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Introduction

Annual global energy demand is 125 PWh according to world energy consumption report [REN21, 2017]. Sun delivers 9944000 PWh energy per year. Earth receives 1800 PWh annual solar energy in form of radiation from Sun [Thirugnanasambandam et al., 2010]. So, Sun can be a major alternative to the fossil fuels to tackle global energy demand. At present, renewable energy supplies 20 % of global energy demand but still solar energy plays limited contribution (0.3 %) in energy supplied by renewable energy sources [REN21, 2017]. Solar photovoltaic (PV) systems have emerged as the potential alternative to the conventional energy sources. Solar energy power plants of several GWh capacity are getting installed worldwide [REN21, 2017]. It all started with recognition of photovoltaic process in 1893 [Williams, 1960].

1.1 Photovoltaic Process and Photovoltaic Cell

Photovoltaic process was discovered by Edmund Becquerel in 1893 [Williams, 1960]. In photovoltaic power conversion process, electron in semiconductor valence band is excited to conduction band on the absorption of solar photon having energy more or equal to bandgap of semiconductor. In this process, photoexcited electron-hole pair gets generated. These photoexcited carriers get transported to the selective contacts of a solar cell and get collected at respective terminals. A photovoltaic cell is normally a P-N junction device that converts solar energy into electrical energy directly [Solanki, 2013]. Incident solar radiation creates an electron-hole pair in the depletion region of a P-N junction and these photogenerated carriers are swept across junction with the help of a built in field of junction and collected at the selective contacts. This result in voltage difference at the selective contacts and this difference in voltage at terminals is utilized as electrical energy [Solanki, 2013].

1.2 Evolution of Photovoltaic Cells

Solar photovoltaic power generation plants need efficient and robust PV modules those are cheap enough for solar photovoltaic plants to remain competitive with conventional mode of electricity generation [Raman et al., 2012]. Evolution of photovoltaic cells has been classified in generations. Each generation is different in terms of underlying technology for PV device fabrication and targeted cost goals for electricity generation. Each successive generation of photovoltaic cells was focused to bring cost down for electricity generation as shown schematically in Figure 1.1 [Reddy et al., 2014]. First generation of solar cells was focused on moderate solar cell efficiencies in 10-20 % range with energy cost in range of 3.5 US$/watt. First generation of photovoltaic cells were mostly based on Si wafer, hence these cells were much costlier. Due to the higher processing costs involved in Si wafer preparation, it was not possible to bring cost down further [Alsema and de Wild-Scholten, 2005]. To bring the cost further down, second generation of photovoltaic cells were introduced. Second generation solar cells were mostly based on thin film of alternate semiconductor material like Cadmium Telluride (CdTe), Copper Zinc Tin Sulfide (CZTS), Copper Indium Gallium Sulfide (CIGS), Gallium arsenide (GaAs) or even including Silicon as well [M. A. Green, 2004]. These second generation photovoltaic cells utilized normally physical vapor deposition processes for preparation of semiconductor material absorber, hence cost was reduced but still efficiency was in moderate range as shown schematically in Figure 1.1 [Aberle, 2009]. After second generation, third generation of solar cells were introduced to reduce cost further targeting higher theoretical efficiencies in range of 20-60 % as shown schematically in Figure 1.1 [Martin A. Green, 2001]. Figure 1.1 also shows present limit of solar cells efficiencies faced by current manufacturing technology for single junction based solar cells. However, this current limit of photovoltaic process can be improved further using advance concepts like multi-junction solar cells, multi-exciton generation etc. Figure 1.1 also shows thermodynamic limit for solar energy conversion that is the highest theoretical thermodynamic limit for solar energy conversion with keeping Sun as energy source and Earth as energy sink in consideration. Normally solar cells are categorized in two categories based on broad working principle of solar cells. These cells are broadly categorized as conventional or P-N junction based solar cells and excitonic solar cells.

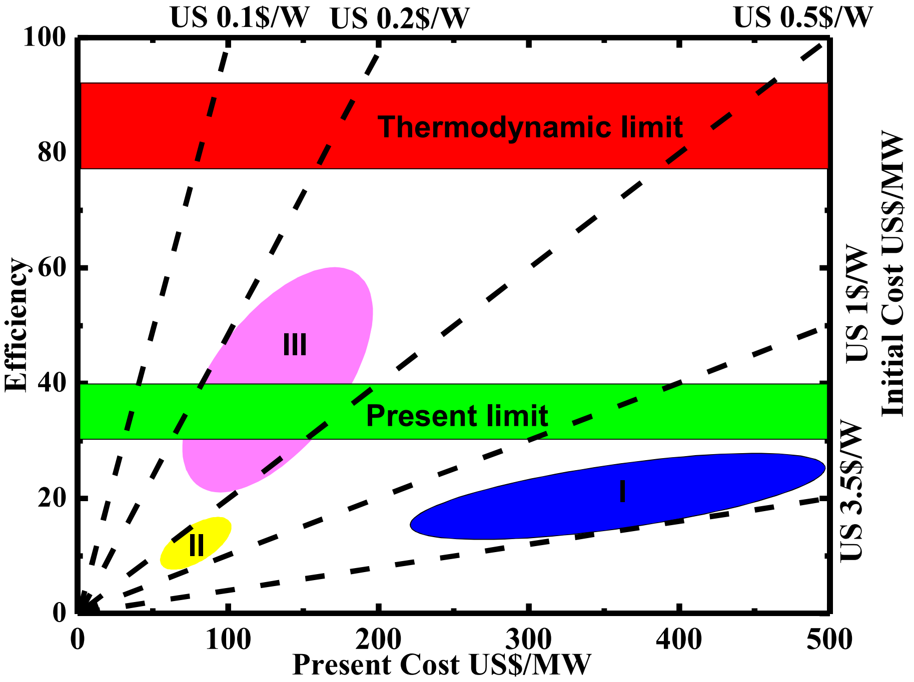

Figure 1.1 Schematic diagram showing development of solar photovoltaic cells in generations along with targeted cost and present cost for power generation along with thermodynamic limit of solar cells [Reddy et al., 2014].

1.3 Conventional Photovoltaic Cells and Excitonic Solar Cells

Conventional solar cells are photovoltaic devices those are based on P-N junction of same or different semiconductor materials as shown schematically in Figure 1.2(a) [B.A. Gregg, 2003]. At P-N junction, a depletion region is formed. These semiconductors are lightly doped to have larger width of depletion region. A built-in field exists at depletion region that opposes movement of majority carriers and assists in the movement of minority carriers. Incident solar photons at depletion region of the P-N junction are absorbed by semiconductor material and electron and hole pairs are generated. These photogenerated electron and hole pairs are minority carriers in the P-N junction and these minority carriers are swept across P-N junction due to presence of built in field. These carries are transported through the semiconductor material and collected at respective contacts at P and N type semiconductors. A photovoltage is developed at terminals of P-N junction because of photogenerated carrier collection at selective contacts, which leads to a load current flow across the device. This results in conversion of solar radiation into electrical energy. Excitonic solar cells are different in fundamental working principle with respect to conventional solar cells. A schematic diagram of excitonic solar cells is shown in Figure 1.2 (b)[B.A. Gregg, 2003]. Excitonic solar cells make use of excitonic absorbers and a bound electron-hole pair, called exciton, is generated instead of a free electron and hole pair in conventional solar absorbers after absorbing an incident solar photon with energy above or equal to bandgap [Powell and Soos, 1975], [B.A. Gregg and Hanna, 2003]. Excitons are dissociated at interface in free electrons and holes, where proper band/energy levels alignments allow them to move across the external circuit [B. Gregg et al., 1990]. An electron transport material is normally utilized to collect electrons from excitonic absorber. Here, the electron transport material (ETM) and excitonic absorber interface governs the dissociation rate of excitons and extraction of electrons in electron transport material. Thus, a suitable band alignment at ETM and excitonic absorber will assist in extraction of electrons more efficiently. Similarly, a hole transport material (HTM) is used to collect holes from excitonic absorber and the interface at hole transport material and excitonic absorber will govern the extraction of holes from excitonic absorber. The photogenerated carrier from electron and hole transport materials are collected at selective contacts [González-Pedro et al., 2010]. These collected photogenerated carrier generate photovoltage at solar cell terminals and thus solar energy is converted into electrical energy. Quantum dot sensitized solar cell (QDSSC) is an example of excitonic solar cell that converts solar energy into electrical energy by making use of Quantum Dots (QDs) as excitonic absorber [Kamat, 2008].

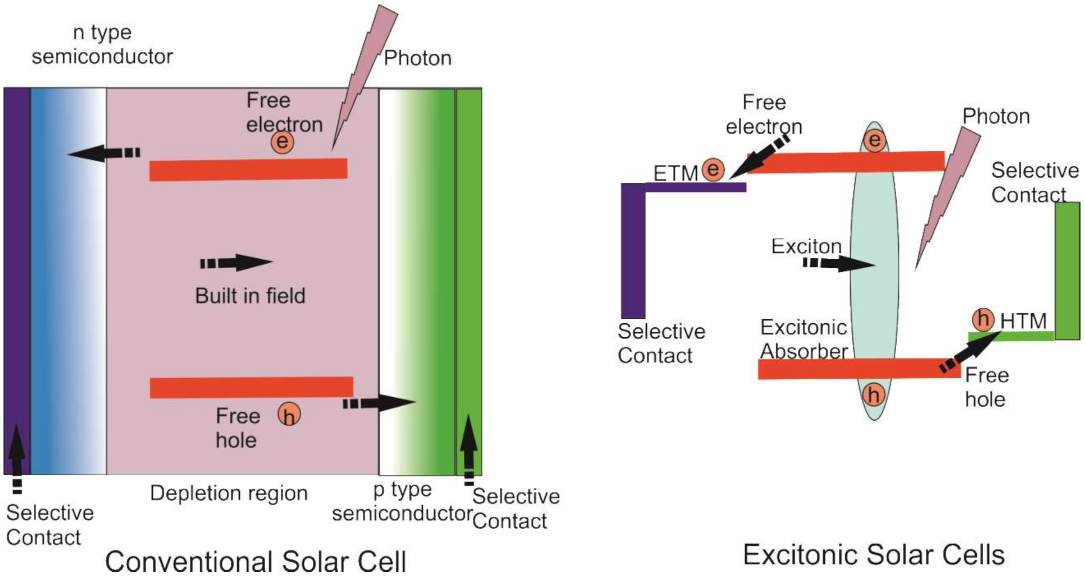

Figure: 1.2 Schematic diagram showing the working mechanism of (a) conventional P-N junction solar cell and (b) excitonic solar cell.

1.4 Quantum Dot Sensitized Solar Cells

A schematic diagram of Quantum Dot Sensitized Solar Cell is shown in Figure 1.3. Here, bottom half of the diagram shows the side view of QDSSC, with respective sub-components. Normally, fluorine doped tin oxide (FTO) coated glass is taken as substrate for depositing electron transport material. Mesoporous TiO_2 is normally utilized as an electron transport material although photoelectrode materials such as ZnO [Tian et al., 2013], SnO_2 [Hossain et al., 2011] and $ZnTiO_3$ [J. Yu et al., 2016] have been utilized as electron transport material as well.

This mesoporous electrode is sensitized with quantum dot absorbers and these QDs work as excitonic absorber. Polysulfide electrolyte is normally utilized as a hole transport material although several other red-ox electrolyte and solid hole conductor have also been utilized. A spacer is used to separate sensitized photoelectrode and counter electrode and redox electrolyte is filled in the gap. In top panel of Figure 1.3, the respective energy levels are shown schematically. Incident photons, having energy more than or equal to QD bandgap, are absorbed and excitons or Coulombic coupled electron and hole pairs are generated. The photoexcited electrons are transferred to the electron transport material due to their favorable energy offset between electron transport material and QDs absorber. Similarly, a favorable energy offset at redox electrolyte and QDs absorber helps extraction of hole or regeneration of QDs absorber. Counter electrode works as catalytic material for red-ox reaction of polysulfide electrolyte and hole is finally captured at counter electrode [Hod and Zaban, 2014]. Semiconductor Quantum Dots have been utilized as excitonic absorber and they are reported to be very efficient in multiexciton generation [R. D. Schaller and Klimov, 2004]. Multiexciton generation could enhance the photovoltaic efficiency of quantum dot sensitized solar cells beyond the single junction limits as predicted by Klimov using detailed balance calculation [Klimov, 2006].

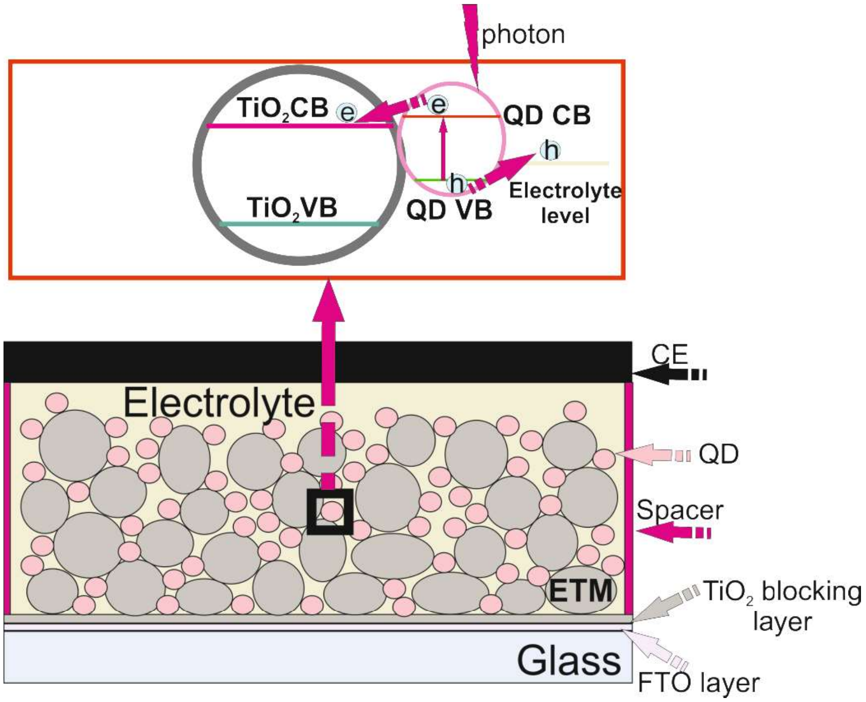

Figure : 1.3 Schematic diagram of quantum Dot Sensitized Solar Cells, lower panel shown side view of QDSSC and top panel shows working mechanism in brief.

1.5 Carrier Multiplication in Semiconductor Quantum Dots

The generation of more than one electron-hole pair due to the impact ionization is called carrier multiplication [Landsberg et al., 1993], [Kolodinski et al., 1993]. Figure 1.4 shows a schematic diagram, explaining the carrier multiplication. After absorption of incident photon having energy more than QD bandgap, hot carriers are generated [R. D. Schaller and Klimov, 2004]. These hot carriers can generate another electron hole pair by impact ionization. This process is called carrier multiplication or multiexciton generation in semiconductor Quantum Dots. Carrier multiplication is also observed in bulk materials as well, but carrier multiplication in semiconductor quantum dots is more efficient due to the lowering of energy offset for carrier multiplication in confined systems [Guyot-Sionnest et al., 1999], [Klimov et al., 2000]. In bulk semiconductor, threshold for carrier multiplication is so high that any useful contribution in solar cell utilizing bulk absorbing material is negligible. Thermodynamic limit for carrier multiplication for semiconductor quantum dots is close to twice of bandgap of a bulk semiconductor. In semiconductor quantum dots having large difference in effective mass of electron and holes, threshold for carrier multiplication is close to twice of semiconductor bandgap [Nozik, 2001]. Such lower threshold of carrier multiplication can enhance photovoltaic performance of semiconductor quantum dots as shown in detailed balance calculation done by Klimov.

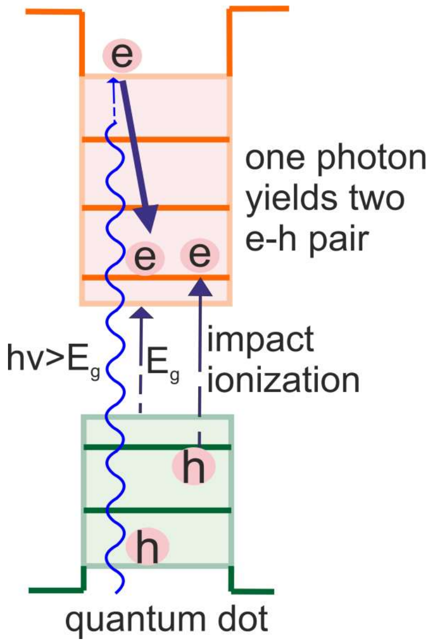

Figure: 1.4 Schematic diagram showing carrier multiplication with impact ionization along with energy requirement of incident photon for multiexciton generation.

1.6 Objective

This thesis work focuses on fundamental aspects of quantum dot sensitized solar cells and contributes towards understanding of Quantum Dot Sensitized Solar Cells working mechanism. Work also focuses on estimation of the detailed balance efficiency estimation of QDSSCs. The objective of work can be summarized in following points.

1. Investigation of in-situ hydrothermal sensitization of CdTe quantum dots for enhanced photovoltaic performance of CdTe QDs Sensitized Solar Cells.
2. Investigation of transition metal doping in CdS quantum dot based QDSSCs and rationale behind their selection and respective consequences.
3. Investigation of alternative photoelectrode material named zinc titanate that is prepared using sol-gel process for QDSSCs application.

4. Calculation of detailed balance efficiency of quantum dot solar cell with TiO_2 as electron transport material and polysulfide electrolyte as hole transport material under realistic/practical energy levels consideration.

1.7 Outline of Thesis

The subject matter covered in this thesis is divided in nine chapters. The second chapter gives literature review on the development of solar cells followed by excitonic solar cells and subsequently development of Quantum Dot Sensitized Solar Cells. It also discusses the improvements made in each component of Quantum Dot Sensitized Solar Cells in detail. Third chapter discusses the methodologies to be adopted for tackling problems identified in chapter 2. Fourth chapter discusses the experimental processes adopted in this thesis work. Fifth chapter discusses the in-situ hydrothermal sensitization of CdTe quantum Dots and estimation of photovoltaic performance of CdTe sensitized photoelectrode. Sixth chapter discuss about transition metal doping in CdS QDs sensitized TiO_2 photoelectrode and impact of transition metal doping in photovoltaic performance of Quantum Dot Sensitized Solar Cells. This chapter also discusses the rationale behind selection of a transition metal dopant. Seventh chapter discusses about the sol-gel synthesis of zinc titanate photoelectrode material and its application as photoelectrode material in CdS sensitized QDSSCs. Eighth chapter discusses detailed balance calculation of Quantum Dot Sensitized Solar Cell efficiency with TiO_2 as electron transport material and polysulfide electrolyte as hole transport material. Ninth chapter discusses the conclusion of entire work done at IIT Jodhpur and annexure shows MATLAB code, written for calculating detailed balance efficiency of Quantum Dot Sensitized Solar Cells with practical electron transport material (TiO_2) and hole transport material (polysulfide electrolyte).

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