2
Review of Literature

Solar photovoltaic systems have evolved significantly in last few decades. Various solar cell architectures with different absorber materials have been developed in last few decades. Figure 2.1 shows the introduction year of different type of solar cells since 1976 reported by National Renewable Energy Laboratory (NREL) in its report in 2015.

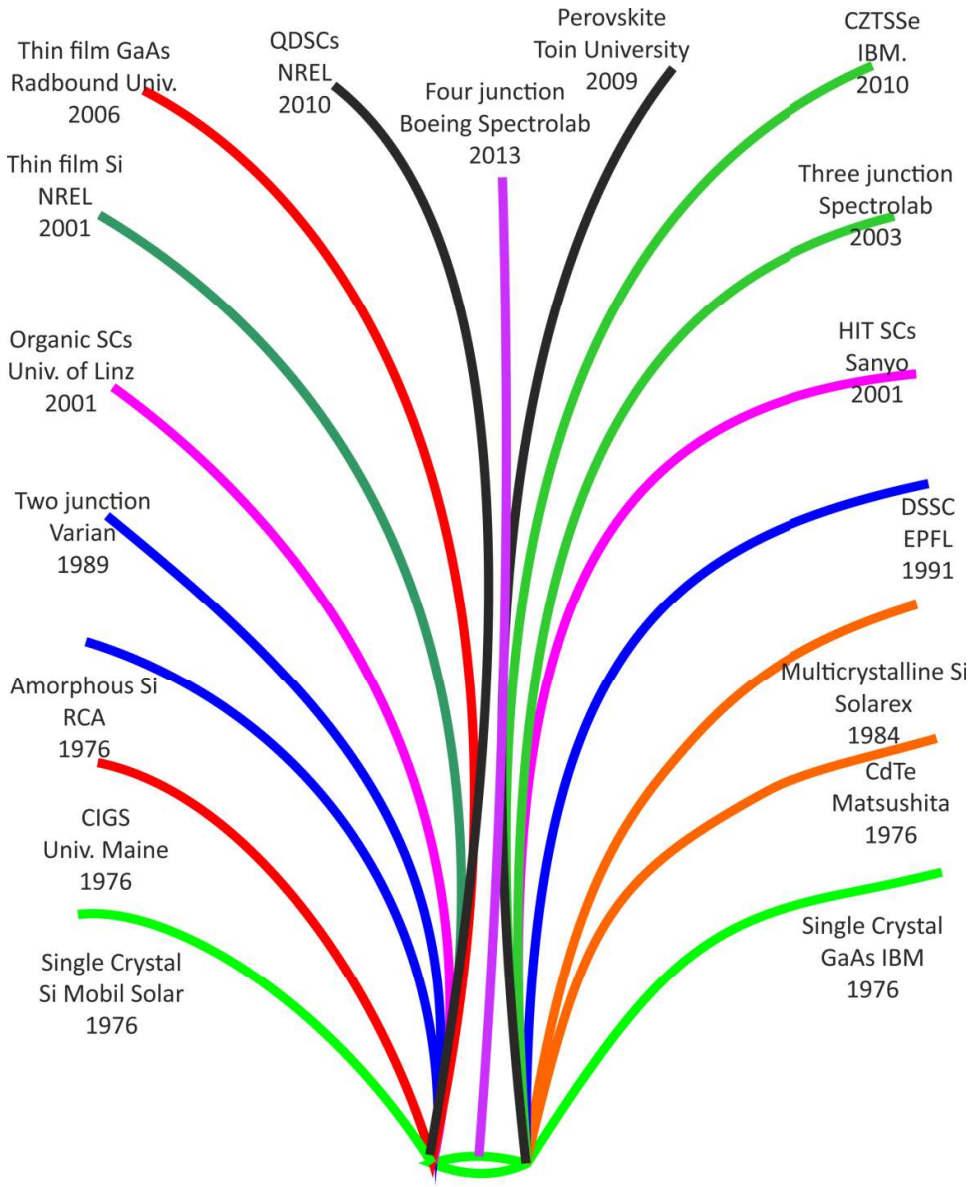

Figure: 2.1 Schematic representation of introduction of various photovoltaic cell technology since 1976.

2.1 Evolution of Solar Cells in Generations

Solar cell evolutions can be classified in four generations according to the underlying device physics, structure and operating principle [Jayawardena et al., 2013]. These generations are shown schematically in Figure 2.2 and detailed photovoltaic parameters for most efficient solar cell from different generations are summarized in Table 2.1. First generation solar cells include Si wafer based solar cells. These cells are also known as conventional solar cell and are well commercialized. These cells are categorized in monocrystalline and polycrystalline solar cells. Second generation of solar cell is based on thin film based solar cells. Second generation solar cells include Cadmium Telluride (CdTe) based solar cells, amorphous Si based solar cells, Heterojunction with Intrinsic thin layer (HIT) solar cells, Copper Indium Gallium Selenide (CIGS) based solar cells, Gallium Arsenide (GaAs) based solar cells etc. Third generation solar cells include advanced concepts to cut down the cost of solar energy generation and simultaneously advancing towards higher efficiencies. Third generation solar cells include Dye Sensitized Solar Cells (DSSCs), Quantum Dot based solar cells (QDSCs), multijunction solar cells and perovskite solar cells etc. Fourth generation solar cells include inorganic in organic nano particle polymer based hybrid solar cells.

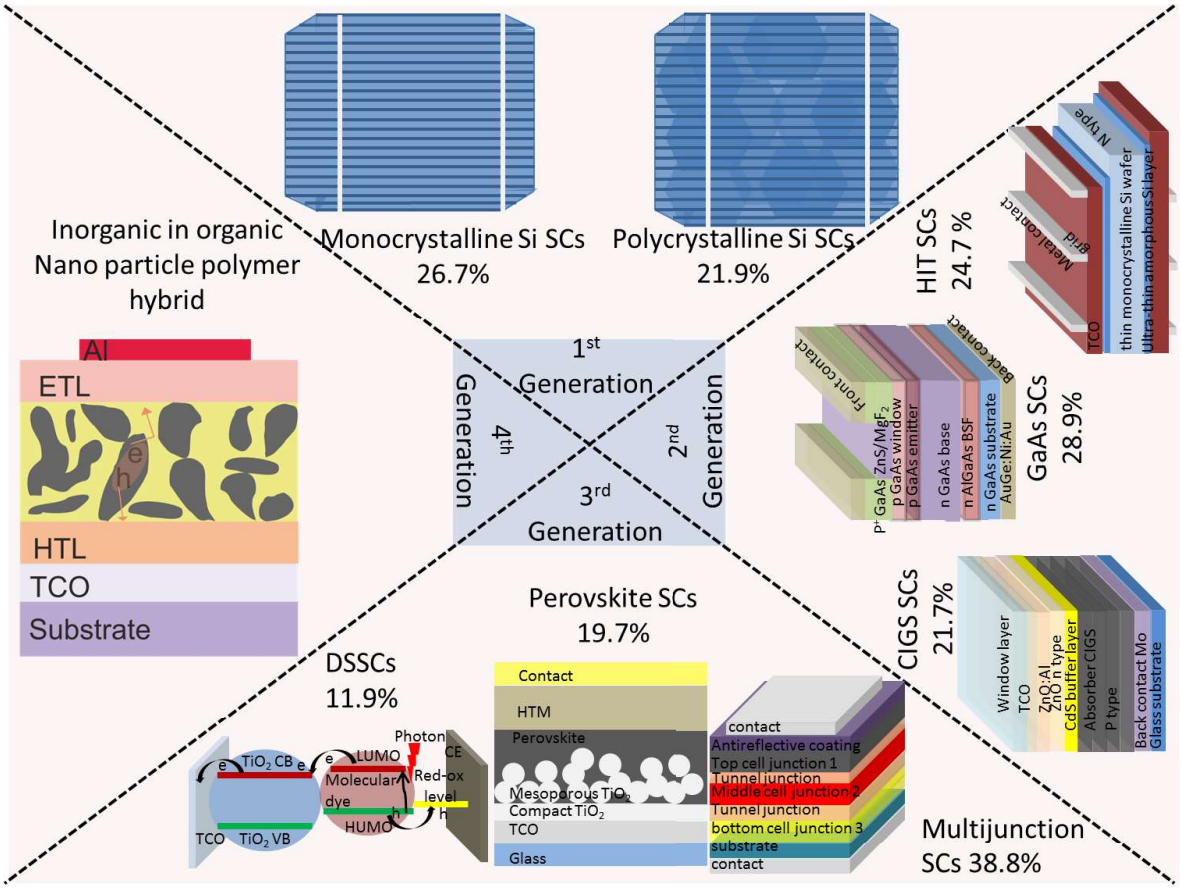

Figure: 2.2 Schematic representation of four generation for solar photovoltaic with schematics of representative devices.

The highest performing devices from each generation are summarized in Table 2.1 with their respective device performance parameters.

Table: 2.1 Summary of some solar cells from all generations along with best solar cells and their respective photovoltaic parameters.

Solar cell generation	Device architecture	Photovoltaic performance parameter for best reported device		
		J_{SC}(mA/cm^2), V_{OC} (Volt)	FF	Efficiency (%)
1st	Monocrystalline Si based Solar cell[Yoshikawa et al., 2017]	42.65, 0.738	84.9	26.7±0.5
	Polycrystalline Si based Solar cell [Benick et al., 2017]	40.76, 0.6726	79.7	21.9±0.4
2nd	Amorphous Si based Solar Cell [Matsui et al., 2015]	16.36, 0.896	69.8	10.2±0.3
	Microcrystalline Si based Solar cell [Sai et al., 2015]	28.72, 0.55	75.0	11.9±0.3
	CIGS Solar cells [Kato et al., 2017]	40.7, 0.718	74.3	21.7±0.5
	CdTe solar cells (First Solar Press release 23 Feb 2016)	30.25, 0.88	79.4	21.0±0.4
	CZTS solar cell [Sun et al., 2016]	21.77, 0.71	65.1	10.0±0.2
	GaAs Solar cell [Kayes et al., 2011]	29.68, 1.12	86.5	28.8±0.9
	HIT Solar cells [Wakisaka et al., 1991], [Taguchi et al., 2014]	39.5, 0.75	83.2	24.7
3rd	Multi-junction solar cell [Chiu et al., 2014]	9.56, 4.77	85.2	38.8±1.2
	Dye sensitized solar cell [Mathew et al., 2014]	18.1, 0.91	78	13±0.4
	Perovskite solar cell [Yang et al., 2015]	24.67, 1.104	72.3	19.7±0.6
	Organic solar cell [Mori et al., 2015]	19.30, 0.78	74.2	11.2±0.3
	Quantum Dot sensitized solar cell [Du et al., 2016]	25.18, 0.742	62.4	11.66±0.17
4th	Nano-particle polymer hybrid solar cells [Liang et al., 2010]	14.50,0.74	68.97	7.4 (representative)

Solar cells can be classified in another category based on their operating principles. First category includes conventional solar cells based on a P-N junction. These types of solar cells make use of built in field in a P-N junction to separate the photogenerated carriers in depletion region in a P-N junction based solar cells. Another category includes excitonic solar cells. In these type of solar cells, excitons are generated instead of free electron and hole pair and these excitons dissociate in free carrier at interface and dissociated photoexcited charge carrier are

transferred by electron transport material and hole transport material and get collected at respective selective contacts as discussed in section 1.3. Excitonic solar cells include dye sensitized solar cells, quantum dot sensitized solar cells, perovskite based solar cells etc.

The sensitization of wide bandgap semiconductor with semiconductor QDs has been a topic of active research from sixties. Molecular dyes have been used as the sensitizers over the last few decades. Photogenerated carriers could be efficiently accepted by electron transport material made of wide bandgap semiconductor while positive holes were captured by a liquid red-ox couple. In 1990, Vogel et al. sensitized titanium oxide (TiO_2) by cadmium sulfide (CdS) using successive ionic layer adsorption and reaction (SILAR) method [Vogel et al., 1990]. Weller et al. in 1991 reported the sensitization of TiO_2 by PbS QDs using SILAR process [Weller, 1991]. They reported reduction in current after five cycles of SILAR as injection of electrons to TiO_2 reduced due to quantum confinement effect. Kamat et al. reported photovoltaic properties of zinc oxide (ZnO)/CdS film over conducting glass. Vogel et al. in 1994, reported the sensitization of TiO_2, tin oxide (SnO_2), niobium pentoxide (Nb_2O_5), tantalum pentoxide (Ta_2O_5) and ZnO wide bandgap semiconductor electrodes using lead sulfide (PbS), CdS, silver sulfide (Ag_2S), stibanylidynestibane sulfide (Sb_2S) and bismuth sulfide (Bi_2S_3) QDs using SILAR. They also reported enhanced stability for PbS quantum dot sensitized TiO_2 after coating with wide bandgap material like TiO_2. Jinghui et al. reported co-sensitization of TiO_2 mesoporous electrode with cadmium selenide (CdSe) and dye molecule [Fang et al., 1997]. Zaban et al. reported sensitization of mesoporous electrode using pre-synthesized indium phosphide (InP) QDs [Zaban et al., 1998]. After these early developments in QDSSCs, research accelerated over different aspects of quantum dot sensitized solar cells, including the different geometrical configurations.

Quantum Dot sensitized solar cells are similar in structure to a dye sensitized solar cells with few structural differences. A schematic diagram of dye sensitized solar cells and quantum dot sensitized solar cells are shown in Figure 2.3.

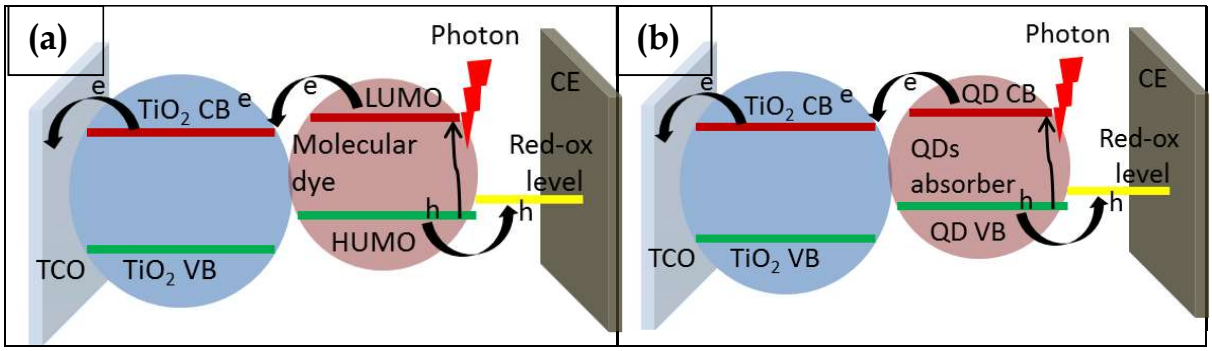

Figure: 2.3 Schematic diagrams showing structure and brief working mechanism for (a) dye sensitized solar cells and (b) quantum dot sensitized solar cells.

These both types of solar cells make use of electron transport material like TiO_2 and hole transport material like red-ox electrolyte. Dye sensitized solar cells make use of molecular absorber dyes while quantum dot sensitized solar cells make use of semiconductor quantum dots as absorber as shown in Figure 2.3. Quantum Dot absorber also participate actively in interfacial recombination with surface states while molecular dyes do not have surface states to participate in interfacial recombination making a fundamental difference in recombination processes [Hodes, 2008].

Quantum Dot Sensitized Solar Cells include several building blocks and advancements in the respective building blocks are summarized in following subsections.

2.2 Building Blocks of a Quantum Dot Sensitized Solar Cells

The sub-components of a Quantum Dot Sensitized Solar cells are considered carefully for efficient design of QDSSCs. These components are excitonic absorber, electron transport material, sensitization of mesoporous electrode, hole transport material and counter electrode. Each of them is discussed in the following sections including the respective issues and challenges to realize an efficient QDSSC.

2.2.1 Excitonic Absorber

Absorber material is a very important part of the solar cell. This is responsible for absorbing incident solar photons and producing photogenerated carriers. Shockley and Queisser calculated the dependence of absorber bandgap on the detailed balance efficiency for a single P-N junction solar cell [Shockley and Queisser, 1961]. In 2006, Klimov calculated the detailed balance efficiency for a quantum dot based solar cell and shown the dependence of detailed balance efficiency on QDs absorber bandgap and is shown in Figure 2.4 [Klimov, 2006].

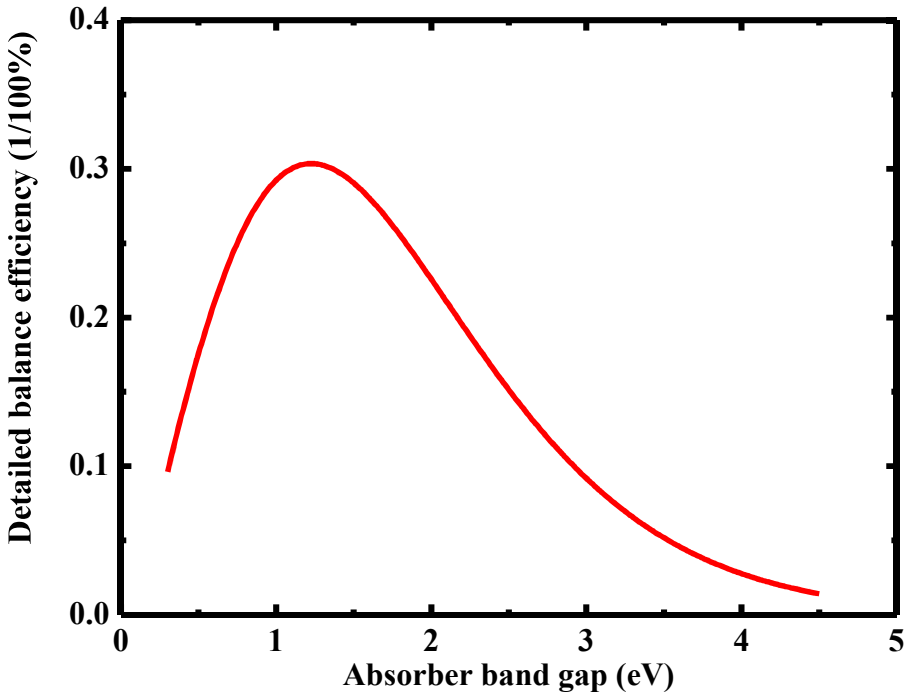

Figure 2.4 Dependence of detailed balance efficiency of quantum dot solar cell over QDs absorber bandgap.

Apart from excitonic absorber bandgap, composition of constituent materials and structure of quantum dots are also important for an efficient quantum dot solar cell. Composition and structure of QDs absorber decide their optoelectronic properties and will govern the recombination mechanisms. Core-shell structure [Jiao, Shen, Mora-Sero, et al., 2015] and alloying of quantum dots [Pan et al., 2013] have been utilized to tune their optical properties for efficient photovoltaic response. Transition metal doping of quantum dot

absorbers also changes their charge dynamics as shown by previous studies and also shows strong effect on their photovoltaic properties [Santra and Kamat, 2012]. The introduction of transition metal energy states was discussed in reports and these dopant states governs optoelectronic properties of quantum dots absorber and thus, photovoltaic response of quantum dot sensitized solar cells [Santra and Kamat, 2012]. However, a rationale behind selection of such dopants was not discussed. So, it is still a problem to decide a suitable transition metal dopant for efficient photovoltaic response. Conduction band minima of electron acceptor material and electrochemical level of red-ox electrolyte decides the minimum bandgap required for the quantum dot absorbers. Table 2.2 summarizes some of quantum dots utilized and their corresponding efficiency along with respective device configuration. This table shows wide range of available QDs excitonic absorbers.

Table: 2.2 Performance of some QDs absorber along with photovoltaic performance parameter with respective QDSSCs configuration. (FTO= Fluorine doped Tin oxide, S^{2-}-S_n^{2-} represents polysulfide electrolyte, FF= Fill factor, J_{sc}= current density, V_{oc}= open circuit voltage, RGO= Reduced graphene oxide, Pt= Platinum)

QDs absorber	Configuration of QDSSCs	J_{SC}(mA/cm^2),V_{OC}(Volt)	FF	Efficiency (%)
CdS [Santra and Kamat, 2012]	FTO/TiO_2/CdS/ZnS/S^{2-}-S_n^{2-}/RGO-Cu_2S/FTO	7.2, 0.496	0.46	1.63
CdS-Mn [Santra and Kamat, 2012]	FTO/TiO_2/CdS-Mn/ZnS/S^{2-}-S_n^{2}/RGO-Cu_2S/FTO	8.9, 0.583	0.49	2.52
CdSe [H. Zhang et al., 2012]	TiO_2/CdSe-MPA/ZnS/S^{2-}-S_n^{2-} /Cu_2S/Brass	16.96, 0.561	0.566	5.42
CdS/CdSe [X.Y. Yu et al., 2011]	TiO_2/CdS/CdSe/ZnS/S^{2-}-S_n^{2-}/Pt/FTO	18.23, 0.489	0.54	4.81
CdTe/CdSe [Wang et al., 2013]	TiO_2/CdTe/CdSe/ZnS/S^{2-}-S_n^{2-} /Cu_2S/Brass	19.59, 0.606	0.569	6.76
CdSeTe [Ren et al., 2015]	TiO_2/CdSeTe/$TiCl_4$/ZnS/S^{2-}-S_n^{2-}/$Cu_{2-x}S$/Brass	20.69, 0.700	0.622	9.01
ZnTe/CdSe [Jiao, Shen, Mora-Sero, et al., 2015]	TiO_2/ZnTe/CdSe/ZnS/S^{2-}-S_n^{2-}/$Cu_{2-x}S$/Brass	19.35, 0.646	0.551	6.89
Zn-Cu-In-Se [Du et al., 2016]	TiO_2/Zn-Cu-In-Se/ZnS/S^{2-}-S_n^{2-}/MC/Ti	25.18, 0.742	0.624	11.66

2.2.2 Electron Transport Material

Electron transport material (ETM) is another important part of a quantum dot sensitized solar cell. Electron transport material accepts photoexcited electrons from excitonic QDs absorber and transfers them to the selective contact often transparent conducting oxide. Thus, position of conduction band minima and conductivity of electrons in electron transport material is very important for the selection of electron transport material [Chakrapani et al., 2010]. Position of conduction band minima with respect to an excitonic absorber decides the exciton dissociation rate to free electron and hole. In absence of proper band alignment at electron transport material and excitonic absorber interface, photogenerated excitons will not be efficiently accepted by electron transport material and photoconversion efficiency will be poor. Conductivity of electron transport material governs the recombination rate of accepted photogenerated carriers. If conductivity of electron transport material is poor then photoexcited carrier will recombine with trap states or electrolyte. So, good conductivity of carriers in electron transport material is desirable. Excitonic QDs absorber is often deposited over mesoporous electrode made of electron transport material. So, porosity and surface morphology of the electron transport material as the electrode, are also another important parameters that dictate efficiency of quantum dot sensitized solar cell [Singh et al., 2018]. Considering wide range of available excitonic absorber as discussed in section 2.2.1, there is a requirement for alternative electron transport materials apart from widely used TiO_2 to achieve efficient exciton dissociation rate and loading fraction. Table 2.2 summarize few electron transport materials utilized in quantum dot sensitized solar cell along with morphology of electron transport material and cell configuration showing wide range of available electron transport material but not limited to these systems.

Table: 2.3 Summary of the some photoelectrodes material utilized as electron transport material for QDSSCs and their performance parameter along with electrode morphology.

ETM electrode material	Morphology	Quantum Dot utilized	Photovoltaic performance		
			J_{sc} (mA/cm^2), V_{oc} (Volt)	Fill factor	Efficiency (%)
TiO_2	Mesoporous layer of nano particle and scattering layer [Du et al., 2016]	Zn-Cu-In-Se	25.25, 0.739	0.622	11.61
	Nanotube [L. Yu et al., 2017]	CdS	12.64, 0.41	0.42	2.16
	Nano-rods [Z. Zhang et al., 2017]	PbS	12.94, 0.43	0.56	3.11
	Nano beads [Zhou et al., 2014]	CdS/CdSe	13.85, 0.54	0.54	4.05
	Nano particle [Tian et al., 2013]	CdS/CdSe	15.42, 0.62	0.49	4.68
	Nano flower [Tian, Uchaker, et al., 2014]	CdS/CdSe	10.74, 0.61	0.5	3.28

ZnO	Nano-rod [Hou et al., 2016]	Mn-CdSe	12.6, 0.74	0.44	4.64
	Nano wire [Jean et al., 2013]	PbS	17.9, 0.6	0.40	4.3
SnO_2	Nano particle [Hossain et al., 2011]	CdS/CdSe	17.40, 0.48	0.44	3.68
	Nano flower [Lan et al., 2015]	CdS	11.56, 0.6	0.43	3
Zn_2SnO_4	Nano particle [Y. Li et al., 2011]	CdS	0.5, 0.5	0.36	0.1
	Nano-rods [L. Bin Li et al., 2013]	CdS/CdSe	11.32, 0.49	0.37	2.08
Zinc titanate	Nano particle [J. Yu et al., 2016]	CdS/CdSe	5.96, 0.59	0.56	1.95
Strontium titanate	Nano particle [C. Chen et al., 2015]	CdS	1.53, 0.76	0.67	0.78

2.2.3 Sensitization Schemes

Apart from optoelectronic properties of QDs absorber, their mode of attachment with electron transport material and loading fraction over mesoporous electrode surface are also important for efficient operation of quantum dot solar cells [Nestor Guijarro et al., 2009]. Sensitization scheme governs the mode of attachment of QDs to electron transport material and loading fraction. Mode of attachment governs the charge transfer from excitonic absorber and loading faction decides the amount of light that will be absorbed by the excitonic absorber. Ideally, a sensitization scheme should offer uniform monolayer covering of excitonic absorber over mesoporous electrode. Such sensitization scheme will have sufficient loading fraction due to the availability of large surface area on mesoporous electrode and enough loading of excitonic absorber to absorb all the incident photons with suitable energy equivalent or greater than QD bandgap. However, as discussed in section 2.2.2, optoelectronic properties of excitonic absorber are also very important. So sensitization scheme should also offer precise control over optoelectronic properties of excitonic absorbers. Sensitization schemes are broadly classified in in-situ and ex-situ (post synthesis) sensitization schemes [Szemjonov et al., 2016]. In in-situ sensitization scheme, QDs are directly grown on mesoporous electrode like successive ionic layer adsorption and reaction, chemical bath deposition etc. In in-situ sensitization schemes, control of optoelectronic properties and loading fraction are difficult and often optoelectronic properties are sacrificed for good loading fraction of quantum dots over mesoporous electrode. In post synthesis scheme, pre-synthesized quantum dots are adhered by various schemes like direct adsorption, linker assisted direct adsorption, electrophoretic deposition. These sensitization schemes normally preserve the optoelectronic properties of prepared quantum dots, so control over optoelectronic properties is very good but they often result in bad control on quantum dots loading fraction in mesoporous electrode. So there is a need to develop new sensitization scheme or to optimize precisely these techniques to overcome such barriers form these sensitization scheme.

2.2.4 Hole Transport Material

Hole transport material (HTM) is another important component of quantum dot sensitized solar cells. It accepts holes from excitonic absorber which are collected at counter electrode. So, electrochemical level of hole conductor and hole conductivity are very important for efficient design of quantum dot solar cells [Makarov et al., 2014]. Conduction band minima of electron transport material and electrochemical potential of hole conductor often decides the maximum photovoltage available from quantum dot sensitized solar cells. So, the electrochemical potential level of hole conductor is very crucial for the efficient acceptance of hole from excitonic absorber together with the maximum photovoltage available. Conductivity of ionic hole conductor is often very good in comparison to the solid hole conductors which normally show relatively poor conductivity. A poor hole conductivity may result in increased recombinations and hence, lower photovoltaic performance. Quantum dot sensitized solar cells are often prepared with mesoporous electron transport material electrode, so the penetration of hole conductor in case of a solid hole conductor is also difficult because of limited diffusion lengths. Liquid hole conductor, solid hole conductor and quasi solid hole conductor are explored in quantum dot solar cells. Table 2.3 summarizes few hole conductors utilized in quantum dots sensitized solar cells. Considering wide range of available excitonic QDs absorbers as discussed in section 2.2.1, a wide range of hole conductors can be adopted, provided their electronic properties, especially the suitable energy levels and their alignment at interface are meeting the discussed criteria.

Table: 2.4 Performance of QDSSCs with different hole conductor utilized and their respective photovoltaic performance (FTO= Fluorine doped Tin oxide, S^{2-}-S^{n2-} represents polysulfide electrolyte, FF= Fill factor, Jsc= current density, Voc= open circuit voltage, MC= mesoporous carbon , Pt= Platinum).

Hole Conductor	Cell configuration	Photovoltaic performance		
		J_{sc}(mA/cm^2), V_{oc} (Volt)	FF	Efficiency (%)
Iodine/Iodide electrolyte[Ogermann et al., 2012]	$TiO_2/CdS_6Se_1/S^{2-}$-S_n^{2-}/Pt/FTO	1.38, 0.565	0.34	0.32
Cobalt electrolyte [H. Lee et al., 2009]	$TiO_2/CdSe_5Te_1$/cobalt electrolyte /Pt/FTO	4.94, 0.67	0.54	4.18
Polysulfide electrolyte [Du et al., 2016]	TiO_2/Zn-Cu-In-Se/ZnS/S^{2-}-S_n^{2-} /MC/Ti	25.18, 0.742	62.4	11.66
Ferrocene electrolyte [Tachibana et al., 2008]	TiO_2/CdS/ZnS/Ferrocene/Pt/FTO	2.45, 0.68	0.60	1.0
Spiro-MeOTAD [H. Lee et al., 2009]	$TiO_2/CdSe_5Te_1$/spiro-MeOTAD /Pt/FTO	2.15, 0.70	0.55	0.84

Poly 3-hexylthioophene [Qian et al., 2011]	TiO_2/CdS/P3HT /Au/Polymer	4.31, 0.67	0.55	1.42
Dextran-polysulfide gel [H.Y. Chen et al., 2013]	TiO_2/CdS/CdSe/ZnS/dextran-S^{2-}-S_n^{2-}/Pyrolized-Pt	15.86, 0.466	0.44	3.23

2.2.5 Counter Electrode

Counter electrode in quantum dot sensitized solar cell decides the catalytic activity for efficient reduction of red-ox electrolyte (hole conductor). If it is not able to accept holes from hole transport material, then it gives rise to the resistance at counter electrode and photovoltaic efficiency of QDSSC is affected [Radisch et al., 2011]. If it is catalytic enough, then good fill factor is observed along with lower series resistance. So, efficient counter electrode is a key requirement for a quantum dot sensitized solar cell. Numerous materials have been utilized as a counter electrode material in quantum dot sensitized solar cells and Table 2.4 summarizes some of them to show wide range of available counter electrode material for preparation of counter electrode.

Table: 2.5 Performance of QDSSCs prepared with different counter electrode material and their respective photovoltaic efficiencies (FTO= Fluorine doped Tin oxide, S^{2-}-S^{n2-} represents polysulfide electrolyte, FF= Fill factor, Jsc= current density, Voc= open circuit voltage, NP= Nano particle, Pt= Platinum).

Counter Electrode	Cell configuration	Photovoltaic performance		
		J_{sc} (mA/cm^2), V_{oc} (Volt)	FF	Efficiency (%)
Cu_2S/Brass [Ren et al., 2015]	TiO_2/CdSeTe/$TiCl_4$/ZnS/S^{2-}-S_n^{2-}/$Cu_{2-x}S$/Brass	20.69, 0.700	62.2	9.01
Pt [H. Lee et al., 2009]	TiO_2/$CdSe_5Te_1$/cobalt electrolyte /Pt/FTO	4.94, 0.67	54	4.18
Au [Y.L. Lee and Lo, 2009]	TiO_2/CdS(3)/CdSe(4)/ZnS/S^{2-}-S_n^2/Au	16.8, 0.5137	49	4.22
PbS [Tachan et al., 2011]	TiO_2/CdS/CdSe/ZnS/S^{2-}-S_n^2/PbS/Pb	9.28, 0.554	59	3.01
Graphene [Dao et al., 2015]	ZnO-NW/CdS/CdSe/S^{2-}-S_n^2/Au NP-Pt NP -Graphene nano platelets -grade C	15.2, 0.720	41	4.5
Carbon [Fan et al., 2010]	TiO_2/CdSe/ZnS/S^{2-}-S_n^2/activated-Carbon/FTO	11.47, 0.60	47	3.34
Poly(3,4ethylenedioxythiophene)[Yeh et al., 2011]	TiO_2/CdS/ZnS/S^{2-}-S_n^2/PEDOT/FTO	5.66, 0.435	47	1.16

2.3 Theoretical Efficiency of Quantum Dot Sensitized Solar Cells

Quantum Dots sensitized solar cells evolved significantly over the years. The journey of QDSSCs started from less than 1 % photovoltaic efficiency and reached up to 12 %, very close to their counterpart dye sensitized solar cells. However, they are still far from the theoretical detailed balance efficiency of QDSSCs, as predicted by Klimov in 2006 [Klimov, 2006]. Klimov in his detailed balance calculation considered ideal electron and hole transport materials, but in practice electron and hole transport materials are very far from ideal. This shows that there is a requirement to revisit the detailed balance calculation from Klimov, considering the commonly employed electron and hole transport materials, to get insight about the detailed balance efficiency. This will assist in finding limiting efficiencies of quantum dot sensitized solar cells and identify the reasons behind the photovoltaic efficiency obstacles.

2.4 Summary

Quantum dot sensitized solar cells have shown good progress in their photovoltaic efficiency along with improvement in their basic building blocks. Still ideal QDs absorber, sensitization schemes and photoelectrode materials have not been shorted out for realizing large scale devices. Thus, there is a requirement to work over sensitization schemes, alternative photoelectrode materials, ideal QDs absorbers, counter electrode and hole conductors. Detailed balance efficiency calculation may predict very optimistic values under ideal conditions, which may be achievable for quantum dot solar cells but still current efficiencies are far behind the predicted values. There is a requirement to revisit detailed balance calculation to find actual feasible detailed balance efficiency for quantum dot sensitized solar cells.

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