“This chapter is dedicated to the fabrication of QDSSC using pre-synthesized ZnO nanoparticles, CdS and CdSe QDs. Section - A describes the fabrication and characterization QDSSC using CdS as sensitizer and Section - B discusses the same using CdSe QDs as sensitizer. Effect of QD size on the performance of QDSSC is also studied. An Energy level diagram of the QDSSC is depicted to understand the working of the cell efficaciously.”
5.1 Introduction

QDSSCs have attracted extensive interest as a means of fabricating highly efficient, stable and low cost PV device because of the tuneable bandgap of the QDs [1]. From the last few decades, most of the research in the field of solar energy is focused on DSSCs in which the problem of wastage of photon energy above the difference between LUMO and HOMO energies is dominant, because one photon gives rise to one exciton only and rest of the energy contained in the photon is wasted as heat [2-5]. QDs have specific advantages over dyes to be used as sensitizers in DSSCs. It is observed that if dye in DSSC is replaced by QDs, then the energy contained in a photon can be fully utilized because in QDs single photon gives rise to multiple excitons [6, 7]. As discussed in earlier chapters also, this effect is known as MEG effect. The production of multiple excitons by a single photon in quantum confined systems may improve the efficiency of solar cells. Researchers have already accomplished the production of 2 or more excitons per photon with energy greater than the bandgap in a PbSe QD based system [8].

However, in spite of the fact that different sized (different bandgap) QDs are available, the energy conversion efficiency of QDSSCs is still low. The less conversion efficiency of the QDSSCs may be due to the difficulty of embedding the QDs into the mesoporous ZnO structure. Another problem is the selection of efficient electrolyte in which the QDSSC can function without degradation. But if suitable linking molecule which could link QDs to ZnO surface and electrolyte be used, then QDs can be used to improve the efficiency of DSSCs. As discussed in chapter 4 also, that broadly three methods of assembling QDs in mesoporous ZnO films have been reported so far: in-situ growth of Qds on ZnO surface using CBD or SILAR, deposition of presynthesized colloidal QDs by direct adsorption and deposition of presynthesized colloidal QDs by using bifunctional linking molecule such as MPA [9]. Research is been going on the
fabrication of QDSSCs using all three methods. But growth of QDs using CBD has been rigorously studied. Direct adsorption of QDs on ZnO surface results in poor linking of the QDs with nanoporous structure of ZnO. So, a suitable bidirectional linking molecule is used whose one end is attached to the QDs and other end is attached to ZnO nanoporous structure. Use of suitable linking molecule enhances the power conversion efficiency because of the proper adsorption and linking of QDs with ZnO structure.

Much research has been done on the fabrication of QDSSCs in which QDs are embedded in mesoporous ZnO/TiO$_2$ structures by in-situ and ex-situ methods. Sudhagar et al. have reported nanospherical TiO$_2$ mesoporous layer combined with CdS QDs as a QDSSC application and the resulting efficiency was 1.2% [10]. Chang et al. have reported a energy conversion efficiency of 1.84 % using $I_3^-$ electrolyte in CdS based QDSSC [11]. Zhang et al have reported a maximum power conversion efficiency of 0.34% for 10 CBD cycles of CdS /ZnO nanowire system [12]. Tak et al. have reported the CdS/ZnO nanowire structure as an enhanced photocatalytic activity, because the CdS/ZnO system can efficiently separate photogenerated electron-hole pair and reduce their recombination [13]. Chen et. al have reported an efficiency of 1.4% in CdS and CdSe co-sensitized QDSSC based on ZnO nanowire [14]. Chen et al have also reported a QDSSC based on ZnO nanorod coated vertically aligned CNTs and a power conversion efficiency of 1.46% was obtained [15]. Chang et al. have recently reported a Cu$_2$S-CuInS$_2$-ZnSe QDSSC with cascaded energy gap structures and obtained a power conversion efficiency of 2.52% [16]. Wang et al. have reported CdS QDs assembled onto the compressed TiO$_2$ layers with a maximum power conversion efficiency of 4.49% [17]. Zhang et al. have reported a ZnO/CdS/CdSe composite nanowire array working as photoanode in QDSSC and obtained a power conversion efficiency of 3.45% [18].
Section – A

Fabrication and Characterization of ZnO Based CdS – QDSSC

5.2 Experimental Details for Fabrication of CdS - QDSSC

The degree of cleanliness of the substrate affects the adherence and the morphology of the film. Substrate cleaning is therefore an integral part of any film deposition. So, before depositing the ZnO nanoparticles on ITO, the ITO substrates were cleaned properly. Different methods have been suggested for semiconductor substrate cleaning in literature. They include chemical cleaning, heat treatment and ultrasonic cleaning. Ultrasonic cleaning uses the local stirring action of the shock waves created solvent to dissolve the residues and thus relatively better cleaning results. We used a very simple method for cleaning the beakers and the substrate as described below.

5.2.1 Beaker Cleaning

In the beakers (500 ml) pour DI water (400ml) + 50ml hydrogen peroxide (H₂O₂) + 20 ml ammonia (NH₃). Cover with foil and heat at 80°C for 1 hour. After that fill the beakers with DI water only, cover it and again heat using hot plate for one more hour. Empty the beakers and bring them to room temp. Now we will proceed with TCO cleaning.

5.2.2 Substrate Cleaning

Substrates were immersed in acetone in the cleaned beakers and cleaned in ultrasonic bath for 15 minutes. After that the substrates were further cleaned using ethanol for 10 minutes in the ultrasonic bath. Then at last substrates were dried under nitrogen flow.
5.2.3 Preparation of Gel Electrolyte

All the reagents used were of analytical grade and no further purification was done before use. The gel electrolyte was prepared by using 10% PEO solution in acetonitrile and CNT with 0.1M of LiI, and 0.015M of I₂. The whole mixture was placed for sonication to disperse the CNTs into the matrix of polymer. The mixture was stirred for 10 h by a magnetic stirrer for complete mixing between CNTs and polymer molecules. Flowchart of the preparation of gel electrolyte is shown in figure 5.1.

Gel electrolyte was used because it does not corrode easily unlike liquid electrolyte, charge transport is better unlike solid electrolyte and it offers the prospect of possible benefits in manufacturing processes, e.g. less stringent requirements for sealing and interconnection schemes on the module level and safe handling in a production process.
Fig. 5.1 Flowchart for the synthesis of gel electrolyte
5.2.4 Preparation of ZnO Electrode

There are a number of methods which can be used to apply the ZnO on ITO such as doctor blade, spray coating, spin coating, vapour deposition, screen-printing. In the present work, we used doctor blade method. ZnO nanopowder (1.2g) was ground by a mortar and pestle with 4 ml DI water and PEG$_{20,000}$ (0.5 g). PEG was used to break up the aggregated particles into a dispersed paste. Thus prepared uniform slurry was coated on ITO glass by doctor blade technique using an adhesive scotch tape to control the thickness of the ZnO film and to provide non-coated areas for electrical contact as spacers [19, 20]. The freshly prepared slurry was uniformly spread in the form of film on ITO. The porous ZnO electrode was typically 10 µm thick. After natural drying of the film at room temperature, it was sintered in air at 450°C for 30 min.

5.2.5 Treatment of ZnO Electrode with Quantum Dots

The present work utilizes the ex-situ growth approach for the synthesis of QDs for QDSSC to attach the pre-synthesized QDs onto the mesoporous ZnO electrode by a bifunctional linker molecule. The prepared ZnO film electrode as explained in the previous step, was first immersed in MPA, which acts as linker molecule between ZnO film electrode and QDs [9]. The modified ZnO electrode was immersed in CdS QD colloidal solution consisting of all the three synthesized QDs of varying sizes (varying bandgap) for 24 h at room temperature. The colloidal solution of QDs was formed in toluene by ultrasonication for 2 h. The QD adsorbed electrode was then rinsed with toluene and dried at room temperature. To minimize adsorption of impurities from moisture in the ambient air, the electrode was dipped in the QD solution while it was still warm (~80 °C). The colour of ZnO electrode changes to yellow after adsorption of CdS QDs.
5.2.6 Treatment of Quantum Dot Adsorbed Electrode with Electrolyte

I\textsuperscript{-}/I\textsubscript{3}\textsuperscript{-} electrolyte was spread on the QD coated ZnO electrode [21, 22]. A sandwich type QDSSC was fabricated with the CdS QDs adsorbed ZnO electrode, a thin Pt sheet as counter electrode, a spacer and an electrolyte. The schematic diagram of the sandwich type QDSSC so obtained is shown in figure 5.2. The flowchart for the fabrication of QDSSC is shown in figure 5.3.

![Fig. 5.2 Schematic diagram of QDSSC](image)

In QDSSCs, QDs such as CdS, CdSe, PbS and InP which absorb light in visible region work as sensitizers because they are able to inject electrons to larger bandgap semiconductors such as ZnO, TiO\textsubscript{2} and SnO\textsubscript{2} etc [8, 10-14]. The injected electron in the conduction band of ZnO percolates through the porous ZnO structure and is fed to the ITO layer which acts as the charge collecting electrode in the cell [23]. The porous ZnO electrode is typically 10 µm thick. Through ITO, the electron moves to the external circuit. At the Pt counter electrode, triiodide (I\textsubscript{3}\textsuperscript{-}) is reduced to iodide (I\textsuperscript{-}) by taking the electrons from Pt electrode. I\textsuperscript{-} is transported through the electrolyte towards the ITO photodeode, where it reduces the oxidized QD. The QD is then ready for next excitation/oxidation/reduction cycle.
Fig. 5.3 Flowchart for fabrication of QDSSC
5.3 Analysis of CdS - QDSSC

5.3.1 Morphological Study of Bare ZnO Electrode

SEM image of ZnO electrode is shown in figure 5.4. The image clearly exhibits the porous nature of the ZnO layer. This porous structure of ZnO helps in the sensitization of QDs in QDSSC because when QDs are embedded on ZnO electrode, QDs actually go and sit in these pores where they get adsorbed. That is why the cell is known as quantum dot sensitized solar cell because when light falls on such structure, ZnO electrode on the top does not absorb light in the visible region (wide bandgap~3.37 eV) but passes it into the next QD layer where it gets absorbed and sensitizes the QDs.

![Fig. 5.4 SEM image of bare ZnO electrode](image)

5.3.2 Absorbance Study of Bare ZnO Electrode

The optical absorption spectra of ZnO nanoparticles as a function of energy in the visible region are shown in figure 5.5. Graph shows that ZnO does not absorb light in the visible region, which means that prepared ZnO samples are transparent to visible light. We can see that proper light absorbance takes place above bandgap energy of approximately 3.4 eV. Below this energy, absorption level decreases stating that below
3.4 eV photons does not possess enough energy to excite the electrons from valence band to conduction band. The overall analysis of the absorbance spectrum concludes that the synthesized ZnO nanoparticles can be successfully used as a photoelectrode in QDSSC.

![Graph](image)

Fig. 5.5 Absorbance of bare ZnO electrode (a) wavelength and (b) energy

5.3.3 Absorbance Study of CdS Adsorbed ZnO Electrode

The optical absorption spectrum of CdS QDs embedded on ZnO electrode is shown in figure 5.6. It is seen from the figure that the absorbance of the CdS QD embedded ZnO electrode covers a wide range of visible spectrum (400 – 600 nm). Thus using CdS QDs as sensitizers onto ZnO nanoparticles resulted enhanced light harvesting of the solar energy.

![Graph](image)

Fig. 5.6 Absorbance of CdS QD adsorbed ZnO electrode
5.3.4 Current-Voltage Measurement

QDSSC was fabricated using the synthesized of ZnO nanoparticles and CdS QDs. The cell was illuminated under one sun illumination (AM 1.5, 100 mW/cm²) and I-V characteristic of the cell (Fig. 5.7) was obtained by using keithley source meter. FF and power conversion efficiency were evaluated using the equations (5.1) and (5.2) respectively.

\[
FF = \frac{I_m \times V_m}{I_{sc} \times V_{oc}}
\]  

(5.1)

\[
\eta = \frac{I_m \times V_m \times 100}{P_{in}} \%
\]

(5.2)

Where, symbols have their usual meanings. The values of \(I_{sc}, V_{oc}, P_m, FF\) and \(\eta\) as obtained from the I-V curve are 5.43 mA, 0.64 V, 1.3 mW, 0.4 and 1.3 % respectively.

![Fig. 5.7 I-V characteristic of CdS sensitized QDSSC](image-url)
5.3.5 Working Mechanism of CdS - QDSSC

The energy level positioning of the ZnO based CdS QDs sensitized QDSSC is shown in figure 5.8. When the QDSSC is illuminated, excitons are generated in CdS QDs and charge separation is performed by ZnO/CdS QDs/electrolyte interface. The resultant electrons are conducted to the ITO layer through ZnO layer and the holes are recovered by I/\text{I}_3^- electrolyte. \text{I}_{sc} depends on number of incident photons. Adsorbing PVA capped CdS onto ZnO, could result in the hindrance of charge transport. In the present case the PVA capping molecules were removed by repeated washing with de-ionized water before incorporating them in ZnO electrode in QDSSC which provides a better charge carrier exchange between QDs and the conducting polymer [24].

![Energy level diagram of ZnO based CdS sensitized solar cell](image)

*Fig. 5.8 Energy level diagram of ZnO based CdS sensitized solar cell*
Section – B

Fabrication and Characterization of ZnO Based CdSe - QDSSC

5.4 Experimental Details for Fabrication of CdSe - QDSSC

The fabrication process is exactly the same as in the previous case except that in this case CdSe QDs were used instead of CdS QDs. Firstly, QDSSCs using individual QDs of different sizes were fabricated and I-V measurements were taken. Then the individual QDs were mixed together in equal amounts to form a blended colloidal solution and then those mixed QDs were used as a whole to fabricate QDSSC, which absorbed the entire visible range in the solar spectrum.

In the first part, the I-V characteristics of the different sized QDSSC are shown and analyzed. After that the analysis of blended CdSe sensitized QDSSC is done.

5.5 Effect of Dot Size on Efficiency of CdSe - QDSSC

QDSSCs were fabricated using the different sized QDs individually. The cells were illuminated under one sun illumination (AM 1.5, 100 mW/cm²) and I-V characteristics were obtained (Fig. 5.9). The FF and η were evaluated using equations (5.1) and (5.2) respectively. The values of I_{sc}, V_{oc}, P_m, FF and η are given in table 5.1.

The decrease in efficiency with increase in QD size may explained by simplified charge injection model (Fig. 5.10). Larger size QD has smaller bandgap as compared to the larger bandgap of smaller size QD. So rate of charge injection in case of smaller sized QD is higher because of high energetic driving force which injects the electron into the conduction band of ZnO. Smaller sized QDs are more energetic in their excited state and are capable of transferring more electrons at a faster rate than a larger sized QD.
Fig. 5.9 I-V characteristic of QDSSC using different sized CdSe QDs

<table>
<thead>
<tr>
<th>QD size (nm)</th>
<th>$I_{sc}$ (mA)</th>
<th>$V_{oc}$ (V)</th>
<th>$P_m$ (mW)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.81</td>
<td>5</td>
<td>0.71</td>
<td>2.06</td>
<td>0.6</td>
<td>2.06</td>
</tr>
<tr>
<td>1.13</td>
<td>4.5</td>
<td>0.68</td>
<td>1.96</td>
<td>0.64</td>
<td>1.96</td>
</tr>
<tr>
<td>1.2</td>
<td>3.7</td>
<td>0.66</td>
<td>1.97</td>
<td>0.8</td>
<td>1.97</td>
</tr>
<tr>
<td>1.29</td>
<td>3.1</td>
<td>0.62</td>
<td>0.89</td>
<td>0.5</td>
<td>0.89</td>
</tr>
<tr>
<td>1.34</td>
<td>2.19</td>
<td>0.58</td>
<td>0.66</td>
<td>0.52</td>
<td>0.66</td>
</tr>
<tr>
<td>1.45</td>
<td>1.53</td>
<td>0.44</td>
<td>0.37</td>
<td>0.55</td>
<td>0.37</td>
</tr>
<tr>
<td>2.26</td>
<td>1.17</td>
<td>0.38</td>
<td>0.25</td>
<td>0.56</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Table 5.1 various parameters of QDSSC with increasing order of size

Fig. 5.10 Simplified charge injection model
5.6 Analysis of Blended CdSe - QDSSC

5.6.1 Morphological Study of ZnO Electrode

The surface morphologies of bare ZnO electrode and CdSe sensitized ZnO electrode were studied using scanning electron microscope (SEM). SEM images (Fig. 5.11) show that bare ZnO electrode has porous structure which is necessary for CdSe adsorption. After adsorption of CdSe QDs on the mesoporous ZnO electrode, the pores of ZnO are filled by the QDs. So, we can see that after QD adsorption, the ZnO nanoporous structure is partially blocked so as to provide the necessary pathway for the movement of charge carriers as well as electrolyte redox couple ions.

![SEM images of ZnO electrode](image)

Fig. 5.11 SEM image ZnO electrode (a) bare (b) CdSe adsorbed

5.6.2 Absorbance Study of ZnO Electrode

Absorbance spectra of ZnO electrode before and after CdSe sensitization is shown in figure 5.12. ZnO electrode absorbed light in only UV region of less than 400 nm, due to its wide bandgap (3.37 eV for bulk). Absorbance increased in the visible region and covered almost entire visible spectrum from 350 to 700 nm with sensitization of ZnO electrode with CdSe QDs. Size quantization effect red shifted the absorption edge.
indicating the adsorption of all CdSe QDs having different absorption wavelength, thereby covering the entire visible spectrum.

![Graph showing absorbance comparison between ZnO electrode and CdSe coated ZnO electrode](image)

**Fig. 5.12 Absorbance of ZnO electrode without and with CdSe adsorption**

### 5.6.3 Current-Voltage Measurement

QDSSC was fabricated using the synthesized CdSe QDs. The cell was illuminated under one sun illumination (AM 1.5, 100 mW/cm²) and I-V characteristic of the cell (Fig. 5.13) was obtained by using keithley source meter. The FF and η were evaluated using equations (5.1) and (5.2) respectively. The values of J_sc, V_oc, P_max, FF and η are obtained to be 10.5 mA/cm², 0.78 V, 3.6 mW, 0.45 and 3.6 % respectively.

![Graph showing I-V characteristic of CdSe sensitized QDSSC](image)

**Fig. 5.13 I-V characteristic of the CdSe sensitized QDSSC**
5.6.4 Working Mechanism of CdSe - QDSSC

The energy level diagram of ZnO based CdSe sensitized solar cell is shown in figure 5.14. When QDSSC is illuminated with light of energy equal to or greater than bandgap of the QDs, then excitons are generated in CdSe QDs (Eq. 5.3 & 5.4).

\[
\text{CdSe} + h\nu \rightarrow \text{CdSe}^* \quad (5.3)
\]

\[
\text{CdSe}^* \rightarrow \text{CdSe}^+ + e^- (\text{ZnO}) \quad (5.4)
\]

Charge separation is performed by ZnO/CdSe QDs/electrolyte interface. The resultant electrons are conducted to the ITO layer through porous ZnO and the holes are recovered by I\(^{-}/I_3^-\) electrolyte. Through ITO, the electron moves to the external circuit. At the Pt counter electrode, triiodide (I\(^3^-\)) is reduced to iodide (I\(^-\)) by taking the electrons from Pt electrode.

\[
I_3^- + 2e^- (\text{Pt}) \rightarrow 3I^- \quad (5.5)
\]

I\(^-\) is transported through the electrolyte towards the ITO photoelectrode, where it reduces the oxidized QD. The regeneration of QDs can be understood by equation (5.6).

\[
2\text{CdSe}^+ + 3I^- \rightarrow 2\text{CdSe} + I_3^- \quad (5.6)
\]

![Energy level diagram of ZnO based CdSe sensitized solar cell](image)

*Fig. 5.14 Energy level diagram of ZnO based CdSe sensitized solar cell*
The major mechanism of charge separation is the energy level position of the whole system (Fig. 5.14). The excited state of the QDs should lie above the conduction band edge of the ZnO and similarly, the ground state of the QDs should lie below the chemical potential of redox pair $\text{I}^-/\text{I}_3^-$ in the electrolyte due to which there exists an energetic driving force for electron and hole separation. Due to this energy level positioning in the system, the cell is capable producing voltage between its electrodes and across the external load. $I_{sc}$ depends on number of incident photons. The significant value of $I_{sc}$ can be attributed to the light absorption by QDs in the whole visible spectrum and multiple exciton generation due to a single photon. Due to MEG effect the number of electrons injected into the conduction band of ZnO is larger than the photons absorbed by QDs. So, the overall conversion efficiency enhances than in the case of DSSC because in DSSC single photon gives rise to single exciton wasting the excess energy as heat [2-5].

Decreasing QD size also increases photocurrent as the shift in conduction band to more negative potential increases the driving force to charge injection. The smaller sized particles being more energetic in their excited state are capable of injecting electrons in ZnO at faster rate. Also, the injection of hot electrons from the quantized particles increases the overall conversion efficiency. The smaller value of FF as compared to DSSCs which is usually approximately 0.7, may be attributed to the resistance losses in the system due to ZnO/CdSe interface, CdSe/electrolyte interface, electrolyte/Pt interface and those in electrolyte.

### 5.7 Summary

ZnO based QDSSC were fabricated using CdS and CdSe QDs as sensitizers. When CdS QDs were used as sensitizer, then the power conversion efficiency was
obtained to be 1.3% at AM 1.5. When CdSe QDs were used as sensitizer, then the power conversion efficiency was obtained to be 3.6% at AM 1.5. The increased power conversion efficiency in case of CdSe QDs may be attributed to the efficient light harvesting and charge collection resulting from enhanced light absorption and faster charge transport in CdSe QDs due to their larger distribution in size.
References


