table>

The comparative study conducted to investigate the influence of the structural and dynamical aspects of AOT and CTAB microemulsions on the morphology and photophysical properties of the CdSe QDs showed profound and contrasting results, as shown below.

<table>
<thead>
<tr>
<th>CdSe QDs synthesis in CTAB microemulsions</th>
<th>CdSe QDs synthesis in AOT microemulsions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Poor correlation between the size of the QDs and the $\eta_0$ values</td>
<td>1. Good correlation between the size of the QDs and the $\eta_0$ values</td>
</tr>
<tr>
<td>2. Less stable and weakly photoluminescent; Maximum QE, $\eta \sim 1 %$</td>
<td>2. Relatively more stable and photoluminescent; Maximum QE, $\eta \sim 9 %$</td>
</tr>
<tr>
<td>3. Ultrasmall QDs (size &lt; 2 nm) could be grown but difficult to stabilize due to agglomeration.</td>
<td>3. Blue light emitting ultrasmall QDs obtained and stabilized</td>
</tr>
<tr>
<td>4. Average PL lifetime less</td>
<td>4. Average PL lifetime values are relatively more</td>
</tr>
</tbody>
</table>

The interplay of different experimental parameters such as precursor concentration, absorbed dose, $W_0$ values and nature of the surfactant of the microemulsions facilitated the maneuvering of the morphology, PL, surface composition and carrier recombination
dynamics of as grown CdSe QDs. Taking into account of the broad PL spectra, the as grown QDs may have potential applications in WLEDs, which can also be realized from their CIE x, y co-ordinates. Apart from this, the less reported fundamental role of the chemical nature of water pools (i.e. nature of surfactant and its counter ions) and the interfacial fluidity of microemulsions in influencing the photophysical properties of QDs has been illustrated in this chapter. These results emphasize the judicial selection of the host matrix (or the template) in the synthesis of QDs.