Chapter 1

Introduction

“This chapter deals with the brief overview of solar cell technologies. The various generations of solar cells are also discussed. The construction of Quantum Dot Sensitized Solar Cell, its operating principle, charge carrier separation, charge transport and recombination losses have also been explained.”
1.1 The Energy Problem

The supply of the secure, clean and sustainable energy while limiting the global temperature increase is the biggest challenge of the 21st century. For the many thousands of years and till about three hundred years ago, mankind used exclusively renewable energy sources. Wood was used for heating, animals were used for transportation, and wind & water supplied mechanical energy. During the 19th century, the industrial revolution brought new machines and new energetic needs. Coal was found to satisfy the increasing demand of energy. The early 20th century saw the first exploitation of petroleum, natural gas and later nuclear energy as energy sources to cover the continuously growing demand. Nowadays, fossil energies cover 95% of the total energy demand worldwide, which exceeds $10^5$ TWh per year. However, the major drawbacks of fossil fuel based energy are – drastic depletion of fossil fuels, challenges ahead on needs for specific requirements and emission of CO$_2$. During the past many thousands of years, the atmospheric CO$_2$ concentration has been between 200 and 300 ppm [1]. Anthropogenic CO$_2$ emission from 50 years of fossil fuel combustion has raised the concentration to above 380 ppm. It has been estimated that CO$_2$ concentrations will reach more than double the pre-anthropogenic values within the 21st century [2]. Such high CO$_2$ concentrations have been predicted to lead to an increase of the average temperature of the earth surface with 3-5°C. This forecast is based on natural climate changes in the past, by looking at ancient glacial cycles (going back millions of years in time) [1]. The effect of this temperature rise on the weather is not exactly known due to uncertainties in climate models, but climate scientists predict extreme rainfall and droughts, and increasing intensity of hurricanes due to rising temperatures. A substantial rise of sea-levels can be predicted with higher accuracy, since historical climate data documents show a clear correlation between CO$_2$ concentrations and the sea level [1].
To prevent the collapse of our current climate, greenhouse gas emissions from developed countries must be strongly reduced, while newly industrialized countries must limit increase in CO₂ emissions. To achieve this goal, alternative energy sources (renewable energy) to coal, oil and gas must be provided, such as power from wind, water, biomass, or solar energy. Figure 1.1 depicts some of the important sources of non-renewable and renewable energy. While a future energy mix will most likely be based on all these sources, only the sun provides our planet with about 10,000 times more energy than our global daily consumption. Solar energy can be converted to heat, which can be used directly for warm-water supplies. Higher temperatures can be achieved by light concentration with optical elements like mirrors and lenses, and this provides the opportunity to operate a steam engine and to convert heat into motion and subsequently electricity.

Fig. 1.1 Some non-renewable and renewable energy resources
1.1.1 Solar Energy

Among all the technologies allowing the production of renewable energy such as solar, wind, water, biomass; the present work is focused on solar energy. Solar energy is the energy derived from the sun in the form of solar radiation. A partial list of solar applications includes space heating and cooling through solar architecture, daylighting, solar hot water, solar cooking, and high temperature process heat for industrial purposes. Solar technologies are broadly characterized as either passive solar or active solar depending on the way they capture, convert and distribute solar energy. Active solar techniques include the use of PV panels and solar thermal collectors to harness the energy. Passive solar techniques include orienting a building to the sun, selecting materials with favourable thermal mass or light dispersing properties, and designing spaces that naturally circulate air.

1.1.2 Advantages of Solar Energy

- Solar electric generation has the highest power density (global mean of 170 W/m²) among all the renewable energy sources.
- Solar power is pollution free during use. Production end wastes and emissions are manageable using existing pollution control.
- Solar electric generation is economically superior where grid connection of fuel transport is difficult, costly and impossible. Examples include satellite, island communities, remote locations and ocean vessels.
- When grid connected, solar electric generation can displace the highest cost electricity during times of peak demand (in most climatic regions), can reduce grid loading, and can eliminate the need for local battery power for use in times of darkness.
Grid connected solar electricity can be used locally thus reducing transmission/distribution losses.

Operating costs of solar power plant are extremely low compared to existing power technologies.

Experimental high efficiency solar cells have efficiencies of over 40% and efficiencies are rapidly rising while mass production costs are rapidly falling.

1.2 Solar Cell

A solar cell is a solid state electronic device that converts the solar energy directly into electricity by Photovoltaic (PV) effect. That is why solar cell is also known as PV cell. PVs is the field of technology and research related to the practical application of PV cells in producing electricity from light, though it is often used specifically to refer to the generation of electricity from sunlight. Cells are described as PV cells when the light source is not necessarily sunlight (lamplight, artificial light, etc.). The emergence of an electric potential between two electrodes attached to a solid or liquid system, upon light irradiation has been discovered by Bequerel in 1839 and is ever since known as PV effect [3]. This discovery has been the base for a variety of concepts to convert solar radiation into electricity and has opened a new domain of alternative energy generation. It took more than one hundred years after the discovery by Bequerel to develop the first solid state solar cell in 1954 by Chapin, Fuller and Pearson with 6% efficiency [4]. They used a diffused silicon (Si) p-n junction. Up to now, the common solar power conversion efficiencies of this type solar cell are beyond 15% [5].

The PV market has shown exponential growth over the last few years. Nevertheless, PV electric power cannot compete with the price of electricity from the grid and is therefore supported by national subsidy programs with the aim of reducing the cost
of PV systems by increasing production volume. Consequently, further advancement in the research and development of new PV cells is required to increase the light to electric power conversion efficiencies and to reduce prices. Solar cells are commonly classified as follows -

1. First generation solar cells,
2. Second generation solar cells,
3. Third generation solar cells and
4. Fourth generation solar cells

1.2.1 First Generation

The classification depends on the underlying technology. Single or multicrystalline p-n junction Si cells are today the most common PV converters with a market share of about 85% and are so called first-generation solar cells. The first generation solar cells consist of large area, single crystal, single layer p-n junction diode, capable of generating usable energy from light sources with the wavelength of sunlight. These are typically made by diffusion process with Si wafers. High purity requirements for the Si crystals, high fabrication temperatures and the large amount of material which is needed for a wafer based cell are major cost factors.

Advantages

- Broad spectral absorption range
- High carrier mobilities

Disadvantages

- Requires expensive manufacturing technologies
- Growing and sawing of ingots is a highly energy intensive process
- Fairly easy for an electron generated in another molecule to hit a hole left behind in a previous photo excitation
Much of the energy of higher energy photon at the violet end of the spectrum is wasted as heat.

1.2.2 Second Generation

The second generation solar cells are based on the use of thin epitaxial deposits of semiconductors on the lattice of semiconductors. Second generation PV modules have currently a market share of about 15% and are mostly based on CdTe. However, also PV panels based on CuInS$_2$, CuInSe$_2$, CuInGaSe$_2$ or amorphous and nanocrystalline Si have reached the stage of commercialization and have entered the PV market. The thermodynamic limit of the light to electric power conversion efficiency ($\eta$) of a single junction PV cell (1st or 2nd generation) which is optimized to the AM 1.5 spectrum is 32.9%. This limit, also known as Shockley–Queisser limit [6] originates from the fact that photons with energies below the bandgap energy are not absorbed, while photons with energies above the band-gap energy release the additional energy ($E_{\text{photon}} - E_{\text{bandgap}}$) mostly as heat.

Advantages

- Lower manufacturing costs
- Lower cost per watt can be achieved
- Reduced mass
- Less support is needed when placing panels in roof tops
- Allows fitting panels on light or flexible materials

Disadvantages

- Typically, the efficiencies of thin film solar cells are lower as compared with Si solar cells
- Amorphous Si is not stable
- Increased toxicity
1.2.3 Third Generation

Third generation solar cells aim towards conversion efficiencies beyond the Shockley–Queisser limit through advanced PV concepts but still use thin film, second generation deposition method. Third generation PVs include multi junction cells also known as tandem cells, Dye Sensitized Solar Cells (DSSCs) also known as Gratzel cell [7], Organic Solar Cells (OSCs) also known as polymer solar cells, Hybrid (organic/inorganic) Solar Cells (HSCs), hot carrier solar cells such as Quantum Dot Sensitized Solar Cells (QDSSCs) [8]. Record conversion efficiencies slightly above 40% have been reported for multi junction cells using concentrated sunlight. Over the last few years Quantum Dots (QDs) have attracted widespread attention due to their outstanding opto-electronic properties [9]. Their absorption spectrum can be tailored by changing their size, which makes them attractive for PV applications [10]. Numerous architectures for QD based solar cells were proposed including photoelectrochemical cells based on QD sensitized wide bandgap nanostructures [11], QD films immersed in electrolyte [12], solid state cells based on QD/polymer blends [12] as well as QD layers sandwiched between electron and hole conductors [13]. QD based devices were also proposed to realize third generation PVs and to achieve conversion efficiencies beyond the Shockley–Queisser limit. Single junction PV cells based on QDs absorbers are potential candidates as building blocks in third generation devices due to the tunability of the absorption spectrum.

Advantages

- Low energy, high throughput processing technologies
- No elaborate apparatus required
- Gratzel cell – Attractive replacement for existing technologies in low density applications like roof top solar collectors
Gratzel cell – Low material cost, works even in low light conditions

Polymer cell – Solution processable, chemically synthesized

Polymer cell – Low material cost

**Disadvantages**

- Efficiencies are lower compared with Si based p-n junction solar cells
- Efficiency is decreased over the time due to environmental effects
- High bandgap material required, so fewer photons are able to produce current

**1.2.4 Fourth Generation**

It is upcoming generation of solar cell which may consist of composite PV technology, in which polymers with nanoparticles are mixed together to make a single multi-spectrum solar cells. Then the thin multi-spectrum layers can be stacked to make multi-spectrum solar cells more efficient and cheaper. The first layer is one which converts different types of light. Another layer passes the light. Last is an infrared spectrum layer for the cell, thus converting some of the heat for an overall solar cell composite. Companies working on fourth generation PVs include Xsunx, Konarka technologies, Nanosolar, Dyesol and Nanosys.

**Advantages**

- Solution processable
- Low material cost (polymer)
- Self-assembly
- Printable nanocrystals on a polymer film
- Improved conversion efficiency (potentially)

**Disadvantages**

- Efficiencies are lower compared to Si based solar cells
- Potential degradation problem
Present thesis focuses on the fabrication and characterization of ZnO based quasi-solid state QDSSC (third generation solar cell) sensitized with semiconductor QDs (CdS and CdSe). The importance of interface chemistry and physics is also emphasized. Experimental strategies to increase the conversion efficiency of QDSSCs are presented. The next section focuses on the working principle of DSSC due to conceptual similarities with QDSSC.

1.3 Dye Sensitized Solar Cell

The first work on semiconductor sensitisation was reported by in 1873. They investigated the sensitisation of silver halide emulsions with dyes, finding the photoresponse significantly extended into the red and even infrared. He applied his findings to photography. In 1887, Moser carried this concept to the photoelectric effect by using the dye erythrosine on silver halide electrodes. Until the 1960’s, the theoretical understanding of the process was under dispute. It was not clear whether the mechanism was an electron transfer or an energy-coupling process. The electron injection process was proved by Tributsch and Gerischer with their work on ZnO in 1968. In the following years, the chemisorption of the dye on the surface of the semiconductor was developed to enhance the function of the dye. The first reported efficiency was 7.1%. In the more recent publications, efficiency about 10.4 % are reported [14-16]. DSSC realizes the optical absorption and the charge separation processes by the association of a sensitizer as light absorbing material with a wide bandgap semiconductor of nanocrystalline morphology [17-19]. DSSC is a promising alternative energy source and is expected to significantly contribute to overall energy production over the coming years. DSSC is composed of four main layers: (1) a 2-20 μm thick, porous, wide bandgap semiconductor
film (typically TiO₂ or ZnO) composed of crystalline nanoparticles abutting one another on Transparent Conducting Oxide (TCO) glass. The nanoparticle film is referred to as the photoanode as is deposited on TCO substrate. (2) a monolayer of dye adsorbed onto these nanoparticles. (3) a hole conductor electrolyte interpenetrating the nanocrystalline semiconductor network and (4) a counter electrode forms the cathode. This arrangement creates the large area semiconductor/dye/electrolyte interface needed for cell operation. The semiconductor nanoparticles and the electrolyte form continuous pathways to the anode and cathode respectively. The electrolyte fills the pores in semiconductor. The schematic of DSSC is shown in figure 1.2.

![Schematic of dye sensitized solar cell](image)

Fig. 1.2 Schematic of dye sensitized solar cell

The schematic diagram for energy flow in DSSC is shown in figure 1.3 to clearly understand the operation of DSSC. Photons enter DSSC through top TCO layer and are absorbed by dye molecules (D) which is attached to the wide bandgap (> 3 eV) semiconductor. The dye molecule after absorbing photon are promoted to excited state (D*) - Lowest Unoccupied Molecular Orbital (LUMO) from ground state - Highest Occupied Molecular Orbital (HOMO) leaving an oxidized dye molecule (D⁺) on the semiconductor surface. Electrons excited to the LUMO levels are injected into the
semiconductor nanoparticles. The injected electrons percolate via the interconnected nanoparticles to the substrate and are fed into an electrical circuit, where they can deliver work. Subsequently, the electrons, which now carry less energy, enter the cell again via the counter electrode and are transported to hole conductor medium (commonly the electrolyte containing iodide/triiodide (I\textsuperscript{-}/I\textsubscript{3}\textsuperscript{-}), this process can be described by equation (1.1)

\[ \text{I}_3^+ + 2e^- \rightarrow 3 \text{I}^- \]  

(1.1)

The oxidized dye (D\textsuperscript{+}) is then reduced back to its original state by hole conductor medium. This process can be described by the equation (1.2)

\[ 2D^+ + 3 \text{I}^- \rightarrow 2D + \text{I}_3^- \]  

(1.2)

Then the cycle is completed. The voltage generated under illumination corresponds to the difference between the Fermi level of the electron in the wide bandgap semiconductor and the redox potential of the electrolyte. Overall the device generates electric power from light without suffering any permanent chemical transformation.

![Fig. 1.3 Schematic diagram of energy flow in dye sensitized solar cell](image-url)
Because the nanoparticles are smaller than the Debye length in the semiconductor and the electrolyte has high ionic strength, the electric fields within the nanoparticles are very effectively screened and charge transport in the nanoparticle network is thought to be diffusive. The driving force for the carrier transport through the nanoparticle film and electrolyte is the chemical potential difference created across the cell, which is due to the build up of carriers at the semiconductor/dye/electrolyte interface.

1.3.1 Fundamental Differences between Si Solar Cell and Dye Sensitized Solar Cell

Light absorption and charge transport occur in same material in p-n junction solar cell. DSSC separates these functions. Photons are absorbed by the dye molecules and charge transport is carried out in wide bandgap semiconductor and electrolyte.

The two main modes for charge carrier separation in any solar cell are drift and diffusion. Drift of carriers is driven by the electric field established across the device. Diffusion of carriers occurs due to gradient of electrochemical potential from zones of high carrier concentration to low concentration. While charge separation in p-n junction solar cell is induced by the electric field across the junction (drift), no such long range electric field exists in DSSC. The charge separation occurs via other kinds of kinetics and energetic reasons at the semiconductor /dye/electrolyte interface (diffusion).

In p-n junction solar cell, the generated opposite charges travel in the same material, while in DSSC the electrons travel in nanoporous wide bandgap semiconductor network and holes travel in electrolyte.

Requirement of pure and defect free semiconductor is relaxed in case of DSSC unlike p-n junction solar cell.
1.3.2 **Drawbacks of Dye Sensitized Solar Cell**

The main drawback of DSSC is its low practical efficiency than Si based solar cells. The absorption spectrum of dyes is quite narrow which directly affect the efficiency of the cell. Dye has absorption peak at only one particular wavelength. So, in DSSCs the entire visible spectrum is not absorbed by the cell rather a small portion of the visible spectrum is absorbed corresponding to LUMO-HOMO difference of the dye. To make the absorption spectrum broader, one needs to blend several different dyes which in total absorb a broader range of visible spectrum. But again, blending different dyes having different chemical compositions in a proper ratio to cover the entire visible spectrum requires great efforts [20]. And even after that, the rate of absorption in different portions of visible spectrum is not same (high) because of different values of absorption coefficients in different dyes due to which the efficiency does not compete with traditional Si based solar cells. Moreover breakdown of dye may occur.

Although ZnO possesses high electron mobility, low combination rate, good crystallization into an abundance of nanostructures and almost an equal bandgap and band position as TiO$_2$, the photoconversion efficiency of ZnO based DSSC is still limited. The major reason for the lower performance in ZnO based DSSCs may be explained by – (1) formation of Zn$^{2+}$/dye complex in acidic dye and (2) the slow electron injection flow from dye to ZnO. Zn$^{2+}$/dye complex formation mainly occurs while ZnO is dipped inside the acidic dye solution for the dye adsorption for a long time. Ru based dye molecules consist of carboxylic functional group for coordination, dye solution mostly existing in acidic medium. Therefore, the Zn$^{2+}$/dye complex is inevitable. The formation of Zn$^{2+}$/dye complex has been attributed to the dissolution of surface Zn atoms by the protons released from the dye molecules in an ethanolic solution.
Moreover, the thermostability and long-term stability is also low in case of DSSC and needs to be improved. Dyes in these cells suffer from degradation under heat and UV light and cell is difficult to seal due to solvents in assembly.

1.4 Semiconductor Quantum Dots

With each passing year, more flexibility of the dye is required and dyes are often unable to meet the expectations [21]. So, now a days, dyes are being replaced by QDs. A QD is a portion of matter (e.g. semiconductor) whose excitons are confined in all three spatial dimensions. Consequently, such materials have electronic properties intermediate between those of bulk semiconductors and those of discrete molecules [22]. QDs discovered at the beginning of the 1980s by Alexei Ekimov in a glass matrix and by Louis E. Brus in colloidal solutions [23]. The term "Quantum Dot" was coined by Mark Reed. QDs have a diameter between approximately 2-10 nm. At this size, quantum effects are evident as a result of the nanocrystal radius being smaller than the exciton Bohr radius. The exciton Bohr radius is the average distance an electron will be from a hole when an exciton is created. For example, in CdS, the Bohr radius is 2.8 nm [24]. When the size of a CdS nanocrystal is reduced below ~ 2.8 nm radius, energy levels are no longer continuous and become split into discrete energy levels. This quantum confinement phenomenon results in size tuneable absorption and emission properties, which can be taken advantage of in many applications such as transistors, LEDs, photodetectors, diode lasers, biological labelling, biological sensors and solar cells. The quantum confinement induced size tuneable properties are very useful in PVs. The absorption spectrum of such QDs can be adjusted by changing the QD size (Fig. 1.4).

In QDs, the electronic characteristics are closely related to the size and shape of the individual crystal. Generally, the smaller the size of the crystal, the larger
the bandgap, the greater the difference in energy between the highest valence band and the lowest conduction band becomes, therefore more energy is needed to excite the dot, and concurrently, more energy is released when the crystal returns to its ground state. The emergence of semiconductor QDs has opened up new ways to utilize them as a possible replacement for dyes in DSSCs. QDs have many advantages over dyes including good thermal stability under rigorous conditions which allows less photobleaching, tuneable bandgaps by changing their sizes and compositions, sharp absorption onset, large absorption coefficients and hence higher absorption, broad absorption spectrum in contrast with the narrow absorption spectra exhibited by dyes [25], high extinction coefficient allowing for use of thinner films of the mesoporous oxide and low cost etc [26]. QDs are brighter owing to their high extinction coefficient. Hence, QDSSCs are attracting more attention now a days. It has been estimated that QDs are 20 times brighter and 100 times more stable than traditional fluorescent dyes [27]. Being zero dimensional, QDs have a sharper density of states than higher dimensional structures. QDs may be able to increase the efficiency and reduce the cost of today's typical Si PV cells.

Fig. 1.4 Energy Vs size relationship in a quantum confined system
According to an experimental proof from 2006 [28], QDs of lead selenide (PbS) can produce as many as seven excitons from one high energy photon of sunlight (7.8 times the bandgap energy) [29]. The generation of more than one exciton by a single photon is called **Multiple Exciton Generation (MEG) or Carrier Multiplication (CM)**. This compares favorably to today's PV cells which can only manage one exciton per high-energy photon, with high kinetic energy carriers losing their excess energy as heat. MEG effect in QDs could push the thermodynamic efficiency limit of these devices up to 44% [28] instead of the current Schockley-Queisser limit. MEG can occur when absorption of a high energy photon leads to production of an excited electron or a hole with an excess energy at least equal to or greater than the QD bandgap. These hot carriers can transfer the entire excess energy, or part of it, to one or more valence electrons, and excite them across the bandgap. In this way, absorption of a single photon leads to generation of two or more electron-hole pairs. The quantum yield for exciton generation is defined as the average number of electron-hole pairs produced by absorption of a single photon.

QD PVs would theoretically be cheaper to manufacture, as they can be made using simple chemical reactions [30]. In the past few years, a rapid increase of the conversion efficiency of QDSSCs has been reported, reaching values of around 4-5% at 1 sun [31]. Recently, various QDs (CdSe, PbSe, CuInS$_2$, etc.) as sensitizers have been proposed, and various strategies have been developed for maximizing photoinduced charge separation and electron transfer [32-38].

**1.4.1 Carrier Recombination and Relaxation in Bulk Materials and Quantum Dots**

The transition in which a charge carrier is transferred from a high energy to a low energy state is called carrier recombination or relaxation. In a bulk semiconductor, excited state electrons can relax via various relaxation pathways (Fig. 1.5), the most important of which are listed below -
1. **Radiative Recombination** - Electron in conduction band recombines with hole in the valence band by emitting a photon. The associated relaxation rate strength depends on the coupling between the initial and the final state and on the number of pathways via which the transition can occur (i.e. the density of final states).

2. **Auger Recombination** – Three particle process in which an electron for instance recombines with a hole by simultaneously transferring the recombination energy to a third particle. Auger rates typically depend on carrier density. In this case also, relaxation rate depends on the coupling between the initial and the final state and on the number of pathways via which the transition can occur.

3. **Thermalization** - Relaxation of hot carriers via sequential emission of phonons (thermalization). Thermalization of hot carriers in bulk material occurs via interactions of hot carriers with the crystal lattice, i.e. the hot carrier relaxes by sequential emission of Longitudinal Optical (LO) phonons. This relaxation process typically occurs on a < 1 ps timescale [39].

4. **Trapping into Defects** - Electrons in the conduction band relax to defect levels in the bandgap. Recombination is possible into physical defects (vacancies, dislocations, grain boundaries, surface states, etc.) and chemical defects in the form of impurities. This relaxation process can in principle be avoided by using a perfect crystalline sample with passivated surfaces.

   Relaxation of carriers in QDs proceeds via the same pathways as in bulk. However, the relaxation rates of the various relaxation processes change considerably in QDs as a result of the discretization of energy levels and the spatial confinement of electronic wave functions [40]. First, by confining the wave functions in the small QD volume, carrier-carrier Coulomb interactions are strongly enhanced in QDs, leading to higher relaxation rates of radiative and Auger processes. Second, leakage of wave
functions outside the QD enhances recombination rates, since the dielectric constant outside the QDs is typically smaller than within the QD material. As a result, the leaking parts of the wave function experience strongly reduced dielectric screening and the Coulomb interaction is further enhanced. Third, the spacing between discrete energy levels is rather large, typically 250 - 550 meV for the electron $1S_e \rightarrow 1P_e$ transition [41].

Thermalization of hot carriers in bulk occurs by sequential emission of LO phonons (~ 40 meV energy) [42]. To accommodate relaxation of a hot carrier in the $1P_e$ state of a QD, however, the simultaneous emission of about 10 LO phonons is required, which is a phenomenon with a very low probability. The absence of a phonon mediated relaxation channel for hot charge carriers in QDs is usually called the ‘Phonon Bottleneck’. Finally, the surface to volume ratio is much higher in QDs leading to large amount of surface defects via which relaxation and recombination processes can proceed. The next section describes how QD can replace a dye molecule to make QDSSC. The structure and working principle on the basis of energy level diagram is also explained.

**Fig. 1.5 Carrier recombination in a bulk semiconductor**
1.5 Quantum Dot Sensitized Solar Cell

A QDSSC incorporates QDs as the photon absorber. Dyes in DSSC are replaced by QDs in QDSSC. Since QDDSC utilizes hot carriers (electrons) for MEG, it is also known as Hot Carrier PV Cell. When QD is excited with a photon having energy at least twice more than the bandgap of QD, then this excess energy creates effective temperature of the photogenerated charge carriers much higher than the lattice temperature. Such high energy carriers are called Hot Carriers (hot electrons and hot holes) and their initial temperature upon photon absorption can be as high as 3000 K with lattice temperature at 300 K. In Shockley-Queisser analysis, a major factor limiting the efficiency to 32.9% is that the absorbed photon energy above the semiconductor bandgap is lost as heat through electron-phonon scattering and subsequent phonon emission, as the carriers relax to their respective band edges and equilibrate with the phonons. This results in carrier cooling. As already discussed in the previous section, the process of electron-phonon scattering and subsequent phonon emission is termed as thermalization.

To reduce thermalization losses in PV cells, the approach has been taken to utilize muti-bandgap structures such as QDSSC to more closely match the absorption range of PV cell to solar spectrum. The larger bandgap QD absorbs the higher energy photons and the smaller bandgap QD absorbs the less energy photon. For such structures the efficiency increases many folds depending on the number of different bandgap QDs available in the system. Other ways to avoid cooling losses is to utilize the excess kinetic energy directly by extracting the photogenerated carriers before they cool to produce higher photovoltage and to utilize the excess kinetic energy of hot carriers to produce a second electron hole pair via impact ionization process. The first approach requires that the rate of carrier transport and collection in the PV device be faster than their cooling rates. In QDs, slowed hot electron cooling is theoretically possible by “phonon bottleneck” effect.
Slowed cooling could make the rate of impact ionization an important process in QDs [43].

The architecture of QDSSC is similar to that of DSSC except that in case of QDSSC, QDs act as the light absorber instead of organic dyes (Fig. 1.6). Semiconductors such as CdS, CdSe, CdTe, CuInS₂, Cu₂S, PbS, PbSe, InP, InAs, Ag₂S, Bi₂S₃ and Sb₂S₃ have been synthesized by various research groups as QDs and deposited onto wide bandgap nanostructures as sensitizers [44-53]. Depending on their size, these materials can absorb photons over a broad spectral range or within a confined window of the solar spectrum. The QDSSC is composed of four main components: (1) a 2-20 μm thick, porous, wide bandgap semiconductor film (typically TiO₂ or ZnO) composed of crystalline nanoparticles abutting one another on TCO glass. The nanoparticle film is referred to as the photoanode as is deposited on a TCO substrate. (2) QDs adsorbed onto these nanoparticles, (3) a hole conductor electrolyte interpenetrating the nanocrystalline semiconductor network and (4) a counter electrode.

![Schematic diagram of quantum dot sensitized solar cell](image)

*Fig. 1.6 Schematic diagram of quantum dot sensitized solar cell*
1.5.1 Wide Bandgap Nanostructures

Mesoporous nanoparticles, nanorods, nanowires and nanotubes are the most common nanostructures for providing a large microscopic surface area for QD deposition. Mesoporous films consist typically of crystals with a diameter of tens of nanometres which are sintered or pressed together to form a continuous network [54, 55]. A number of low cost methods are available to produce nanostructures with strongly enhanced microscopic surface area to deposit thin absorber materials.

1.5.2 Quantum Dot Sensitization

QD sensitizers can be synthesized by two fundamentally different techniques: in-situ and ex-situ. Chemical Bath Deposition (CBD) and Successive Ionic Layer Adsorption and Reaction (SILAR) are widely used in situ methods for preparation of QDs on nanostructured wide bandgap semiconductors which provide high surface coverages of QDs. The in-situ approach depends on the nucleation mechanism inside the nanostructure followed by QD growth, which usually leads to a polydisperse QD size distribution. The direct connection between the QD and the wide bandgap semiconductor leads to efficient charge injection from the QD into the wide bandgap material. In general higher surface coverages can be achieved with in-situ methods. Pre-synthesized monodisperse QDs, on the other hand, are usually prepared ex-situ approach and are either bound to wide bandgap semiconductor by molecular linkers or deposited directly without linker molecules. There are two limiting factors for colloidal QDSSCs. First, the chemical nature of the bifunctional molecular linker plays a significant role in charge separation and subsequently in the light to electric power conversion efficiency of the cell [56]. Secondly, the surface coverage of QDs on the wide bandgap nanostructured oxide is usually poor when ex-situ QD preparation is used [57]. For efficient solar cell operation,
strong light absorption followed by efficient charge separation is required, which so far has been more difficult to achieve with QDSSCs based on ex-situ QD preparation.

1.5.3 Electrolytes - Hole Conductors

The most common electrolytes used in QDSSCs are aqueous organic electrolyte with I$_1$/I$_3$ redox couple and polysulfide [58]. Besides, the Fe$^{3+}$/Fe$^{2+}$ and the Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ redox systems, have also been investigated in conjunction with CdS-sensitized cells [59]. Recently a cobalt complex redox couple was proposed in conjunction with CdSe, PbS and CdS sensitized cells [60-62].

1.5.4 Counter Electrodes

Platinized TCO layers have been used in conjunction with the redox electrolytes. For the polysulfide electrolyte, Pt counter electrode leads to a rather low fill factor and Au has been used alternatively [63-66]. Shen et al. have investigated metal sulfides (especially Co, Cu and Pb) as suitable counter electrode materials, measured their long term stability and pointed out that Cu$_2$S and CoS may poison the surface of the photoelectrode [67].

1.5.5 Protective Coatings

The low stability of QDs in corrosive electrolytes, recombination by surface traps and the need for enhanced charge extraction from the QD have motivated research to passivate the QD surface in contact with the electrolyte. Inorganic amorphous coatings can be deposited in a conformal and continuous fashion onto mesoporous wide bandgap semiconductor electrodes, and for DSSCs it was shown that coatings can improve solar cell performance [68, 69]. Stable and reproducible I–V measurements on using the corrosive I$^-$/I$_3^-$ redox couple were reported when CdS sensitized mesoporous TiO$_2$ electrodes were coated with an amorphous TiO$_2$ shell by electrophoretic deposition [70].
Photocurrent measurements under periodically switched light for a coated and uncoated electrode demonstrate that inorganic coatings can be used to drastically improve the stability of QDs. The recent advances in chemical stability and solar cell performance due to the use of coatings are encouraging, and further research is needed to better understand the interface energetics and kinetics.

1.5.6 Working Principle of Quantum Dot Sensitized Solar Cell

QDSSCs are based on a nanostructure of a wide bandgap semiconductor material that is sensitized with QDs. The operating principle of the QDSSC is similar to that of DSSC. The schematic to understand the operating principle of QDSSC is shown in figure 1.7. When QDSSC is illuminated by sunlight then excitons are generated upon light absorption by the QDs. If the exciton recombination is slow compared to electron injection rate, the electron will be transferred to the conduction band of wide bandgap semiconductor. The hole remaining behind in the QD will be reduced through an electrochemical reaction with the reductant in the electrolyte. The electrons injected into the semiconductor flow to the contact at the anode, through the load and to the cathode where they reduce the oxidant in the electrolyte to complete the circuit. This process can be explained using chemical reactions as follows.

When QDSSC is illuminated with light of energy equal to or greater than bandgaps of the QDs, then excitons are generated in QDs (Eq. 1.3)

\[ \text{QD} + h\nu \rightarrow \text{QD}^* \]  \hspace{1cm} (1.3)

\[ \text{QD}^* \rightarrow \text{QD}^+ + e^- (\text{ZnO}) \]  \hspace{1cm} (1.4)

When the energy contained in a single photon is greater than the bandgap of the QDs sensitizing the cell, multiple excitons are then generated. Charge separation is performed by ZnO/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 (Eq. 1.5).

\[
I_3^- + 2e^- (Pt) \rightarrow 3I^-
\]  

(1.5)

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 (1.6).

\[
2 \text{QD}^+ + 3I^- \rightarrow 2 \text{QD} + I_3^-
\]  

(1.6)

![Diagram of energy flow in quantum dot sensitized solar cell](image)

**Fig. 1.7 Schematic diagram of energy flow in quantum dot sensitized solar cell**

The major mechanism of charge separation is the energy level position of the whole system (Fig. 1.7). The excited state of the QDs should lie above the conduction band edge of the ZnO and ground state of the QDs should lie below the chemical potential of redox pair $I^-/I_3^-$ in the electrolyte, due to which there exists a 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.

There is no electric field to drive the transport because electric fields cannot be sustained in the semiconductor nanoparticles or in electrolyte, except in few angstroms thick space charge layers near solid surfaces. QDSSC have been made by various research groups with several different types of semiconductor QDs, wide bandgap semiconductors and electrolytes [71]. For example, QDSSC have been made using PbS, CdS, CdSe, InAs, InP, Ag$_2$S, Sb$_2$S$_3$ and Bi$_2$S$_3$ QDs on TiO$_2$ nanoparticles using polysulfide, cobalt, ferricyanide, and iodine electrolytes [72-79]. QDSSC have also been made with ZnO, SnO$_2$, Nb$_2$O$_5$ and Ta$_2$O$_5$ nanoparticles as the wide bandgap semiconductors [80-87]. The photovoltage in QDSSC is limited by the energy difference between the conduction band edge of wide bandgap semiconductor and the redox potential of the electrolyte, analogous to DSSCs.

The charge transfer rate in QDSSC depends on the band alignment of the two materials, which changes as the size of the QD varies. Larger QD will absorb more of the solar spectrum, but may not transfer the generated charges efficiently to the acceptor material. The injection rate of an electron is dependent on the difference in the QD conduction band and the conduction band of wide bandgap semiconductor.

**1.5.7 Efficiency Limit of Quantum Dot Sensitized Solar Cell**

The theoretical efficiency limit of a solar cell depends on the optical bandgap of the absorber and the band alignment within the device. To reach high conversion efficiencies, the difference between the electrical energy of a photogenerated charge and the photon energy at the absorption onset must be minimized. The impact of the loss in potential was recently quantified for DSSCs, and it was pointed out that a reduction of losses from 0.75 to 0.40 eV pushes the theoretical conversion efficiency limit from 13.4%
to 20.3 %, provided that optimized dyes are used in both cases. Similar considerations apply to QDSSCs, that is, high conversion efficiencies in the 15–20% range are realistic when the addressed problems can be solved.

Future high efficiency QDSSCs require smart material selection to provide the desired low loss energy level architecture. Additional methods must be developed which enable systematic energy level alignment between absorber, electron and hole conducting medium. Band offsets must be reduced to the extent that only the driving force for charge separation is maintained, while thermalization effects must be minimized. If this can be realized, QDSSCs will offer a low cost alternative as building blocks in multi-junction third generation PV cells as well as for broadband single-junction PV devices.

1.5.8 Challenges in Quantum Dot Sensitized Solar Cell

In summary, the main working principle of QDSSCs is very similar to DSSCs and QDSSCs can boost the power conversion efficiencies many folds than DSSCs by making use of MEG effect using hot electrons. But all this would happen after the QDs are properly linked with the wide bandgap semiconductor network layer. The aim of the present work is to replace dyes in DSSCs by QDs to fabricate QDSSCs. In case of DSSC, dye molecules have carboxyl groups attached with them to get linked with wide bandgap semiconductor network layer but no such linking molecule exists in case of QDs. To overcome such problem external linking molecule such as Mercapto Propionic Acid (MPA) is used to link QDs with ZnO layer. MPA is a bi-functional linking molecule which attaches itself to QD from the one end and to wide bandgap semiconductor network from another end. Figure 1.8 clearly explains the linking phenomenon.

For large scale applications of QDSSCs, it is desirable to replace the liquid electrolyte by a quasi solid or solid state hole conductor, mainly to reduce difficulties associated with sealing (liquid electrolyte may leak). Additionally, solid state hole
conductors are interesting because the highest photovoltages reported for DSSCs were achieved with solid state devices [88]. So, similar concept is used in the present system of QDSSC. Compact wide bandgap semiconductor layers are required to cover the ITO electrode to prevent recombination.

![Diagram of ZnO, mercapto propionic acid, QDs, and modified ZnO electrode]

Fig. 1.8 Mercapto propionic acid acting as linking molecule between ZnO and QDs

The limited number of semiconducting QDs that have been synthesized up to now leaves the field wide open for materials scientists to identify new semiconducting absorbers. Also the very limited number of redox electrolytes that have been investigated in conjunction with QDSSCs demonstrates the need for further research. The interface properties within the device are critical for its operation. Research in this direction has just started, and further progress is expected in the near future. New methods for energy level alignment should boost the QDSSC efficiency to compete with the conversion efficiency of 15–20 %, of Si solar cells, but at a significant lower cost.
1.6 Brief Outline of the Thesis

This thesis aims at evaluating the potential of QDs as photon absorbing material in solar cells. The objective of this work is to fabricate and characterize QDSSCs for best solar cell performance. The research undertaken in the present work describes synthesis and characterization of ZnO nanoparticles, CdS and CdSe QDs, and fabrication of QDSSCs using the synthesized ZnO nanoparticles and QDs. The thesis has been divided into six chapters as follows:

CHAPTER – 1 Introduction

This chapter provides a brief overview on the necessity of using renewable sources of energy as an alternative to non-renewable sources of energy. A brief description of the various generations of solar cells and the properties of different types of solar cells in different generations is also given. The distinction between conventional Si based solar cell and DSSC is done on the basis of their working principles because of the working similarities between DSSC and QDSSC. The construction of QDSSC, its operating principle, charge carrier separation mechanism, charge transport and recombination losses have also been discussed.

CHAPTER – 2 Experimental Details & Characterization Techniques

The initial part of this chapter is dedicated to the description of each layer used for the fabrication of QDSSCs. The details of Indium Tin Oxide (ITO) substrate, mesoporous ZnO electrode, QDs as sensitzers, electrolytes and counter electrodes are discussed along with the procedure for assembling the cell. The various characterization techniques used during the work were X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), UV-Vis Spectroscopy, Photoluminescence (PL), Class-A Solar Simulator and Keithley Sourcemeter. The chapter also covers the working principles and technical details of the above techniques.
CHAPTER – 3  Synthesis and Characterization of ZnO Nanoparticles

This chapter reports the synthesis of ZnO nanoparticles using sol-gel method and solid state reaction method. The effect of pH variation on sol-gel synthesized ZnO nanoparticles was also investigated. The size of the nanoparticles increased with increase in pH of the sol. Minimum crystallite size of ~28 nm and maximum crystallite size of ~32 nm was obtained for pH value of 7 and 11 respectively. An increase in the bandgap (blue shift) was observed with decrease in the size of the ZnO nanoparticles. The growth mechanism of ZnO nanoparticles from zinc acetate dihydrate precursor has also been discussed in terms of solvation, hydrolysis and polymerization.

CHAPTER – 4  Synthesis and Characterization of Quantum Dots

This chapter gives a detailed description of the synthesis techniques of the CdS and CdSe QDs. Chemical route was employed to synthesize CdS and CdSe QDs. While synthesizing CdS QDs, Poly Vinyl Alcohol (PVA) was used as capping agent to control the size of the QDs. The size of CdS QDs decreased from 5.6 to 2.6 nm with increase in capping agent concentration from 2 to 10 wt%. Bandgap of the QDs increased from 2.5 to 2.74 eV with decrease in QD size from 5.6 to 2.6 nm. CdSe QDs size varied from 0.85 to 2.25 nm with increasing synthesis temperature from 225 to 255°C. Bandgap of CdSe QDs decreased from 3.4 to 1.95 eV with increase in size from 0.85 to 2.25 nm.

CHAPTER – 5  Fabrication and Characterization of Quantum Dot Sensitized Solar Cells

This chapter is dedicated to the fabrication of ZnO based QDSSC using CdS and CdSe QDs as sensitizers. The use of CdS QDs of varying bandgap from 2.5 to 2.74 eV resulted in the absorbance of light in the range 400 to 600 nm. The values of short circuit current density ($J_{sc}$), open circuit voltage ($V_{oc}$), maximum power ($P_{m}$), fill factor (FF) and efficiency ($\eta$) are found to be 5.43 mA/cm$^2$, 0.64 V, 1.3 mW, 0.4 and 1.3 % respectively.
The use of CdSe QDs of varying bandgap 1.95 to 3.4 eV resulted in the absorbance of a broader spectrum of visible light in the range 350 to 700 nm. The values of $J_{sc}$, $V_{oc}$, $P_m$, FF and $\eta$ are found to be 10.5 mA/cm$^2$, 0.78 V, 3.6 mW, 0.45 and 3.6 % respectively.

CHAPTER – 6 Conclusions and Future Aspects

This chapter concludes and summarizes the results of the synthesis and fabrication processes presented in the thesis. The suggestions for future work are also proposed. This includes research on QDSSC based on nanostructures other than nanoparticles such as nanorods and nanotubes etc. New semiconducting QD materials and electrolytes can also be investigated. The possibility of the present work with co-sensitization of the CdS and CdSe dots is also proposed which would be our future work.
References


