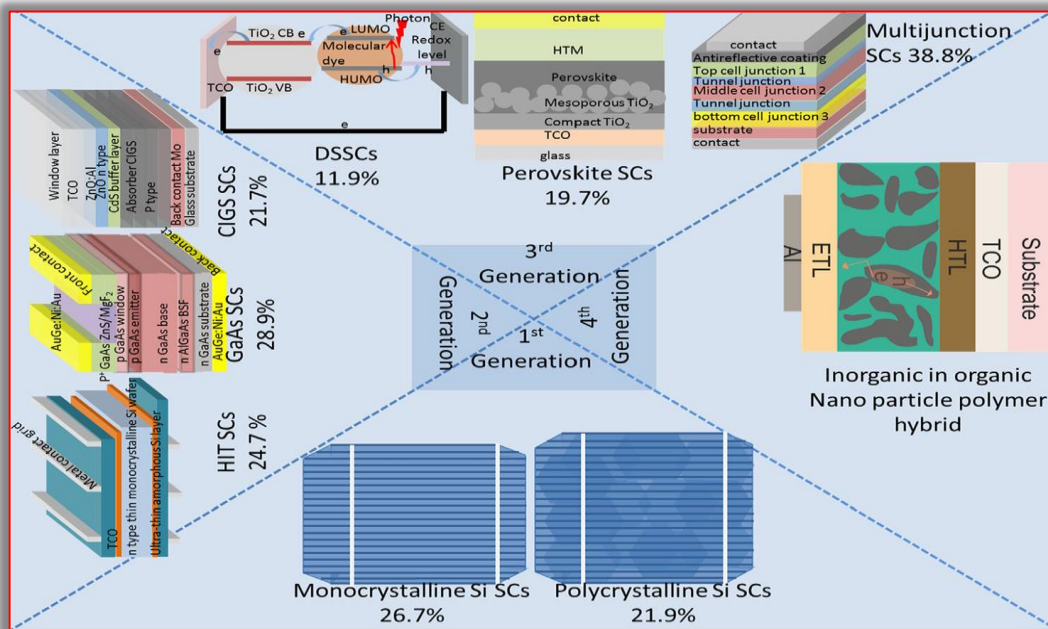


Chapter 1

Introduction and Literature Review



1.1 Introduction

The global energy demand and climate variation can be saturated by an inexpensive, plentiful, and green continuous energy source [1,2]. The fast elevation of global population requires green energy to increase the socialization and economic level [3]. Therefore, research scientists have high curiosity to nullify global warming and greenhouse effect via energy transformation technique due to shortage of fossil fuel. Solar energy is one of the best alternative resources because it is most considerable due to non pollutant nature [4].

1.2. Renewable energy sources and its global distribution

Renewable energy source means natural source derived clean energy which remains always sustainable. Solar energy has several key advantages over other renewable technologies, namely the global distribution of sunlight (in contrast to wind, geothermal, and hydroelectric resources that are localized to certain areas), the lack of hazardous waste generation (in contrast to nuclear energy), and the decentralized nature of solar energy generation. Current global energy is consisted of renewable (19%) and non renewable energy sources (81%). The shares of energy from different sources have been shown in **Figure 1.1a**.

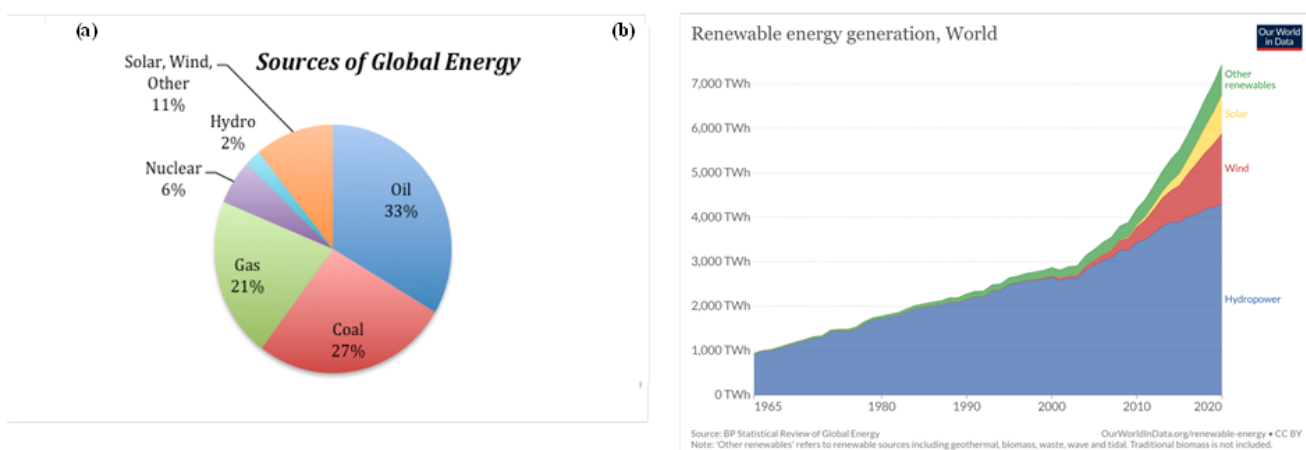


Figure 1.1: (a) The distribution ratio of different energy resources at global scale showing 19% of the total contribution comes from renewable energy sources. Data from International Energy Agency (iea.org) (b) Elevation ratio of renewable energy during 1965-2020 [5].

Solar energy is cheaper and green source of chemical fuel, electrical energy and thermal energy for various activities. It transmits sufficient energy to earth around 360° at a global level. Sun provide 130,000TW of solar radiation to the earth and if 0.1% is harvested for electrical power. The resulting amount will be sufficient to sustain the nature and global. The avrage (1353 Wm^{-2}) solar flux comes at normal incidence outside the Earth's atmosphere and corresponding spectrum seems similar to blackbody radiation at 6000 K. Spectral distribution of solar intensity is altered through surface reaction by aerosol , ozone ,water vapor and CO_2 .The extent of Solar energy almost 99% of total earth energy does not affect geographical variation [6]. Therefore, solar cells can be considered as heart of zero carbon emission which may draw attention to the scientist for upgradation of environmental and energy scenario because of the depletion of fossil fuels. Solar cells are bright as well as boon to accomplish carbon-free energy sources to maintain our civilization of living. The graph of solar power generation is increasing contineously due to limited nonrenewable sources (Figure 1.1b).

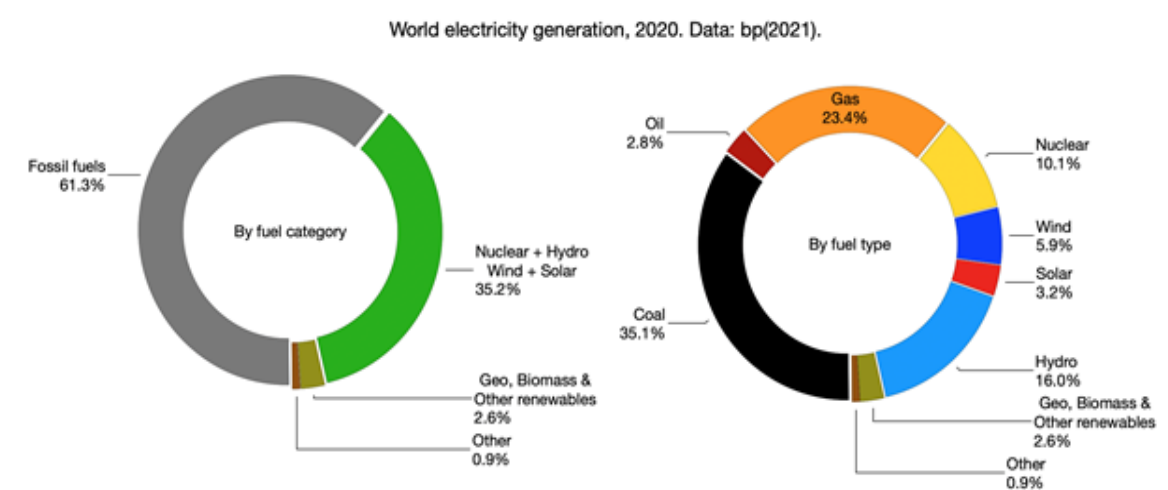


Figure 1.2: Electrical energy generation by energy resources on global level in 2020 [7].

1.3. Solar cell

Solar cell is an electrical device constructed of semiconductor materials that converts the photon energy directly into electricity by the photovoltaic effect. Solar cells are optimistic

technique which offers green and sustainable energy for social development and proper cultivation. The distribution ratio of global electricity generation from solar energy sources contributes 3.2% of total electricity generation as shown in pie chart of **Figure 1.2**. Semiconducting materials offer great opportunity to harvest sun's energy through excitation technique.

1.3.1. Components and design of solar cell

In general, solar cells are composed of photoactive materials sandwich between photoelectrode and counter electrode. Third generation solar cells are composed of photoanode, electrolyte and counter electrode (**Figure 1.3**). Photoanode consists of sensitizer (Dyes, QDs and perovskite) adsorb wide band gap semiconductor materials (TiO_2 , ZnO , SnO_2). Photoanode will absorb photon, excite and transport electrons. Electrolyte is composed of redox active couples or polymer electrolyte and act as transport bridge between two electrodes. The counter electrode consists of conducting metal or metal sulfide deposited transparent conducting glass. Nanostructured materials i.e., Cu_2S , CoS , GeC and NCW (nitrogen doped carbon nanowire) possess higher catalytic activity towards polysulfide electrolyte in 3G QDs sensitized solar cell [8,9].

1.3.2. Working principle of solar cells

In a general solar device, energy conversion involves photon excited charge generation, interfacial separation and transportation towards selective electrodes. Solar cells are a type of p-n junction diode in which p type and n type materials remain electrically connected between electrodes. When light falls on the photoelectrode result in creation of electron hole pair at the interface. If potential barrier is sufficient between two electrodes then electron and hole pair separated and transported towards respective electrodes. Photoexcited electron travels through n-type semiconductor and hole travels through p-type semiconductor leads to conversion of photon energy into electrical energy.

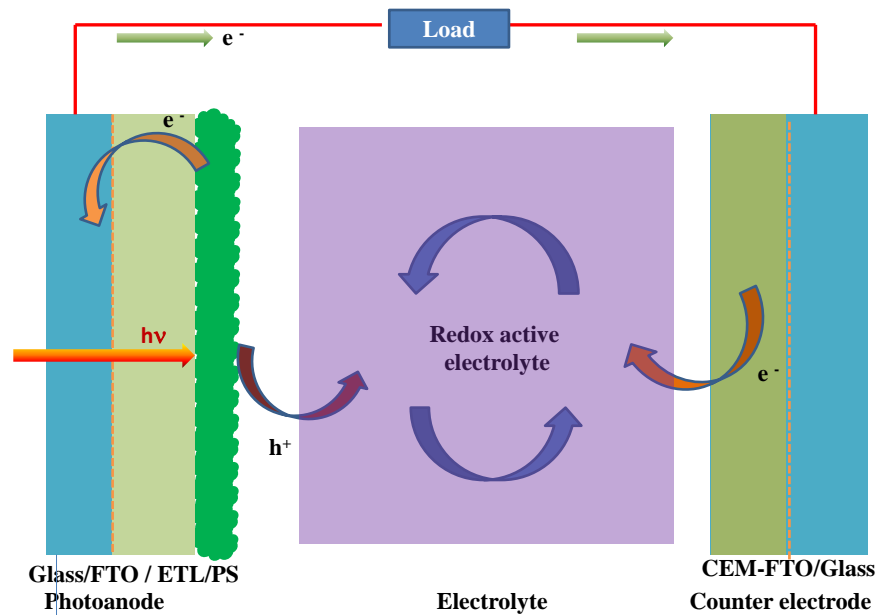


Figure 1.3. Components, configuration and design of third generation (3G) solar cell

1.3.3. General classification of solar cells

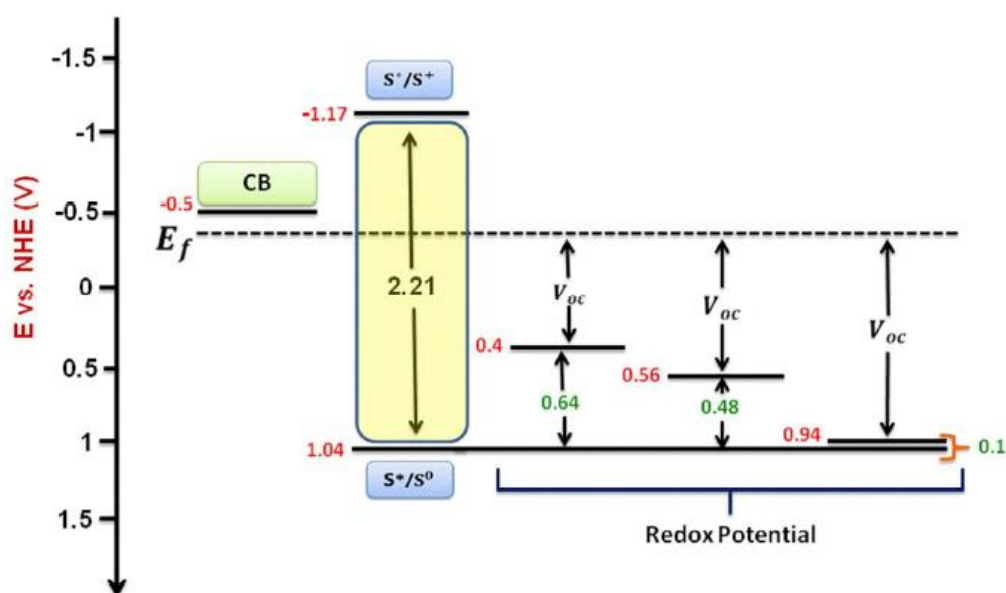
Solar cells are classified on the basis of configuration, materials and fabrication technology as generationwise fashion. First generation solar cells are based on variation of silicon. Monocrystalline or polycrystalline and amorphous silicon. Monocrystalline silicon solar cell is made up of single crystalline which is colored and holds cylindrical shape. They have highest level of efficiency at 15-20% but performance level tends to suffer from increased in temperature. Polycrystalline solar cell composed of number of interlocking silicon crystals. Solar panels based on polycrystalline materials are cheaper per unit area than monocrystalline solar panel. These kinds of solar cell produce conversion efficiencies in the range around 13-16% due to deficiency of silicon purity. Second generation (2G) solar cells are called thin film based solar cells which is produced on wafer dimensions. These kind of thin film based solar panels and cells are made up of amorphous phase of silicon in which the atoms are randomly distributed with irregular dimensions relatively different from ordered crystalline dimensions. These films can also be made from cadmium-telluride (CdTe), copper indium gallium diselenide (CIGS) or organic PV materials. Thin film solar cells are manufactured by

placing several thin layers of photovoltaic on top of each other to create the module. Efficiency tends to vary 7-13% in thin film solar cells. They can be manufactured to be flexible, making them widely applicable to a range of situations and building types. They are not ideal for domestic use as they take up a lot of space. Third generation solar cells are being made from a variety of new materials besides silicon, including nanotubes, silicon wires, solar inks using conventional printing press technologies, organic dyes, perovskite crystal and conductive plastics. The characteristic solar feature possesses multiple junctions made up from layers of different semiconducting materials. In particular, more focus is on third generation of solar cells (Dye, perovskite and Quantum dot sensitized solar cell) since they are of low cost and processing of these cells is relatively easy. However, third-generation QDs sensitized solar cells have received great attention probably because they are a modern extension of traditional dye-sensitized solar cells.

1.3.1. Dye materials and dye sensitized solar cells

Dye materials are organic molecules having multiple functionalities and absorption centers. Organic dyes possess color variation as a function of different absorption chromophores. They are attractive materials due to high absorption centers and effectively can be utilized in 3G solar technology. Dye sensitized solar cells can be fabricated via incorporation of thin film as a photoactive layer. Fabrication procedure is easy to that of fabrication of amorphous silicon based solar cells [10,11]. Liquid redox couples are broadly used in DSSC fabrication. Liquid electrolyte holds better electrical conductivity and lower viscosity and high interfacial wettability. The excellent electrical contact between dye molecule and electrolyte leads to the exploration of dye sensitized solar cells [12]. Chemical environment and redox potential of electrolyte decides open circuit potential in DSSC (Scheme 1.1). DSSC with energy conversion efficiency of 11% has been achieved [13]. However, the potential problems caused by liquid electrolytes, such as the leakage and volatilization of

organic solvents, are considered as some of the critical factors limiting the long term performance and practical use of DSSC. Thus, researchers have been paying attention to find the substitutes of liquid electrolytes with some kinds of higher stable electrolytes such as polymer gel electrolyte [14]. Recently, quasi-solid DSSCs based on *in situ* chemically crosslinked gel electrolytes have attracted interests in the sight of improving electrolyte/TiO₂ interfacial contact [15]. Ahn et al. fabricated DSSCs with electrospun poly (vinylidene fluoride-co-hexafluoropropylene) (e-PVdF-co-HFP) polymer gel electrolyte, with and without doping with the liquid crystal E7 and with a liquid electrolyte. The photovoltaic performances were investigated as 6.82, 6.35 and 7.17%, respectively [16]. Dong et al. developed copolymer matrix [poly (oxyethylene)-segmented amide-imide] to decorate liquid electrolyte as gel polymer electrolyte for DSSCs. Gel polymer electrolyte containing 76.8 wt% of the liquid electrolyte rendered a power conversion efficiency of 9.48% considerably higher than liquid electrolyte only (8.84%) [17]. Tarrannum et al. synthesized efficient polysulfobetaine-based gel electrolyte which showed photovoltaic conversion efficiency of 6.82% slightly lower (7.07%) for liquid electrolyte in dye-sensitized solar cells (DSSCs) [18].



Scheme 1.1: Schematic representation of energy levels (TiO₂, Dye, electrolyte) and open circuit potential in DSS cell with three electrolyte (I/I₃⁻, [Co(bpy)₃]^{2+/3+} and [Cu(dmp)₂]^{1+/2+}) [19]

Wu et al. [20] developed DSSCs through gel polymer electrolyte having Poly (ethylene oxide) (PEO) as conductive matrix. They investigated cell performance with liquid electrolyte and gel polymer electrolyte to suppress interfacial charge recombination (reaction of the injected electrons with the triiodide in the electrolyte at $\text{TiO}_2/\text{electrolyte}$). The cell with gel polymer electrolyte exhibited high photovoltage presumably due to negative shifting of conduction edge band potential of TiO_2 . Electrolyte having 30% polymer matrix exhibited V_{OC} (0.873V) reasonably higher than liquid electrolyte (0.775V).

1.3.2. Perovskite materials and perovskite sensitized solar cells

Perovskite materials ($\text{CH}_3\text{NH}_3\text{PbX}_3$) have been developed as highly sensitized structure in third generation solar technology. They are excellent semiconducting materials and properties are almost comparable to inorganic materials. Materials can be produced through solution processing technique. They possess distinct properties such as light weight, flexible and solution processable [21,22]. Additionally, low cost and flexible feature offers high power per weight properties which is suitable for light harvesting. However, they are sensitive towards air, light and moisture. Thin film undergoes fast degradation under environmental impact. Hydrophobic (non-ionic) polymeric materials are used to prevent the contact of moisture and oxygen with perovskite film. The polymeric structure stabilizes perovskite layer and accelerates photovoltaic redox reaction. But perovskite does not digest polymeric structure and thus, thermal and photo stability are lowered down. Tavokali et al. developed donor type polymer poly (5, 5-didecyl-5H-1, 8-dithia-as-indacenone-*alt*-thieno [3,2-*b*] thiophene)(PDTITT) as hole transport layer to realize the function of photovoltaic redox reaction in perovskite sensitized solar cell. Thiophene acts as electron rich moiety. The cells exhibited photo conversion efficiency of 18.42% comparable to spiro- OMeTAD (19.42%) [23]. However, Solution processable perovskite sensitized solar cell composed with Spiro – OMeTAD materials suffer from poor stability due to presence of unstable surface dopants

and many irregular voids which hinder the Hole transfer activity. In order to solve these critical issues, electrolyte additives have been annexed to the molecular framework of Spiro. Surface coating is adopted on Spiro layer.

1.3.3. Quantum dots and quantum dots sensitized solar cells

Quantum dots are semiconducting nanocrystals roughly 1-10 nm in diameter, having zero dimensions [24]. It has different optical and electronic properties compared to larger (bulk) particle. It emits light of specific wavelength which is a function of size of the particle. QDSSCs have attracted great recognition because of large absorption coefficient tunable absorption features and multiple exciton generation nature due to size quantization effect [25]. Quantum dot is a semiconducting nanocrystal having high molar extension coefficient and size dependent physicochemical property (**Figure 1.4**). The dopants can increase the light harvesting capacity of Quantum dots [26]. Absorption properties vary with band gap which is tailored through capping agent. Capping agents are multifunctional organic ligand which controls the nucleation and size of nanocrystal. Tunable nature of band gap accelerates the photosensitization degree [27]. The nano absorption materials have the benefits of stability due to their large extinction co-efficient and intrinsic dipole moments [28]. It is the surface structure which can be determining factor for conversion efficiency in Quantum dot sensitized solar cell. Color variation depends not only on size but shape, composition, structure also matters.

The incident photon to current conversion efficiency (IPCE) or external quantum efficiency (EQE) provides the idea about the nature and characteristics of sensitizing materials. The IPCE of sensitizer materials can be quantized from the following empirical equation [29].

$$\text{IPCE}(\%) = 1240 \times \frac{J_{\text{sc}}(\text{A}/\text{cm}^2)}{\lambda(\text{nm}) \times I_1 (\text{W}/\text{cm}^2)} \times 100 \quad (1.1)$$

Where notation J_{sc} is the short-circuit photocurrent at specific absorption wavelength and I_1 is the flux density of incident light.

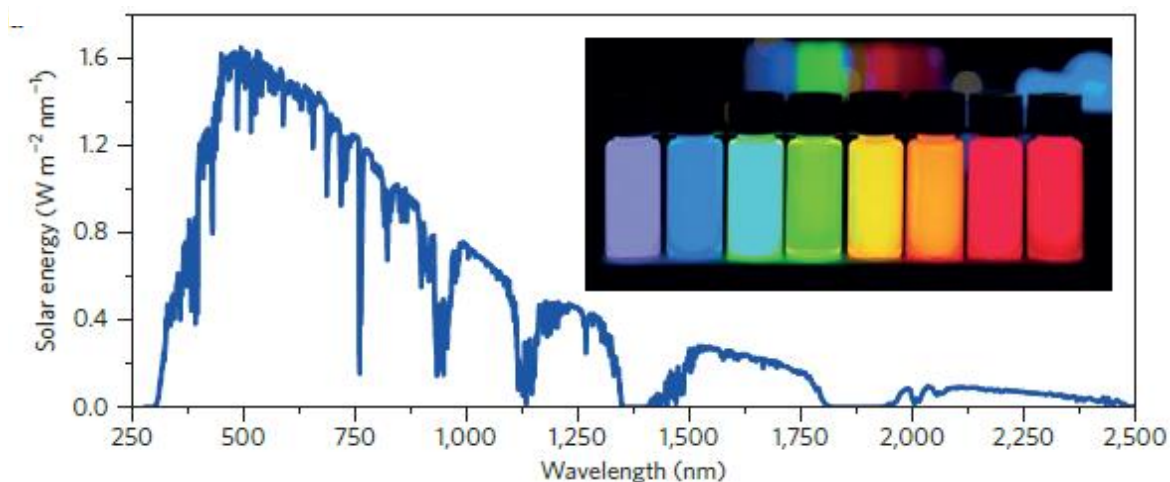


Figure 1.4: Nanoparticle size dependent absorption (color variation) enables tuning of colloidal quantum dot spectrum [30].

As a consequence, quantum dots sensitizers work as a better replacement compared to degradable organic dyes. Quantum dots widen the absorption spectrum and hence energy conversion efficiency [31]. Energy conversion efficiency varies with the capping environment [32]. Capping moiety can control the optical and electrical properties of size-dependent semiconducting nanocrystals. Dimension variation provides the opportunity to tune the performance of solar cells [28,33]. Li et al. developed AgInSe_2 quantum dots (QDs) capped with different types of thiol molecules [thioglycolic acid (TGA), 3-mercaptopropionic acid (MPA), or glutathione (GSH)] to control the optical properties. The GSH-stabilized AgInSe_2 (multidentate chelating environment) QDs are highly efficient light harvesters in a QD-sensitized solar cell (QDSSC), showing ~23% better efficiency (4.94%) than cells using TGA- and MPA-stabilized AgInSe_2 QDs [34]. The basic structure of a QDSSC device consists of three components: a QD-sensitized mesoporous TiO_2 photoanode, sulfide/polysulfide redox couple electrolyte, and electrocatalytic material-loaded counter electrode (CE). The photosensitizer is designed as a thin film photoactive layer in the photovoltaic device (solar cell). The photovoltaic device is composed of a photoanode, redox electrolyte, and

photocathode. QDSCs require an electrolyte with a redox mediator to regenerate native QDs and charge transfer between the photoanode and counter electrode. Redox electrolyte works as bridge between two electrodes.[35] It enhances the efficiency, durability and stability of the device. Redox electrolyte can be used in different phases i.e., liquid phase, gel phase and solid phase. It can be single ion or multi ion redox mediator. The performance of solar cell is related with transport of excitons (electron and hole). Hole transport is assisted through redox electrolyte. Photovoltage depends on the function and nature of redox electrolyte.[36] In QDSSCs, polysulfide redox couples are used as an basic electrolyte to gain remarkable photo to current conversion efficiencies without QD deterioration [37]. The lack of ideal electrolyte is the main factor that limits the efficiency of QDSSC. The accumulations of hole in QDs leading to oxidation degradation which intensifies the interfacial charge recombination phenomenon (**Figure 1.5a, b**). The efficiency of device is lowered down due to poor light harvesting capacity of photosensitizer. Therefore, many organic/inorganic redox active electrolytes such as complexes of Fe and Co in their variable oxidation state and nanomaterials supported polysulfide electrolyte were examined by research scientists in different QDs sensitized solar system [38].

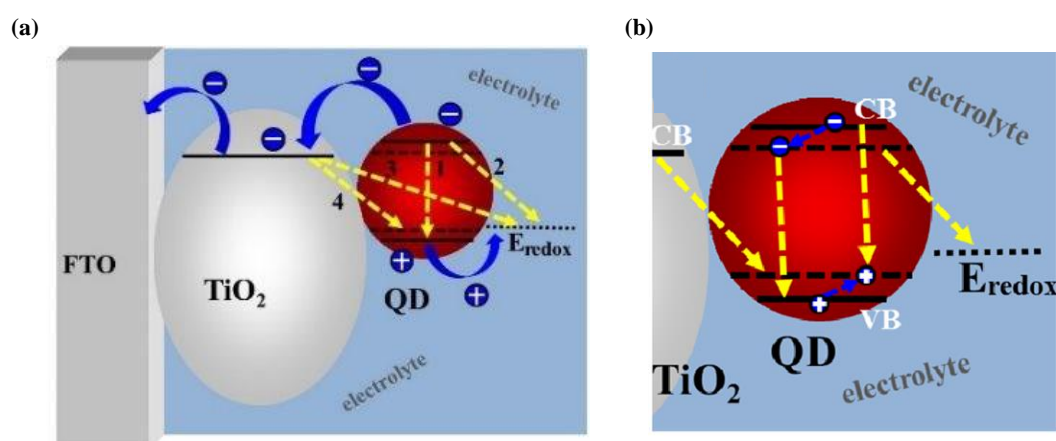


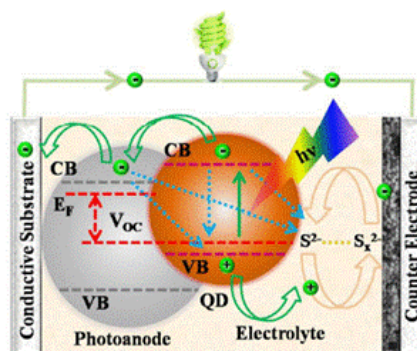
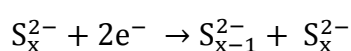
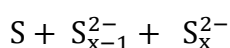
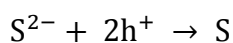
Figure 1.5: (a) Schematic presentation of absorption transition, interfacial charge transport and various recombination pathways occurring at the interface of TiO₂/QDs/electrolyte. (b) Systematic representation of surface trap, defect states and charge recombination happening on the surface of quantum dots [39,40].

1.4. Electrolyte

Redox mediator works as charge bridge between two electrodes. The redox electrolyte is essential to extract the electron reaching the counter electrode and transport it through the electrolyte to regenerate oxidized QD at the photoanode due to electron injection in photovoltaic reaction.

The working principle of this device is relatively simple. First, Sensitizer molecules adsorbed on TiO₂ nanoparticles are excited by photons, followed by an ultrafast electron injection into the conduction band of the semiconductor oxide. Sensitizer cations are regenerated by redox species. Reduction of oxidized redox species is completed at the catalytic Pt layer of the (Scheme 1.2).

The QDSSC works best with electrolytes having polysulphide (S²⁻/S_n²⁻) redox couple. When QDs donate electrons to TiO₂ upon illumination, the S²⁻ ions in the electrolyte will transfer electrons back to the QDs. In the process S²⁻ will transform to S_x²⁻ and diffuse to CE. At photocathode, the electrons arriving from the photoanode will be received by S_x²⁻ ions in the electrolyte so that S_n²⁻ ions will be transformed back to S²⁻ ions.



Scheme 1.2: Operating principle and schematic redox mediation in QDSS cell [41]

Interfacial energy level alignment facilitates diverse change in Open circuit potential due to contact of electrolyte between photoanode and counter electrode. Although the

polysulfide electrolyte has superior hole-extraction ability, the devices fabricated with this electrolyte suffer from lower V_{oc} and FF when compared to DSSC as a result of its negative redox potential (-0.67 V vs Ag/AgCl) and sluggish interfacial charge transfer at the counter electrode and electrolyte interface. To improve V_{OC} , it is inevitable to consider an alternative electrolyte whose redox potential is significantly more positive compared to the polysulfide redox potential. Redox potential is key parameter which decides efficient function of electrolyte and photovoltage of solar cell [42]. Redox potential used so as to define the donor energy level of the redox electrolyte in a photovoltaic device generally refers to the standard hydrogen electrode (SHE). The IUPAC has established that the origin of the SHE scale is-- located at 4.44 eV in the electron potential energy scale [43].

$$E_{F,redox} = -4.44eV - eE_{redox} \quad (1.2)$$

Where, e is the elementary charge, E denotes the redox potential in the SHE (standard hydrogen electrode) scale, and $E_{F, redox}$ the apparent Fermi level of the redox electrolyte.

The significantly high V_{OC} of solar cell can be explained by the more positive oxidation potential of the redox couple and the more negative potential of the TiO_2 conduction band in QDSS cell.

$$V_{OC} = |V_{CB} - V_{redox}| \quad (1.3)$$

Therefore, the replacement of the polysulfide electrolyte with some other electrolyte, e.g., cobalt complexes or redox active polymer or organic redox couples which have a more positive redox potential can be beneficial, although the device efficiency could not be improved due to severe photo corrosion and fast charge recombination.. An oxidation potential of 1.045 V vs NHE was obtained for the redox couple S^{2-}/S_n^{2-} . This potential is much higher than that for the I^-/I_3^- system. In addition, it was recently reported that the

conduction band (CB) energy (V_{CB}) of TiO_2 was significantly shifted toward negative potentials in the presence of the S^{2-}/S_n^{2-} electrolyte.

1.4.1. Redox active couples/electrolyte and its various hole transporting phase

Redox electrolyte is expressed as medium containing simultaneously oxidised and reduced forms of same materials capable of redox reactions. Redox active electrolyte undergoes reversible change (oxidation and reduction reaction) between photoanode and counter electrode maintaining continuous regeneration of oxidised QDs sensitizer. On the basis of phase dependent properties, various type of redox active hole transport/electrolyte have been classified in **Figure 1.6**. Sulfide/polysulfide redox couple degrades the conductivity and catalytic activity of Pt counter electrode. As a result, Quantum dot sensitized solar cell exhibits poor photovoltaic performance which is attributed to strong interaction and adsorption between sulfide ion and Pt counter electrode causing hindrance in charge transport. Aqueous polysulfide electrolytes are not so prone to conduct reversible charge transport due to high surface tension of water causing insufficient interfacial contact over the junction of photoanode and electrolyte [44]. On other hand, organic electrolyte having electrolyte active ionic liquid have been assessed as redox mediator for Quantum dots sensitized solar cell. Organic electrolyte possess function components which reinforce the conversion process via minimizing charge recombination through functional repulsion of photo-excited charge, Moreover, scientist have developed various QDSSCs through integrating multicomponent hybrid electrolyte such as metal complex solution with their variable oxidation state, iodide/tri-iodide and ionic liquids [45]. However, hybrid organic electrolyte remains failed to produce higher conversion efficiency, probably due to irregular charge recombination and incompatible nature of nanostructured QDs towards hybrid organic electrolytes [46]. Evangelista et al. developed iron based $Fe(CN)_6^{3-/4-}$ complex electrolyte with high photovoltage of 0.8V and solar characteristic conversion efficiency of 2% for CdS

sensitized solar cell [47]. In recent time, inorganic complex electrolytes have been focused to improve photovoltaic properties. Polypyridine supported Co based complex electrolyte have been proposed for QDSSCs and DSSCs. These kinds of electrolyte contains specific functional moiety having nitrogenic ring (bipyridine, terpyridine, and phenanthroline) due to corrosion resistance, ligand steric factor and low positive redox potentials (0.43–0.85 V)[48] compared to the redox potential of polysulfide (0.55 V)[49,50].

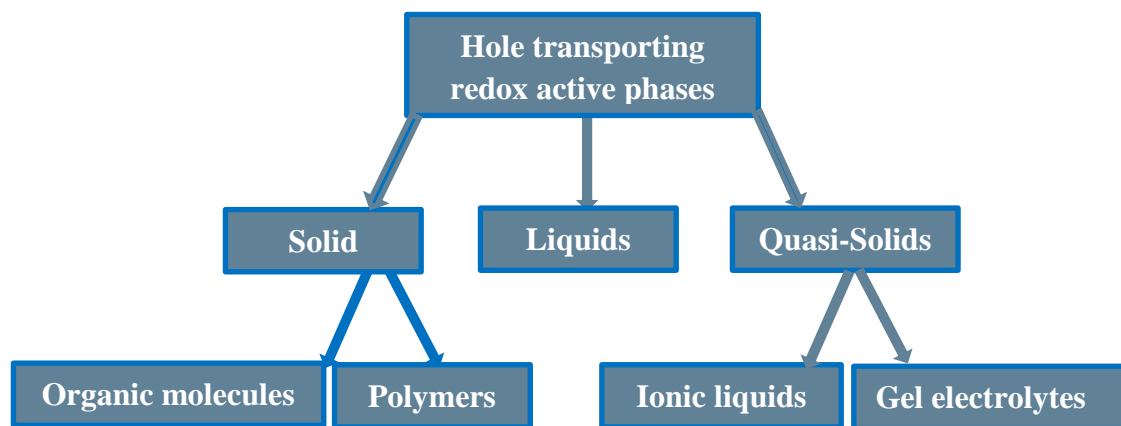
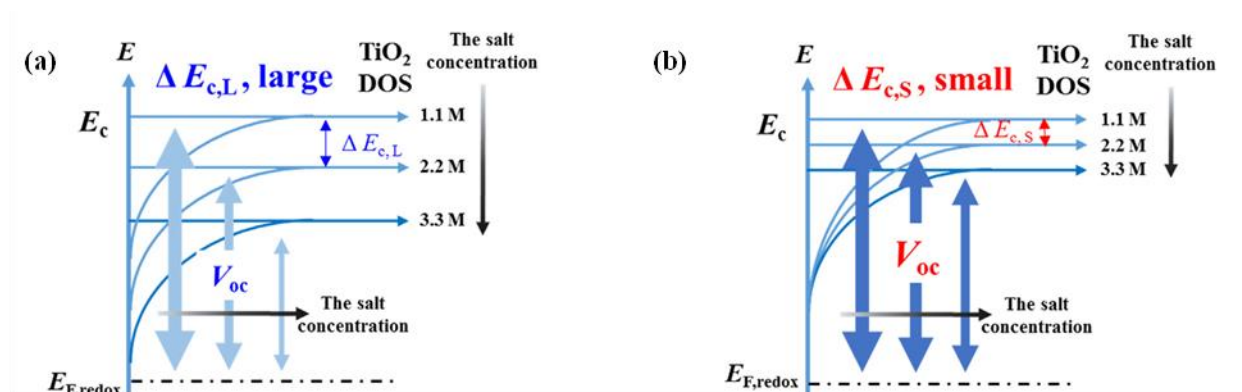


Figure 1.6: Classifications of hole transport redox active phases (materials).

1.4.2 Liquid electrolyte

Liquid electrolyte consisted of oxidizing and reducing components in aqueous or organic medium (solvent) which acts as conductive pathways for photovoltaic redox reaction in QDSSCs and DSSCs. Liquid electrolyte accelerates interfacial band alignment at the junction of different band gap layers. Various liquid electrolytes containing aqueous solution of Sulfide/polysulfide, iodide/tri-iodide have been utilized in 3G solar cell [51]. The complex solution of $\text{Fe}^{2+}/\text{Fe}^{3+}$, $\text{Co}^{2+}/\text{Co}^{3+}$ have also been used to control the photovoltaic property. In general, liquid electrolyte degrades photovoltaic reaction due to interfacial corrosion. Recently, liquid polymer electrolyte and gel polymer electrolyte have improved the photovoltaic performance. Liquid polymer electrolyte and ionic liquid electrolyte are better substitute of intrinsic liquid electrolyte. due to presence of active site enrich center [52]



Scheme 1.3: The comprehensive energetic scheme of the density of states in TiO₂ for different molar concentration of salt in (a) Liquid (b) solid polymer electrolyte [53]

When electrolyte comes in contact with photoanode and counter electrode. Photovoltaic reaction varies with extent of alignment of energy level of CB of TiO₂. Open circuit potential changes according to nature and phase of electrolyte [53]. Redox active electrolyte concentration affects the open circuit potential in cell due to interface tuning of energy (**Scheme 1.3**). In liquid electrolyte, electrolyte cation can preferentially adsorb on nanoporous photoanode. Therefore, TiO₂ (CB) shifted towards downwards and V_{OC} is decreased and further increased with high concentration of electrolyte couples. In polymer electrolyte, electrolyte cation can be adsorbed on polar functionality of polymer chain and thus, direct adsorption of electrolyte cation on nanoporous photoanode is reduced to little extent which causing upward shifting of TiO₂ (CB) and thus, V_{OC} increases.

1.4.2.1. Polysulfide redox couple

Aqueous sulfide/polysulfide (S₂²⁻/S_x²⁻) electrolyte couple has been explored to realize Quantum dot sensitized solar cell. In general, QDSSC employs a polysulfide electrolyte but various researches have concluded that polysulfide produces lower photovoltage (V_{OC}) of up to 0.6 V and fill factor (FF) of up to 0.55 because of relatively negative polysulfide redox potential (around -0.65 V vs. Ag/AgCl). However, majority of the highly efficiency QDSCs utilized with polysulfide aqueous electrolyte. Since, aqueous polysulfide electrolyte does not prone to puncture into the nanostructure and property can be rationalized through high

surface tension of water. Therefore, it is interesting to consider an alternative electrolyte having positive redox potential compared to the polysulfide redox potential. Interestingly, quantum dot sensitized solar cells based on alternative electrolyte are also finite on global research scale. Different surface group (functional group) grafted chemical functioned as electrolyte carrier which facilitate the improvement of open circuit potential [54,55]. Shu et al. studied comparative performance through incorporating polysulfide electrolyte and organic $C_7H_5N_4S^-/C_{14}H_{10}N_8S_2$ (AT^-/BAT) modified electrolyte in CdS QDSSCs and found not only higher Voc and FF but also enhanced conversion efficiency from 0.52% to 0.7% over Pt counter electrode [25]. Liquid electrolyte can penetrate strongly to photoanode leading to enhancement of high charge recombination reaction. Proper interfacial electrolyte contact can increase the efficiency of charge separation in QDs. Therefore, it is crucial to modify the surface structure of polysulfide electrolyte. Ning et al. selected intrinsic organic redox couple $McMT^-/BMT$ in CdS sensitized solar cell and found that it intensified the photovoltage and conversion efficiency. In addition to this organic $C_2H_3N_4S^-/C_4H_6N_8S_2$ (T^-/T_2) and $C_7H_5N_4S^-/C_{14}H_{10}N_8S_2$ (AT^-/BAT) have been used as redox couple for QDSS cells [56]. Li et al. developed modified polysulfide $[(CH_3)_4N]_2S/[(CH_3)_4N]_2S_n$ electrolyte for TGA capped CdS QDSS cell. The solar cell exhibited photovoltage of 1.2 V and conversion efficiency of 3.2% with modified polysulfide having efficient wettability and penetration capacity in organic solution [57]. Thus, organically modified sulfide/polysulfide electrolyte improves PCE due to change of redox potential.

1.4.3. Gel polymer electrolyte

Gel polymer electrolyte contains liquid electrolyte, plasticizer and polymeric host as integral components. Gel polymer electrolytes are semi-solid phase in which active liquid electrolyte couples are imbedded within the chain extended framework of the polymeric host. Redox responsive gels are capable of controlled redox reaction and maintain reversible changes. Gel

polymer electrolyte can be tailored through proper operation into various shapes, color centers, mixing features and variable gel transition temperature [58]

Polymer matrix	Repeat unit	Glass transition temperature (°C)	Melting Temperature (°C)
PEO	$-(\text{CH}_2\text{CH}_2\text{O})_n-$	-64	65
PAN	$-\text{[CH}_2\text{CH(CN)}]_n-$	125	317
PVP	$-\text{[CH}_2\text{CH(NC}_4\text{H}_6\text{O)}]_n-$	110	180
PVDF	$-(\text{CH}_2\text{CF}_2)_n-$	-40	171
PVDF-HFP	$-\text{[(CH}_2\text{CF}_2)_n\text{CF}_2\text{CF(CF}_3)_n]_n-$	-90	135
PS	$[\text{CH}_2-\text{CH(C}_6\text{H}_5)]_n-$	90	240
PMMA	$-\text{[CH}_2\text{C(CH}_3\text{)COOCH}_3]_n-$	-105	-
PVC	$-(\text{CH}_2\text{CH)}_n-$	85	-

Table 1.1: Properties and repeating structures of the most common polymer matrices used to prepare gel electrolytes [59–61]

The polymer offers intrinsic strength to the electrolyte by increasing the viscosity and internal energy, while, the plasticizers provides softness and flexibility to the polymer backbone. Polymer electrolytes are employed in various electronic devices such as batteries, electrochromic windows, supercapacitors, and solar cells in order to solve common problems such as leakage, volatility, flammable properties of liquid electrolyte. Polymer electrolytes can be developed easily with their desired function. Polymer matrices having lower glass transition temperature facilitates chain segmental motion and collaborates towards electrical conducting performance with redox active couples (**Table 1.2**). Gel polymer electrolyte is a promising solution to replace organic liquid electrolyte in 3G solar cell technology. Various technological approaches have been introduced to modify activity of polymer electrolytes, ionic conductivity and stability issues. Gel electrolyte is designed as redox responsive unit by the process of gelation, adsorption, inflation and network expansion[62]. The formation of gel involves many interaction forces such as intermolecular hydrogen bonds, van der Waals, electrostatic interaction and physical cross-linking [63]. It depends on the temperature. Thermoplastic gel electrolyte possess higher ionic conductivity because of presence of amorphous content and electrolyte absorbent center in polymer chain

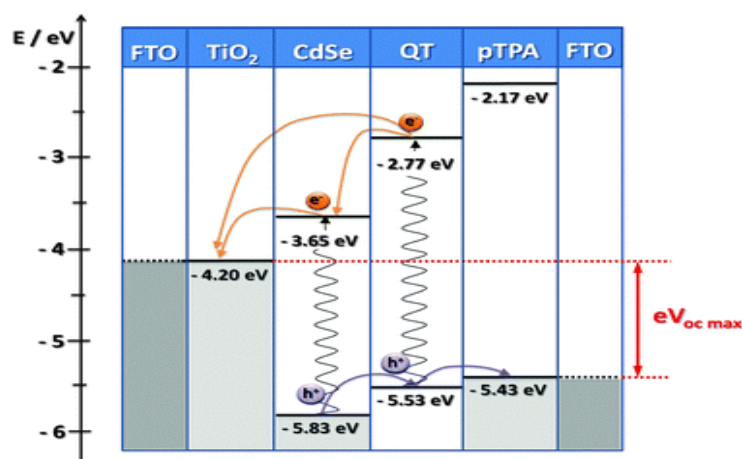
[64]. The gel electrolyte can be reversibly changed from the sol state to gel state by tuning temperature scale. Sol to gel transition is influenced through variation of structural integrity in polymer host. This kind of gel polymer which shows temperature dependent features is known as thermoplastic gel polymer electrolyte. On other hand, different kind of polymer gel electrolyte is thermosetting polymer electrolyte (TSPEs), in which electrolyte active centers are created through chemical or covalent cross-linking of organic molecule leads to the formation of three-dimensional extended polymer network which possess high affinity to wrap liquid electrolytes in the core structure. Thermosetting polymer electrolyte does not display temperature dependent physical states transition. In consequence, thermosetting polymer electrolyte exhibits lower electrical conductance than liquid electrolyte and thermoplastic polymer electrolyte. *Yu et al.* developed chemically crosslinked polyacrylamide-based hydrogel to uptake polysulfide electrolyte in CdS/CdSe co-sensitized solar cell with power conversion efficiency of 4.0% [65]. Jin et al. developed polyacrylamide (PAAm) supported polysulfide gel electrolyte with power conversion efficiency of 1.78% using CoSe as counter electrode in CdS/CdSe QDSS cells. However 0.9% GO incorporated composite gel electrolyte extended the conversion efficiency of 4.10% due to better electron conducting nature [66]. Duan et al. developed graphene doped polyacrylamide (PAAm) supported polysulfide composite gel electrolyte with power conversion efficiency of 2.34% comparatively higher than pure PAAm incorporated gel (1.36%) using CoSe counter electrode in CdS QDSS cells [67]. Yang et al. developed PAAm –PANi gel electrolyte with conversion efficiency of 2.33% using CoSe counter electrode in CdS/CdSe QDSS cell [68]. The remarkable change in conversion efficiency is due to expanded conducting interface between electrolyte and counter electrode

Composite Polymer Electrolyte	J_{SC} mA/cm ²	V_{OC} (V)	FF	η (%) (GPE)	η (%) (LE)	Ref.
PAAm-PAA	12.05	0.36	0.41	1.80	-	[3]
PAAm-G	9.63	0.590	0.39	2.34	1.36	[67]
PAAm-PANi	13.60	0.520	0.329	2.33	1.74	[68]
PAAm-GO	12.18	0.513	0.656	4.10	1.78	[66]

Table1.2: various composite polymer electrolytes with polysulfide and photovoltaic values for CdS sensitized solar cell.

1.4.4. Solid polymer electrolyte

Solid polymer electrolyte comprised of solvent free salt solution supported on chain of polymer matrix. Ion transmission occurs through polymer chain. Conventional, p-type semiconductor[69], hole-conducting organic or inorganic material[70] and solid, solvent-free polymer [71] have been demonstrated as a kind of solid electrolyte for 3G sensitized solar technology [14]. However, solid polymer electrolyte does not possess sufficient ionic conductivity and interfacial wettability result in poor conversion efficiencies. It is predicted that the solid-state or gel state electrolytes may prevent sensitizer corrosion, device degradation causing efficient hole regeneration in QDSSCs. Yang and Wang have developed PEO-PVDF co-polymer blends decorated via novel S/tetramethylammonium sulfate (S/TMAS) redox additive leading to functional realization and better quantum dot sensitized photovoltaic performance than traditional redox couple S/Na₂S [72]. Generally, liquid or gel electrolyte materials possess more conducting features than solid electrolytes. Kniprath et al. communicated photovoltaic properties as ($V_{OC} = 1-1.15$ V, $J_{SC} = 0.05-0.10$ mA cm⁻²; $\eta = 0.020\%$) on CdSe sensitized device via implication of conjugated polymer poly(9,9-dioctyl-fluorene-co-N-(4-butylphenyl)diphenylamine) as a function of hole transporting species [73]. Barceló et al. developed photovoltaic properties ($V_{OC} = 0.9-1.0$ V, $\eta = 0.34\%$) on hybrid solid state TOP capped CdSe QDSSC with 3, 3'-didodecyl-quaterthiophene as hole conducting layer (**Scheme 1.4**) [74]. The lower solar efficiency was assessed for device. It might be due to probable hindrance on charge transport on resistive interface.



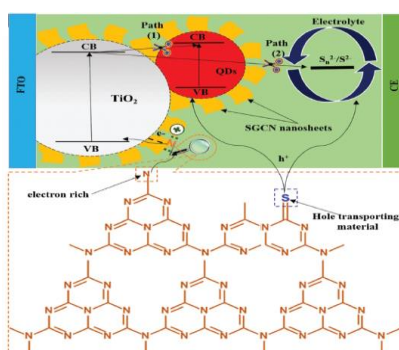
Scheme 1.4: Schematic illustration of energy level diagram, photoexciton generation, potential barrier and hole transport across multiphases within CdSe sensitized solar device showing electron injection with simplified potential diagram [74].

1.5. Electrolyte additives

Additives are intrinsic functional materials containing electron rich repulsive centers. Electrolyte additives reinforce the performance of pristine redox active couples. It has high tendency to passivate defects and surface states available on photoanode. Thus, it works as steric hindrance between photoanode and electrolyte. Some natural electrolyte additives such as dextran [75] Konjac glucomannan [76] and agar [77] contains specific structural framework, porosity and regular dimensions. They can sustain the active electrolyte and cooperates in the performance. Due to presence of various interaction centers, it can solidify the electrolyte also and thus converts liquid electrolyte into gel or quasi-solid state. Natural polymeric additives are used to convert liquid electrolyte (polysulfide) into gel electrolyte.

Sodium polyacrylate [78] or sodium carboxymethylcellulose [79] possess superabsorbent features having higher affinity towards polysulfide electrolyte and transform readily into gel polysulfide electrolyte. Electron-rich oxygenic functional surface behaves as potential barrier and strongly repels electron from recombination into hole and thus suppress back electron transfer reaction in Quantum dot sensitized solar cell (**Scheme 1.5**). Various technical approaches have been incorporated to improve redox properties, open circuit potential and

photovoltaic performance within QDSSCs[80]. Zhong et al. explored polymeric additives i.e., poly(ethylene glycol) [81] or poly(vinyl pyrrolidone) [82] could fill the photoanode defects and prevent undesired charge recombination reaction towards electrolyte. Wei et al. discussed SiO₂ additive in polysulfide electrolytes with enhanced electrolyte activity. 3D silica contains porous and network structure with sufficient chemical barrier which effectively prevents photoexcited electron recombination at the interface of photoanode and electrolyte. Charge recombination phenomenon is effectively reduced because of presence of terminal –OH (hydroxyl group) on the surface of silica. Hydroxyl groups are more susceptible to towards chemical adsorption on QDs sensitized photoanode. Mingsukang et al. developed methylcellulose–polysulfide gel polymer electrolyte with conversion efficiency of 1.42% in CdS QDs sensitized solar cell [83]. Yu et al. reported that the incorporation of tetraethylorthosilicate to polysulfide redox couples leading to the enhancement of photovoltage and characteristic fill factor result in depression of charge recombination [84]. Thus, it is highly interesting to create a chemically decorated/coated polysulfide electrolyte to comprehend high V_{OC} and long-term durability. Thus, photovoltaic characteristic parameters can be boosted by coating electrolyte with suitable chemical structure which confines higher opposition towards more electron recombination. Thus, proper chemical technology should be adopted to develop inexpensive chemical moiety and stable electrolyte preservative which can hamper the deactivated electrons at the interfaces of TiO₂/QDs/electrolyte to accomplish higher photovoltaic conversion reaction.



Scheme 1.5: Schematic diagram of charge transport with role of additive (SGCN) in polysulfide electrolyte in QDSS cell [85].

1.5.1. Variation of redox mediation in polysulfide with different chemical environment

Structural modification can change the electrochemical properties of electrolyte. Chemical environment modify the redox behaviour of polysulfide electrolyte and performance of device (**Table 1.1**). Polysulfide redox electrolyte possesses high redox potential and thus, open circuit potential is observed little lower than the value obtained in dye sensitized solar cell. Photovoltaic performance can be enhanced by using different redox electrolyte having lower redox potential relatively. Electrolyte additive is another choice to tailor the redox potential of electrolyte and stabilization features of QDs. However, sponging charge recombination influences open circuit potential and energy conversion efficiency. Du et al. developed PEG supported polysulfide electrolyte for CdSe sensitized solar cell solar cell with enhanced conversion efficiency of 6.74% [81].

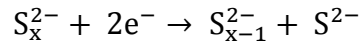
Electrolyte Additive	QDs	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)	Free Electrolyte	Ref.
PIL	CdSe	13.85	0.420	0.35	1.86	-	[51]
PAAS	CdSeTe	19.86	0.650	0.61	7.80	-	[78]
GuSCN	CdS	8.07	0.500	0.50	2.01	1.79	[86]
PEG	CdSe	15.81	0.643	0.66	6.81	-	[81]
SGCN	Cu-in-S	22.36	0.635	0.50	7.13	6.16	[85]
Dextron	CdS/CdSe	15.86	0.466	0.44	3.23	-	[75]
TEOS	Zn-Cu-In-Se	28.36	0.768	0.61	12.34	-	[84]
PVP	CdSe _x Te _{1-x}	20.49	0.723	0.66	9.77	-	[87]
12-HSA	CdS/CdSe	12.18	0.470	0.42	2.40	-	[88]
CMS-Na	CdSe	15.63	0.615	0.65	6.32	-	[89]

Table 1.3: Solar characteristic parameters for various sulfides/Polysulfide based QDSSCs containing chemical additive bearing different passivating group. TEOS: Tetraethylorthosilicate HSA: Hydrostearic acid.

1.6. Electrocatalytic reaction of redox active electrolyte with photocathode

Electrocatalysis converts oxidized redox active couples or electrolyte into native state to maintain photovoltaic reaction [90]. Quantum dot sensitized solar cell can be evaluated by conducting counter electrode. In the QDSSCs, electrolyte active species regenerates

photoexcited QDs via donation of electrons to oxidised state to renew photovoltaic phenomenon and conversion reaction. Thereafter, the oxidized electrolyte reduced back for further reaction at the surface of Quantum dots [90].



The reduction rate of S_n^{2-} ions at the CE is primarily determined by the electrocatalytic activity and electrochemical active area of the CE

However, polysulfide is more susceptible towards counter electrode and blocks the active sites via adsorption phenomenon. Thus, noble electrocatalytic metals are unsuitable for QDSSCs. In the polysulfide redox couple system, sulfur atoms retards the surface activity and conducting capacity [91]. Catalytic activity can be preserved via passivation layer which prevents the corrosion due to activity of sulfide/polysulfide electrolyte. Redox activity can be enhanced via utilization of non corrosive electrolyte mediator. On other hand, nanostructured conducting and composite structure uptakes electrolyte sufficiently leads to fast transmission of charge across multifunctional electrode. Thus, functionalized electrolyte accelerates the conversion reaction over active sites of counter electrode [66].

1.7. Control of interfacial states, defects states and charge recombination phenomenon

Interfacial structure is key point in device fabrication technology. Charge recombination arises at the interfaces of photoanode/electrolyte [92]. It is the surface state or trap state which attracts photoexcited charge and retards the functioning behaviour of electrolyte. Therefore, QDSSCs exhibits still poor conversion efficiency as compared to dye sensitized solar cell. The lower photovoltaic performance is attributed to the relatively lower photovoltage in the cell compared to DSSCs. Interfacial electronic properties can be tuned via surface doping or passivation layer at surface contact of TiO_2 -QD-electrolyte junction. Since, each interface contributes towards recombination and total photovoltaic performance. Therefore, it is essential to understand transport properties at the interfaces. Organic linker

having multiple polar functionalities is more prone towards binding of Photosensitizer and electron transport layer (metal oxide). Short chain organic linkers thioglycolic acid, mercaptopropionic acid and glutathione possess electron rich coordinating center which supports the structural, chemical and electronic variation at the interface. The linker enhances the affinity of wide band gap semiconducting metal oxide towards sensitizer. The large sensitizer coverage is susceptible to capture broad solar spectrum and thus amplify the energy conversion phenomenon. Thus, linker reduces the extent of unwanted contact between photoanode and electrolyte. The charge recombination kinetics is modified at the interface. On other hand, Passivating layer can decrease the extent of charge recombination on defective surface states in quantum dots [93]. Electrolyte structure having passivation group may enhance the photovoltaic performances. Surface coating is another important technique which offers interfacial energy barrier at the recombination site. The recombination barrier suppresses the unwanted backward reaction [94].

1.8. Polyelectrolyte

Polyelectrolytes are ionic polymers having charged electrolyte groups attached with counter ion which readily undergo dissociation in aqueous solutions. Polyelectrolyte solutions offer ionic conductivity as well as cohesive character (**Figure 1.7**). Ionic groups are covalently attached to nonionic polymer chain. The active ionic moieties such as sulfonate, phosphate and carboxylate groups work as pendant groups into the polymer backbone [95]. Though, ionic conductivity values typically lie in the order of approximately 10^{-5} S cm⁻¹ at 25 °C [96–98]. Electrolyte active sulfonated copolymer acts as excellent ion exchanging membrane for fuel cell activity. Ionomeric segment offers controlled features i.e., flexibility, dimensional stability and swellability into hydrophobic polyurethane chain. Polysalt containing functional group (carboxylate, sulphate, phosphate ion) facilitates swelling capacity of polymer matrix. Intrinsic liquid electrolyte cause serious problem in solar cell technology.

Liquid electrolyte degrades the performance of solar device. The photovoltaic performance can be enhanced via utilization of various nanostructured gel electrolyte. Gel electrolyte remains quasi solid at lower temperature (room temperature) and viscous at higher temperature. Gel polymer electrolyte have excellent characteristic features i.e., stability, adhesion and electrical conductivity. Structural stabilization provides higher activity into intrinsic electrolyte liquid electrolyte. On other hand gel polyelectrolyte can be used as better alternative of liquid electrolyte. Polyelectrolyte possess excellent passivation group which may enhance the number density of photoexcited electron into external circuit of solar device. Superabsorbent and proper solvent holding capacity promotes the electrolyte activity into structural segments.

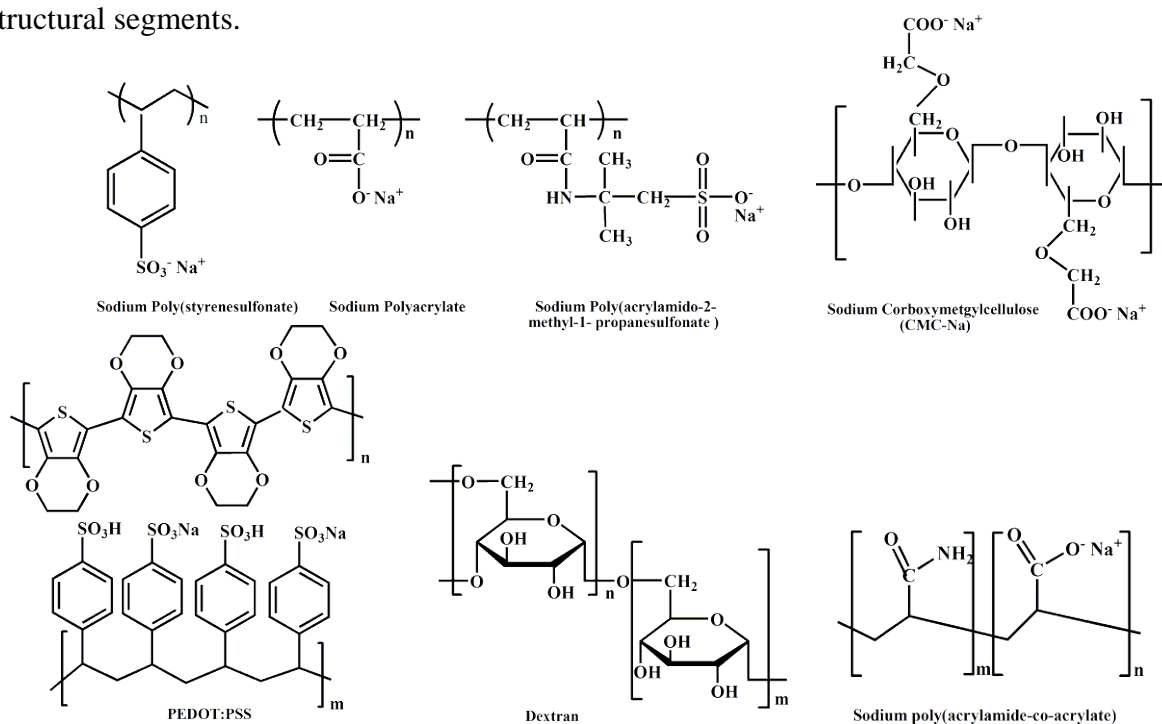


Figure 1.7: Chemical structures of polyelectrolyte polymers [99,100]

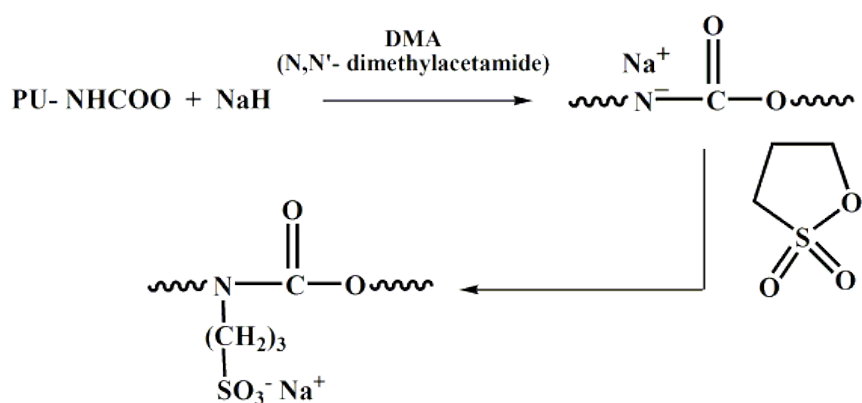
In general, nonionic polymer is used as gelling agent for traditional liquid electrolyte [101]. However, Nonionic polymer does not possess sufficient electrical conductivity which may impedes the diffusion characteristic of intrinsic redox couple. And thus, retards the electrolyte activity of redox couples and hence photovoltaic conversion efficiency also. Therefore, conducting and ionic polyelectrolyte can be adopted as potential

host to solidify polysulfide aqueous solutions characteristics [89]. Oxygenic co-polymers PAAm-PAA matrix has suitable coordinating and adsorption centers (carbonyl and carboxyl groups) which supports water solubility and better gelatinizing capacity. Feng et al. demonstrated that polyelectrolyte possess superior water-absorbing and water-holding capacity, sodium polyacrylate (PAAS) has been used to gelate aqueous polysulfide electrolytes to reorient quasi-solid state QDSSCs [78]. Li et al. developed sodium poly[3-(4-carboxyla- tebutyl)thiophene (P3CT-Na) as hole transport layer) in perovskite sensitized solar cell with higher efficiency of 16.6% [102]. Zhang et al. replaced PEDOT:PSS via CH_3NH_3^+ balanced thiophene based conducting polyelectrolyte for perovskite sensitized solar cells with improved efficiency of 19.76% [103]. Jo et al. studied a series of thiophene containing self-doped conjugated polyelectrolyte in organic solar cell with maximum efficiency of 9.89% via electrolyte activity of poly [1, 4-bis (4-sulfonatobutoxy) benzene-alt-thiophene] (PhNa-1T) compared to PEDOT:PSS (PCE = 8.37%) [104]. Cai et al. utilized PEDOT-S (poly (4-(2,3-dihydrothieno [3,4-b]-[1,4]dioxin-2-yl-methoxy)-1- butanesulfonic acid) as hole transport layer in organic solar cell with a conversion efficiency of 5.12% . Efficiency is higher due to controlled hole injection barrier and electron rich HOMO level [105]. Kwak et al. used polyelectrolyte as additive to improve electrolyte activity and efficiency of organic solar cell and found enhanced performance from 4.63% to 5.26% [106]. Therefore, it will be fashionating to adopt polyurethane ionomers having oxygenic en-rich functionalities and charged alkyl sulfonate group into hard segment content which can be accepted for electrolyte activity in QDSS cells.

1.8.1. Polyurethane ionomers

The polyurethane ionomers are constructed of redox active pendant group incorporated across hard segment (urethane linkages) which is located as framework structure with an alternate fashion. Polyurethane ionomer contains active polar ion into urethane segments.

Polyurethane ionomers behave as polyelectrolytes in polar or aqueous solvents. Polyelectrolyte activity is due to, mobilization, polymer extension and ion dissociation [107,108]. The charge carrier is ionic. Ions are more bulky in size and thus their mobility is low. Ionic segments (pendant group) stabilizes structural framework due to electrostatic interactions between anionic segments and counter ion that reinforce thermal resistance and mechanical strength. Polyurethane ionomers contain inorganic group up to 1-15 mol% into main structural framework (**Scheme 1.6**). This characteristic offers high prospect of self-organization with proper orientation which leads to exploration of variety of nano and microstructures having excellent ionic aggregates and ion conductive nanochannels. The surface volume of the conducting channels is key structural integrity which controls the electrical conductivity of such polyelectrolyte polymers. Ionic group causes structural stabilization and hydrophilic features into polyurethane backbone [109]. Polyurethane ionomers are used as coating, adhesive, ink, building materials, automotive, textile and biomaterials [110]. Thermoplastic polyurethanes (TPUs) are cross-linked elastomers at ambient temperature and thus have unique features causing expansion and shrinkages to transform into various shape and dimensions via application of heat (thermal energy). With recent increasing attention on flexible electronic devices and architecture, flexible polymers having specific functional moieties are of great compulsive. In recent years, the most important solicitations for ionomers have been explored in electronics, environment and medicine.[111]. Recently, we have developed Quantum dot sensitized solar cell with functionalized polyurethane ionomer as a single ion redox mediator. Polyurethanes are composed of hard segment and soft segment moieties. Urethane functionalized entity designed as hole transport moieties.



Scheme 1.6: General schematic reaction pathways for polyurethane ionomer synthesis[107]

Polyurethanes are grafted with γ -propane sultone (pendant group) which improves electrical conductivity due to incorporation of ionic functional and donor group. In particular, zeta potential can be used to measure dispersion stability of hydrophilic polyurethane ionomer. Higher zeta potential indicates increased dispersion stability of polyurethane ionomer [112,113]. Polyurethane ionomers can also be chemically crosslinked e.g. by polyisocyanates or polyfunctional alkylating agent to improve water resistance capacity. Polyurethane anionomer dispersion are more stable than their cationic counterparts towards electrolyte (particularly in the presence of sulfonate groups) [114]. It was established that the trapped charge entity intensifies the activity of functional groups due to mobilization features and enhanced electrical conductivity. Polyurethane ionomer can boost the performance of QDSCs. The electron rich oxygenic functionalities and pendant anion not only reduce charge recombination but also enhances the redox activity. Thus, polyurethane ionomer can be utilized as electrolyte fuel in 3G solar technology. It can be utilized as substitute of polysulfide electrolyte for the redox mediation in QDSSCs. Further, it can be rationalized that pendant group may enhance the redox activity of polysulfide through synergistic adsorption over pendant surface.

1.9. Scope and objective of present work

Present research focuses towards progress on electrolyte engineering, it has been demonstrated that chemical structures play a crucial role to establish reversible redox activity of electrolyte species. Recently, Polyurethanes have been explored due to presence of multi-functionalities in the soft segment and hard segment of polymer framework. Although, less research focused on polyurethane electrolyte because of electrical insulating behaviour, however, functionalization or chemical grafting could impart electrical conductivity. It is the beauty of urethane linkage which has attracted great attention towards chemical modification or composite formation. However, reversible and bidirectional charge charge transports have not been studied at the interface of photoanode and counter electrode in Quantum dot sensitized solar cell. It can be expected that ionically conducting urethane linkage can suppress the photoexcited back electron transfer towards its electrolyte function without hindering the interfacial redox activity. Thus, non-corrosive atmosphere offers suitability to polyelectrolyte which will be promising candidate for redox mediation in Quantum dot sensitized solar cell.

Here, main objective of the thesis is to develop and design the ionomer gel electrolyte by introducing redox active pendant group into urethane linkage or hard segment contents to generate ionic conductivity. The ionic conductivity can be modulated through variation of chain extender, hard segment unit and nature of urethane linkage.

The main objective of the present work explores the following sub-objective.

- ❖ To understand the role of polyurethane chemistry in terms of redox activity and effect of structural variation on photovoltaic conversion efficiency.
- ❖ To develop suitable quantum dots i.e., CdS by changing the organic capping agents.
- ❖ Chemical functionalization of urethane linkage to develop ionomer gel electrolyte for Quantum dot sensitized solar cell.

- ❖ To study the redox potential functionalized polyurethane for controlling the HOMO-LUMO energy levels.
- ❖ To study the composite behaviour of ionomer gel electrolyte for Quantum dot sensitized solar cell
- ❖ Temperature influence (Annealing effect of device) on photovoltaic conversion efficiency
- ❖ Synergistic influence of polysulfide redox couple into functionalized (sulfonation) polyurethane

1.10. Plan of the present work

To perform research work on electrolyte design for Quantum dot sensitized solar cell. The following plans of work have been carried out systematically.

(a) Functionalized Thermoplastic Poly (urethane-urea) as Hole Conductor for Quantum Dot Sensitized Solar Cell.

- ❖ Synthesis of aliphatic thermoplastic polyurethane with combination of hard segment unit (HMDI), soft segment unit (PTMG and chain extender (EDA) at fixed hard segment content of 30%.
- ❖ Functionalization of thermoplastic polyurethane especially on urethane linkage by varying the concentration or composition of sulfonating agents such as NaH/Y-propane sulfone.
- ❖ Optimization of degree of sulfonation on urethane linkage to establish suitable HOMO and LUMO energy levels.
- ❖ Preparation and decoration of sulfonated polyurethane as ionomer gel electrolyte.
- ❖ To study the redox potential of different degree of sulfonated polyurethane

- ❖ Calculations of energy gap for functionalized polyurethanes at different level of sulfonation.
- ❖ Structural characterization for functionalized thermoplastic polyurethanes.
- ❖ Synthesis of CdS QDs through solution phase technique by employing EDTA as a surface stabilizing agents.
- ❖ To study the quantum confinement effect at different level of capping and nucleation for elucidation of particle size for efficient light harvesting.
- ❖ Investigation of surface morphology to analyse size , shape and volume.
- ❖ Fabrication of electrodes (photoanode and counter electrode) for assembly of Quantum dot sensitized solar cell.
- ❖ J-V characteristic measurement of device with light having intensity 100 mW/cm^2 and elucidation of photovoltaic parameter value.

(b) Redox Mediation through Integrating Chain Extenders in Active Ionomer Polyurethane Hard Segments in CdS Quantum Dots Sensitized Solar Cell

- ❖ Synthesis of structurally modified polyurethanes through variation of short and long chain extender (diol and diamine) maintaining hard segment content at 30%.
- ❖ Synthesis of polyurethanes by integrating diol having ester component at constant hard segment and chain extender.
- ❖ Functionalization or chemical modification by pendant group at urethane linkage bearing different electronic environment.
- ❖ Preparation and decoration of ionomer gel electrolyte from different functionalized polyurethane.
- ❖ Structural characterization of sulfonated polyurethanes by different technique.
- ❖ Study of electronic conductivity at thin film phase and ionic conductivity in solution phase.

- ❖ Measurement of lifetime of surface free electron of different ionomer solution
- ❖ Device fabrication and analysis of J-V characteristic measurement.

(c) Multifunctional Graphene Oxide Implanted Polyurethane Ionomer Gel Electrolyte for Quantum Dots Sensitized Solar Cell

- ❖ Synthesis of graphene oxide and reduced graphene oxide
- ❖ Synthesis of composite polyurethane via reaction of NCO- terminated Prepolymer with different content of graphene oxide.
- ❖ Synthesis and incorporation of electrolyte active pendant anion into polyurethane and composite polyurethane matrix.
- ❖ Spectroscopic analysis
- ❖ Investigation of thermal stabilization and glass transition temperature
- ❖ To study morphological features and correlation of structure function
- ❖ Assessment of electrochemical properties
- ❖ Preparation of gel polyelectrolytes
- ❖ Spectroscopic studies of synthesized materials.
- ❖ Synthesis and functionalization of CdS particle via 3-mercaptopropeonic acid
- ❖ Preparation of photoanode, counter electrodes and assembly of QDSSCs.
- ❖ J-V characteristic measurements of device
- ❖ Calculation of power conversion efficiency