CHAPTER 1

Introduction

- Renewable energy and Photovoltaic technologies
- Generations of Photovoltaic
- Dye sensitized solar cell (DSSC)
- Components of DSSC
- Electron transfer kinetic of DSSC
- Generations of DSSC

1.1 A Perception…

“Access to electricity determines the quality of life…!!”

The statement dictates the supreme relationship between the electricity and human kind in the contemporary world. We, the human being rely upon the various energies to survive on this planet in which some are essential and remaining part of energies fashions our life styles. But extreme consumption of crude oil for the generation of electricity has alarmed the species on this planet to move toward safe and green production as well as consumption of energies. In doing so, we have disturbed the nature at greater extent by emitting tons of green house gases leading to the increasing temperature of the earth surface followed by their consequences. Looking to these major issues caused by the conventional energy resources, many government organizations have already started to take measure against the access and consumption of energy. Nuclear power plants are too thought to be the substitute of crude oil since its energy generation efficiencies are quite adorable. Even there are enough rooms in the nuclear power plants but they too suffer from the major issues related to safety and waste disposal.

In this century, Renewable Energy Resources (RER) are thought to be the Holy Grail for the human being as far as electrical energy is concerned. This technology can answer all the questions raised in the energy sector of contemporary world. Renewable energies are defined as the energies which are produced using the natural components like wind, sun, water etc. using appropriate equipments. Wind mills, solar cell and hydrothermal power stations are accompanied by the renewable energy resources like wind, sun and water respectively. It has been fact that nature never raises their price for light, wind and water so the energies generated by using these technologies will be cost effective as well as emission free!!
Even renewable technologies demand much R&D efforts to be an easily accessible for the common living creatures on this earth. A large sum of money is needed to be invested in the installation of solar cells, wind mills and hydrothermal power station. Though the raw materials are free from nature but the maintenances and equipment stability is of main concern during the operation. Amongst all the renewable energy resources, solar energy is easily available and can be produced at the point of consumption or even in the space. Since sun is supplying his radiations constantly on the earth surface while there are some special requirements for the generation of wind energy and hydrothermal energy. So, it can be preclude that the solar cells technology, also known as the Photovoltaic technology would be the future for the electricity.

1.2 What is Photovoltaic..?

Photovoltaic in broad sense can be defined as the technology or science which deals with the conversion of light into DC electricity. In fact, as far as light is concerned, human being relies upon the sun which delivers plenty of light on this earth constantly. Photovoltaic technology (Abbreviated hereafter as PV technology) can be installed at any point of use so power transmission part can be retarded at greater extent. Moreover, working of PV devices neither generate any green house gases nor produce any type of environmental hazards which leads to green approach for the energy production. Though there are certain issues which need to be curbed before making it accessible to the underdogs of society. The generations of PV technology can be broadly classified into the three categories viz. Silicon technology (1st generation), Thin film solar cells (2nd generation) and Organic solar cells (3rd generation).
1.3 Generations of Photovoltaic

The silicon technology is believed to be the first piece in the photovoltaic which utilizes doped Si and generates electricity upon irradiation of light. It has pretty good solar to electricity conversion efficiency (more than 20 % of module) under the full sunlight. First, there was a tremendous worldwide scientific and technical infrastructure for Si starting in the 1960s [1]. Huge government and industrial investments were made in programs for understanding the chemical and electronic properties of Si, how to grow it with the required purity and crystalline structure, and to create the equipment needed to perform all the processing steps. Consequently, a good material with high chemical purity and structural perfection is required to fight the natural tendency of the conduction-band electrons to return to the valence band. This loss process is called \textit{recombination}. To avoid this loss, the electrons must be highly mobile, as they are in perfect silicon. Impurities and imperfections must be avoided as they can absorb the extra energy of the conduction band electrons and convert it into heat, thus eliminating the free electron from traveling through the circuit by immediately restoring it to the valence band energy. Metallurgical Grade (MG) Silicon is obtained by reduction of quartz with coke in an arc furnace [1]. Then it is strongly purified by a method developed by and named after the Siemens Company consisting of the fractional distillation of chlorosilanes, which are obtained from the reaction of HCl with Si. Finally, silanes are reduced with hydrogen at high temperatures to produce hyperpure silicon, usually called \textit{Semiconductor Grade (SG) Silicon}. The lowest (publicly offered) module selling prices in 2002 were about $3/Wp. The major issues associated with production of single crystalline Si solar cells, are their purification and crystallization. Hence the production cost of the Si based solar cell is quite higher along with high payback time (1.5 to 2 year or more).
The simplest answer of above issues is “to achieve lower cost and improved manufacturability at larger scales than could be envisioned for Si wafer based modules.” Throughout the 1970s, progress in Cu₂S/CdS solar cells led to the development of new theories to explain the device performance, new methods of materials processing, and new concepts in semiconductor device manufacturing [2,3]. Between 1981 and 82, four thin-film technologies demonstrated the ability to cross the magical 10% efficiency barrier, thus becoming candidates for serious consideration: Cu₂S/CdS [4], a-Si [5], CuInSe₂/CdS [6], and CdTe/CdS [7]. The main advantage of Thin Film Solar Cell (TFSC) is that they will eventually have lower costs than c-Si-wafer PV technology when they are produced in sufficiently large volumes to offset the initial capital investment. The lower costs of TFSC derive from the following characteristics: they are typically 100 times thinner than Si wafers (\(\sim 1-3 \mu m\) for all the semiconductor layers) deposited onto relatively low-cost substrates such as glass, metal foils, and plastics; they are deposited continuously over large areas at much lower temperature (200 to 500°C vs \(\sim 1400°C\) for c-Si); they can tolerate higher impurities (thus needing less expensive purification of raw materials); and they are easily integrated into a monolithic interconnected module.

With all the advantages of TFSCs, why does c-Si or multi-Si still dominate 90% of the world market? This brings us to the disadvantages of Thin film solar cells: they have lower efficiencies (so far 10-11% of module), and they have a much less-developed knowledge and technology base compared to c-Si. One of the major disadvantages of this technology is the limited resources of raw materials as well as toxicity associated with them.

Photoelectrochemistry for solar to electricity conversion has been studied since couple of years [8] but a sudden report of photoelectrochemical solar cell based on
nanocrystalline titanium dioxide (TiO$_2$) sensitized with dye molecules by Brian O’Regan and Michael Gratzel, have opened up the new horizon in the low cost photovoltaic technology [9] and now a day, recognized as Dye Sensitized Solar Cell (DSSC), A third generation photovoltaic technology in general and DSSC in particular, is believed to be future of low cost photovoltaic. The main counter part of this technology is nanocrystalline TiO$_2$ which is quite abundant in nature. Moreover, these solar cells are fabricated using vacuum less technology as well as capital investment is much less than that of contemporary technology. DSSC have achieved 10-11% solar to electricity conversion efficiency using TiO$_2$ as semiconductor and Ru metal complexed dye as sensitizer (in laboratory scale) [10]. Later on community moved toward many metal free organic dyes to be used as sensitizers in DSSC but none of them can exceed mark of 11% [10]. While recent report by Burshcka et al. have crossed the mark by attaining ~15% photovoltaic efficiency of dye solar cell sensitized with organometallic halide perovskite in conjunction with solid hole conductor [11]. DSSC carries very complex though subtle electron transfer kinetic that is studied using various electrochemical and spectroelectrochemical techniques. Even though the efficiencies of these solar cells are lower than that of contemporary technologies, they offer many advantages over them like roll to roll printing approach, can be fabricated on plastic substrate, have vivid colors and shades, highly suitable for building integrated photovoltaic etc. In view of this, we have attempted to explore the realm of DSSC in detail. Following Table 1.1 gives the brief insight into the development of photovoltaic technology as a function of time [1]. This shows that the journey of photovoltaic was started in the 1839 with the discovery of the photogalvanic effect in the electrolyte solution and reached to the photoelectrochemistry and semiconductor interfaces.
Table 1.1: Timeline for the development of photovoltaic technology

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
</tr>
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<tbody>
<tr>
<td>1839</td>
<td>Becquerel (FR) discovered photogalvanic effect in liquid electrolytes</td>
</tr>
<tr>
<td>1873</td>
<td>Smith (UK) discovered photoconductivity of solid Se</td>
</tr>
<tr>
<td>1954</td>
<td>First 6% efficient solar cells reported: Si (Bell Lab, USA) and Cu$_2$S/CdS (Air Force, USA)</td>
</tr>
<tr>
<td>1963</td>
<td>Sharp Corp (JP) produces first commercial Si modules</td>
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<tr>
<td>1970</td>
<td>First GaAs heterostructure solar cells by Alferov, Andreev et al. in the USSR</td>
</tr>
<tr>
<td>1973</td>
<td>A big year in photovoltaic: Worldwide oil crisis spurs many nations to consider renewable energy including photovoltaic; Cherry Hill Conference in USA (established photovoltaic’s potential and legitimacy for government research funding); World’s first solar powered residence (University of Delaware, USA) built with Cu$_2$S (not c-Si!) solar modules</td>
</tr>
<tr>
<td>1980</td>
<td>First thin-film solar cell &gt;10% using Cu$_2$S/CdS (USA)</td>
</tr>
<tr>
<td>1985</td>
<td>A big year for high-efficiency Si solar cells: Si solar cell &gt;20% under standard sunlight [12]</td>
</tr>
<tr>
<td>1987</td>
<td>Fourteen solar powered cars complete the 3200 km World Solar Challenge race (Australia) with the winner averaging 70 kph</td>
</tr>
<tr>
<td>1994</td>
<td>GaInP/GaAs$_2$-terminal concentrator multijunction &gt;30% (NREL, USA) [13]</td>
</tr>
<tr>
<td>1996</td>
<td>Photoelectrochemical “dye-sensitized” solid/liquid cell achieves 11% (EPFL, Switzerland) [14]</td>
</tr>
<tr>
<td>1998</td>
<td>Cu(InGa)Se$_2$ thin-film solar cell reaches 19% efficiency (NREL, US) [15] comparable with multicrystalline Si</td>
</tr>
<tr>
<td>2002</td>
<td>Cumulative worldwide installed photovoltaic reaches 2000 MW. It took 25 years to reach the first 1000 MW and only 3 years to double it (in 1999, it was 1000 MW..!!)</td>
</tr>
<tr>
<td>2013</td>
<td>Perovskite sensitized photo-electrochemical solar cell achieved approximately 15% solar to electricity conversion efficiency [11]</td>
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</table>
1.4 Dye Sensitized Solar Cell (DSSC)

Dye sensitized solar cell falls in the realm of photoelectrochemical cell which was first pioneered by Prof. Gratzel and owns the name as Gratzel’s cell. This device composed of a nanocrystalline semiconducting material (usually TiO₂) sensitized with organic/inorganic light harvesting materials along with a redox electrolyte/hole conductor and a counter electrode (generally Pt). The sudden report of 6-7% efficient device using photoelectrochemistry had accelerated the efforts of chemist and material scientist to go forward in this technology to achieve better efficiencies [9]. Previous experiments on the photoelectrochemistry was carried out by using thin film of semiconductor (a few nm) hence the charge generation was limited leading to dwindled performance but a subtle logic of O’Regan and Gratzel proved that DSSC is also a potential competitor. **Scheme 1.1** depicts the various parts of DSSC under working condition and is generally assembled in sandwich type configuration.

![Scheme 1.1: Basic components of dye sensitized solar cell](http://electrons.wikidot.com/dye-sensitized-solar-cell)
There are R&D activities going on across the globe on the various aspects of DSSC along with the development of theoretical concepts of the same. 10-11% solar to electricity conversion efficiencies have been reported so far using TiO₂ as semiconductor and Ru-metal complexed dye as sensitizer in presence of a liquid electrolyte [16]. Many efforts have been devoted to enhance the efficiency of the device by changing various parameters like photoelectrode material [17], sensitizers [18], electrolytes [19], counter electrode [20] etc. but little fruits are harvested. Recently, Chandsekaran et al. have claimed to achieve close to 12% solar to electricity conversion efficiency on DSSC by using a co-adsorbate material [21]. Following are the details of different counterparts of DSSC.

1.4.1 Substrates

Generally, DSSC electrodes are prepared onto the Transparent Conductive Oxide (TCO) coated onto the glass surface which acts as current collector in the device. FTO (Flourine doped tin oxide) and ITO (Indium doped tin oxide) are widely used TCO materials which are having good transmittance in visible region without scarifying the conductivity [22]. TCO coated glasses are easily available in the market with the surface resistivity ranging from 7 Ω/cm² to 100 Ω/cm². As the conductivity of TCO increases, transmittance of light decrease but the magnitude depends upon the TCO material used. TCO glass contains the thin layer (in the range of nm) of a doped conductive oxide coated using vacuum deposition or sputtering. The commercially available TCO substrates are generally having transmittance in visible region greater than 80% hence there has always been a reflectance loss in DSSC restricting the performance of device. Moreover, stability of FTO film is higher than ITO since the later gets cracked during calcinations leading to high resistance at collector and thereby lowering the device performance.
Now a day, TCO is also coated onto the plastic substrate to confer flexible DSSC. Polyethylene terphthalates (PET) are used widely for this purpose and are marketed as ITO/PET films [23]. Moreover, TiO₂ is also prepared on Ti foil [24], on various metal substrate [25] as well as on paper substrate [26] and DSSC are illuminated from the back side.

1.4.2 Photoelectrode

Photoelectrode is also known as the anode or negative electrode in the dye solar cell. It is solely responsible for the generation of current upon stimuli with light. Photoelectrode consists of a layer of nanocrystalline semiconductor materials sensitized with dye molecules. There are many semiconductors which can be used in the DSSC but TiO₂ and ZnO are runner up. In DSSC, electron transport mainly occurs through the semiconductor matrix by percolation/diffusion. Peculiarities of better semiconductors for DSSC are having good carrier mobility, wide band gap, abundant in nature, photostable, high refractive index, conduction band energy (above -0.5 V Vs NHE). The semiconductor film used for this purpose is generally made up of nanoparticle form with the thickness ranging from 6-15 µm for efficient DSSC depending upon the molar extinction coefficient of the dye used.

The performance of the photoelectrode depends upon the nature and size of the nanoparticles used and must be prepared with high crystallanity and good dispersion. Anatase TiO₂ particles are better than rutile and brukite. Since the electron transport properties and densities of the anatase form is better than those of other structure [27]. The basic structure of the TiO₂ utilized for DSSC fabrication is in form of sphere having diameter ranging from 20-30 nm. But in recent years substantial progress has been made to synthesize the TiO₂ based nanostructures like nanotubes, naorods, nanoforest, mesoporous materials etc. but power conversion efficiency has not been
improved much [28-31]. Hong et al. have reported a photoanode composed of TiO$_2$ nanoparticles/nanorod composite. They have found that electron diffusion coefficient and interfacial charge transfer are enhanced in presence of nanorods leading to 6.1% electricity conversion efficiency [32]. Krysova and coworkers have prepared TiO$_2$ nanofibres using electrospinning technique for the DSSC application and they have demonstrated remarkable power conversion efficiency using nanofibre based electrode [33]. Generally TiO$_2$ has been synthesized via hydrolysis of titanium alkoxide precursor using sol gel technique using acid or base followed by particle growth and crystallization. Depending upon the various parameters like temperature, humidity, pH, concentration etc. various shape and size of nanomaterial has been obtained. It has been reported that the base catalyzed condition during hydrolysis leads to the mesoporous TiO$_2$ that gave slower recombination in DSSC along with high $V_{oc}$. There are also other methods like micelle templated, hydrothermal, electrodeposition, sonochemical, electrospinning etc for the synthesis of TiO$_2$ nanostructures [34-37]. The synthesized TiO$_2$ particles are formulated in paste using surfactants, binding agents, solvents etc. Generally used binder is ethyl cellulose in $\alpha$-terpeneol while there are reports of different paste recipes but efficient paste formulation has been given in the report by Ito et al. [34]. The polymer in the TiO$_2$ paste performs dual role like binding agent as well as it is responsible for the pore generation in TiO$_2$ matrix during the calcinations in order to form a continuous mesoporous network. Polyethylene glycol with high molecular weight is also good ingredient for the paste formulation and has widely been utilized. The amount of polymer used should be optimized since the lower content will generate less porosity while high content will lead to less interconnects between particles. The optimum amount of polymer in the
paste is 50-60% and changing the polymer concentration one can control the porosity of the network. Application of the paste was carried out by using doctor blading or screen printing technique onto conducting glass substrate followed by sintering of the film at 450°C in order to remove the polymeric material and to generate better contact with particles [34].

There are certain pre and post treatments to the photoelectrode in order to reduce the recombination of electrons and improve the charge collection efficiency. It is fact that the FTO surface exposed to electrolyte may result in the recombination of electron from TCO surface to electrolyte components. In order to overcome this difficulty a dense and thin layer TiO₂ is coated onto the FTO surface before preparing the nanoparticle network. This can be achieved by spin coating of ethanolic solution of titanium precursor or by soaking the TCO in TiCl₄ solution followed by sintering. While post treatment to TiO₂ network is carried out by using TiCl₄ solution which is believed to confer the necking of TiO₂ particles and improves the interparticle contact leading to better charge mobility. This method was reported by Nazeeruddin et al. in 1993 [38] but earlier Kavan et al. [39] had developed a TiCl₃ based method by electrodeposition which was difficult to perform but gave same results as reported by Nazeeruddin et al. It is also proved that the treatment of TiCl₄ lowers the acceptor level in the semiconductor leading to improve electron injection efficiency. Moreover, attempts were made to modify the TiO₂ energy levels by doping the semiconductor with suitable dopants. Zhang et al. have shown the doping of nitrogen and sulfur into the TiO₂ photoelectrode and found that the simultaneous doping of both ions yields good results than individual one [40]. While Huang et al. have shown that the doping of Zn²⁺ ions into the TiO₂ matrix leads to enhanced photocurrent in the device by leaving open circuit voltage intact [41]. Very recently, C. T. Wang and coworkers
have prepared sol gel derived Fe doped TiO$_2$ photoelectrode and utilized it in dye solar cell [42]. Detailed experimental analysis of DSSC based on N719/Fe-TiO$_2$ showed that the electron lifetime and charge collection efficiencies are improved at greater extent. Lee et al. have examined the effect of carbon nanotube incorporated TiO$_2$ photoelectrode in DSSC. They have shown more than 20% enhancement in overall photovoltaic efficiency due to the increased surface area and better charge transfer kinetics [43]. Kim et al. have fabricated DSSC using trench structured TiO$_2$ nanotube electrode in Ti foil substrate achieving 40% enhancement in performance as compared to conventional nanotube based photoelectrode [44].

Scientists have also developed the methods for the preparation of TiO$_2$ network at low temperature which is essential for the fabrication of plastic/flexible dye solar cell. It is fact that polymer substrate can not be heated upto certain temperature i.e. 100-150°C hence it is desirable to prepare the network of TiO$_2$ using alternate method. Lindstrom et al. have developed a compression method in which powderous sample was pressed by applying the 500-1500 kg/cm$^2$ pressure and achieved 3% efficiencies without sintering [45]. Further optimization of this process was carried out by Arakava and coworker who have achieved remarkable solar to electricity conversion efficiency using ITO/PEN substrate i.e. 7.4% [46].

There is one of the prominent semiconductor contender for TiO$_2$ in DSSC is ZnO whose band gap and band edge is quite similar to that of TiO$_2$. Moreover ZnO is having better carrier mobility than TiO$_2$ as well as various nanostructures of ZnO can be synthesized using different methods. The best reported efficiency for the ZnO based DSSC is 6.6% using ZnO nanoparticles sensitized with N719 dye and liquid redox mediator [47]. The main drawback associated with the use of ZnO is the dissolution of Zn$^{2+}$ ions in solution during dye soaking which results in the
precipitation of the dye [48]. In order to overcome this difficulty Park and co-worker have coated the ZnO nanoparticles with SiO₂ core and have achieved 5.2% solar to electricity conversion efficiency [49]. They have found the greater stability of the ZnO in presence of SiO₂ coating. Generally ZnO is grown onto the substrate directly using electrodeposition method from the aqueous solution of Zn²⁺ ions. Lu et al. have shown the effect of rare earth ion modification on the performance of ZnO based DSSC; they have doped ZnO oxide with different rare earth metals like La, Gd, Sm, Ce and Nd [50]. They have achieved enhanced performance in the device modified with Gd ions. Moreover, there are other oxides materials which were used as semiconductor in DSSC like SnO₂, Zn₂SnO₄, Nb₂O₅ etc. The best reported efficiency for the SnO₂ based DSSC is 2.8% using D149 dye as sensitizer while that of Zn₂SnO₄ based device is 3.8% [51,52]. Guo et al. have achieved 5% electricity conversion efficiency using Nb₂O₅ as semiconducting material [53].

1.4.3 Sensitizers

Sensitizers/Dyes are believed to the heart of DSSC since it is the main light harvesting component of the device. There are certain specifications for the dyes to be used as sensitizer in DSSC in order to synchronize with complex mechanism of the device. Following are the basic requirement for a molecule to be fulfilled before putting forward its candidature as sensitizer.

- It should have high molar absorption coefficient and wide optical window in order to harvest the solar spectrum efficiently
- Planar conformation of the molecule is preferred
- It must have LUMO level above the conduction band of TiO₂ and HOMO level lower than the redox potential of electrolyte in order to achieve efficient injection and regeneration respectively
- It must have suitable binding groups like –COOH, -SO₃H, -PO₃H₂ etc. in order to bind with TiO₂ particles
- Dye must have photochemical as well as electrochemical stability
- Dye should not form aggregates onto the TiO₂ surface which result in the charge injection inefficiencies.

There is one unique and acceptable design for the DSSC sensitizer which incorporates Donor, Bridge and Acceptor as shown in Figure 1.1.

**Figure 1.1** A schematic design of the dye used as sensitizer in DSSC (Arrow shows the direction of electron flow upon excitation of molecule by light)

The main role of donor part is to donate the charge upon irradiation, this charge moves toward acceptor via bridge hence the main role of bridge is to separate the charge as much as possible in order to enhance the excited state dipole leading to long lived excited state while the acceptor part is directly attached to the TiO₂ matrix by binding groups. Once the charge reached to acceptor, it has been injected into the conduction band of TiO₂ if the LUMO is well placed above the edge of conduction band.
The first candidate for the sensitizer in DSSC was the Ru based metal complexed dye (N719) which showed the remarkable quantum efficiency and achieved near about 6% photovoltaic performance which was reported by O’Regan et al. in 1991 [9]. Later on many modifications in the Ru based dyes were carried out and now days these dyes are giving more than 10% solar to electricity conversion efficiencies [54]. These complexes are having good optical window with high molar absorption coefficient, suitably placed energy levels, better electrochemical stability etc. Following Table 1.2 shows some Ru based metal complexed dyes with their photovoltaic performance.

**Table 1.2** Some Ru based sensitizers for DSSC with remarkable power conversion efficiencies

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Dye</th>
<th>η</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>01.</td>
<td><img src="image" alt="N3 dye" /></td>
<td>N3 dye = 10%</td>
<td>[55,56]</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="N719 dye" /></td>
<td>N719 dye = 11.2%</td>
<td></td>
</tr>
<tr>
<td>02.</td>
<td><img src="image" alt="Black dye" /></td>
<td>Black dye = 10.4%</td>
<td>[57,58]</td>
</tr>
<tr>
<td>03.</td>
<td><img src="image" alt="CYC B1 dye" /></td>
<td>CYC B1 dye = 8.5%</td>
<td>[59]</td>
</tr>
</tbody>
</table>
The photoelectrochemistry of such dye molecules is based upon the metal to ligand charge transfer process (MLCT) in which electron density is shifted towards the ligand upon absorption of quanta. Table 1.2 summarizes the efficient molecules from the realm of Ru based complexes and shows the molecular modification on the parent compound in order to modify the performance of DSSC. N3 and N719 dye were first reported by Gratzel group in 1993 and are first molecules to attain more than 10% solar to electricity conversion efficiency [55,56]. These both dyes are different in their protonation state and harvest solar spectrum efficiently. Later on many modifications on the ligands were made in order to extend the \( \pi \) conjugation using thiophene and phenyl units but no remarkable performance difference was achieved. Moreover, there were some Os, Fe, Cu, Re and Pt based complexes which too were tested as
sensitizers in dye solar cell [63-67]. But the efficient dyes are having some problem as far as the practical application of DSSC is concerned. It is fact that the Ru is a rare earth and precious metal leading to the economic barrier to device fabrication; moreover, the synthetic protocols and purifications of such dye is quite difficult and tedious which hampers the bulk production of the same. In order to find the alternative, community moved toward metal free pure organic dye molecule which are having potential to bulk synthesis, are having good stability, good light harvesting properties etc [68].

Pioneering progress in organic dye based DSSC was made by Hara et al. and Yanagida et al. who have synthesized dialkylamino containing oligoene donors and cyano acetic acid as acceptor [69,70]. These dyes have achieved more than 6% efficiencies with liquid based redox system and Pt counter electrode [70]. There are many organic donor moieties like carbazole, triaryl amine, coumarine, porphyrines, phthalocyanines, phenothiazine, hemicyanine dyes, anthracene dyes etc which have been utilized as sensitizers in DSSC [68]. The oligothiophene based bridge units and cyano acetic based acceptor units in the dyes have proved to be good candidate in terms of current collection efficiency. Yu and coworkers have recently examined the effect of different acceptor group such as cyanoacetic, ethyl carboxylate, oxalic, sulphonic and hydroxyl amine using same donor unit and they inferred that the cyano acetic is better accepting group in the dye for DSSC application [71]. Following Table 1.3 shows the some selected dyes from purely organic moieties which have outperforms in DSSC along with their solar to electricity conversion efficiency.

This table depicts the efficient molecules from each series along with their structure and efficiencies. It has been found from this table that the metal free organic sensitizers are prominent competitor to the rare earth metal based complex in DSSC.
Among the organic sensitizers, carbazole and triphenyl amine based moieties are runner up since these molecules have attained efficiencies more than 8%. Recently, He et al. have synthesized 3,6-disubstituted carbazole dye bearing alkyl group on nitrogen atom. These dyes were successfully employed as light harvesting material in DSSC and showed remarkable photovoltaic performance in conjunction with liquid electrolyte (~6%) [79].

**Table 1.3** Molecular structure of metal free organic dyes used as sensitizer in DSSC

<table>
<thead>
<tr>
<th>Basic Moiety</th>
<th>Structure</th>
<th>$\eta$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbazole</td>
<td><img src="image" alt="Carbazole" /></td>
<td>8.1%</td>
<td>[72]</td>
</tr>
<tr>
<td>Coumarine</td>
<td><img src="image" alt="Coumarine" /></td>
<td>6.07%</td>
<td>[73]</td>
</tr>
<tr>
<td>Triaryl amine</td>
<td><img src="image" alt="Triaryl amine" /></td>
<td>9.1%</td>
<td>[74]</td>
</tr>
</tbody>
</table>
2-substituted carbazole bearing N-alkyl or aryl group have been designed and synthesized for DSSC application [80]. These dyes showed only 2-3% electricity conversion efficiency under 1 sun. Moreover, macrocyclic dyes like porphyrine and
phthalocyanines are also potential sensitizers but aggregation of the macrocycles onto TiO$_2$ surface has led them to perform poor in DSSC; though the porphyrine based dyes have attained more than 5% solar to electricity conversion efficiencies under the 1 sun illumination. There is also report of D-π-A dye based on isoindigo nucleus with cyanoacetic acceptor. Isoindigo dyes showed better sensitizing properties by achieving more than 3% solar to electricity conversion efficiency [81]. Some imidazole derivatives have also been examined as sensitizers in DSSC with 4% photovoltaic efficiency under 1 sun illumination [82]. Dihydrodibenzoazepine based sensitizers have also been used as sensitizers in DSSC by achieving remarkable solar to electricity conversion efficiency (~4.8%) [83].

1.4.4 Redox mediator

The redox mediator/electrolyte is a crucial component for the charge transport in the DSSC. It usually donates an electron to the dye molecule and regain from the counter electrode via catalytic reactions. Hence the current density and fill factor of the device largely depends upon the composition of the electrolyte. There are certain requirements which need to be satisfied for an electrolyte to be used in DSSC like volatility, ionic mobility, solvent viscosity, and redox properties [84]. Moreover, electrolyte used in DSSC should be non reactive toward the sealing material in order to avoid leaking of the device. The electrolyte of the DSSC generally consisted of a redox mediator, organic additives, solvent (aqueous or non-aqueous). There are mainly four types of electrolytes which have been utilized in DSSC like liquid electrolyte, polymer gel electrolytes, solid hole transporting material and solid polymer electrolyte.

A widely used redox mediator is iodide/triiodide which found to be efficient redox species for the dye solar cell. The formulation of the liquid electrolyte is generally
carried out in organic solvent though primitive photo-electrochemistry was carried out in water [85,86]. Reactive solvents are not the optimal choice for the media since it may react with the dye molecules. Organic solvents are proved to be better media in DSSC leading to efficient device than water. There are certain problems related to the iodine based electrolyte like corrosion of device due to the dissolution of counter electrode component but efficiencies of the devices are only achieved using LiI/I2 in organic solvent. There are many solvents like acetonitrile, ethylene carbonate, propylene carbonate, valeronitrile, 3-methoxy propionitrile etc. but nitrile based solvents are runner up. The problem largely associated with the organic solvents is its volatility and toxicity, leading to environmental issues but the main advantage of the liquid electrolyte is enhanced electron transport and complete dissolution of redox species. Researchers have also investigated the effect of various solvents in DSSC like THF, DMF, DMSO, nitriles, alcohols [87]. But in terms of photo conversion efficiencies, they all were similar but strong donating solvents tend to enhance performance via modifications of TiO2 conduction band. In combination with the plastic substrate, 3-methoxypropionitrile is found to be efficient [88] and it’s a solvent of choice in DSSC now a day due to its high ionic mobility and high boiling point. Recently, a report showed that bromine based (Br2/Br3-) redox mediator in combination with carbazole based dye yields more than 1V in DSSC [89]. Moreover, LiI can be replaced with ionic liquid in electrolyte like 1-butyl-3-methyl imidazolium iodide as an iodine source [90,91]. Ionic liquids are getting more attention due to its low volatility and environmental compatibility. 1,2-dimethyl-3-propyl imidazolium iodide (DMPII) have been widely used in the electrolyte of dye solar cell due to low viscosity and good stability. There is also a new trend in the redox species based on the metal complexes of Ni and Co. Spokoyny et al. have used the Ni based...
Bis(dicarbollide) redox shuttle while Yum et al. have utilized Co-Polypyridyl redox mediator in conjunction with triaryl amine dye (Y123) and achieved more than 8% solar to electricity conversion efficiency along with more than 1V in the DSSC [92,93]. Recently, some groups have successfully reported water based DSSC along with hydrophobic dyes and achieved remarkable solar to electricity conversion efficiency [94-96].

Some additives are used in the electrolyte of the DSSC which are generally having donating tendency. Nitrogen containing heterocyclic compounds are prime choice as additives in DSSC [97]. It has been found that the Nitrogen atoms from the additives adsorbs onto the TiO$_2$ substrate and raise the energy of Fermi level of semiconductor. Open circuit voltage in the DSSC is due to the difference between the TiO$_2$ fermi level and redox potential of electrolyte system. As the Fermi level energy increases, open circuit potential increases. Hence the additives are used to enhance the $V_{oc}$ in the dye solar cell by modifying the TiO$_2$ band structure [98]. One more indirect reason is the suppression of recombination of electron by electrolyte components since the addictives will be adsorbed onto those sites where dye is not available by reducing the direct contact between the electrolyte and TiO$_2$ [99]. Pyridine and benzimidazole based derivatives are generally used for this purpose but efficient additives are 4-tert butyl pyridine and 1-methyl benzimidazole [100].

Earlier we have discussed that the organic solvents are volatile in nature since they are having sufficient vapor pressure even at room temperature. The volatility of the solvent will cause the device to rupture in working condition since the working temperature of the device will be 50-60$^\circ$C. In order to overcome this difficulty, community has moved toward the better alternative which can have good ionic mobility with better mechanical strength. Polymer Gel Electrolytes (abbreviated
hereafter as PGE) are prominent candidates as a better replacement of liquid electrolytes since they have diffusive properties like liquid and cohesive properties like solids. PGE can be prepared by adding suitable gelling agent or polymer into the liquid electrolyte. PGEs have some advantages, such as low vapor pressure, excellent contacting and filling properties between the nanostructured electrode and counter electrode, higher ionic conductivity compared to the conventional polymer electrolytes and excellent thermal stability. Thus the DSSCs based on PGE have outstanding long-term stability. To pursue the use of PGE in DSSC, it must have high ionic conductivity in order to preserve the efficient functioning of DSSC. The ionic conductivity of PGE depends on charge carrier transfer and diffusion efficiency of the redox couple resulting from its own ingredients such as various types of polymer, the concentration of polymers with various molecular weights and conductivities, and the concentration and property of iodide salts. External factors also influence the conductivity to a certain extent, such as the organic solvents and temperature. All the factors mentioned above further decide the photovoltaic performance of the DSSCs based on PGE [101]. The DSSC fabricated using gel electrolytes are termed as Quasi Solid DSSC and was first reported in 1995 using poly (acrylonitrile), ethylene carbonate, acetonitrile and NaI with 4.4% power conversion efficiency [102]. Then after a series of polymer and polymer composites like PEG, Poly(ethylene oxide-co-propylene oxide), Poly(acrylamide)/PEG, Poly(methylacrylate), Poly(vinylidenefluoride-co-hexafluoropropylene) etc. were employed for the solid and quasi solid DSSC fabrication [103-105]. Wang et al. prepared a series of quasi-solid-state DSSCs by adding 5wt% of poly (vinylidenefluoride-co-hexafluoropropylene) (PVDF-HFP) in methoxypropionitrile (MPN) based gel electrolytes [106]. Membrane electrolytes have also been used as redox mediator in dye solar cell. Recent report
showed preparation of electrospun polyacrylonitrile based nanofibres membrane gel electrolyte and its application in DSSC. This report shows that the current density of membrane based electrolyte is comparable with that of liquid DSSC [107]. Li et al. have reported a gel electrolyte based on conducting polymer and neutral polymer block-copolymer as backbone materials. This electrolyte showed 7% electricity conversion efficiency when applied to DSSC as redox mediator [108]. The conductivities of these polymer gels exceeded 10 mS/cm and the cell efficiencies were over 6% at 1 Sun illumination but the sealing problem remained. Recently, Tang and coworkers have designed an ionic liquid imbibed polymer gel electrolyte using 1-butyl-3-methyl imidazolium chloride as solvent, 1-methyl-3-propyl imidazolium iodide as iodide source and poly(hydroxyethylacrylate/glycerol) as placeholder. Resultant polymer gel electrolyte showed ionic conductivity 14.28 mS/cm at room temperature and they have achieved more than 15% enhancement in the performance of DSSC using this gel electrolyte [109].

In order to avoid the volatile liquid counterpart in the electrolyte, community moved toward the solid hole conducting materials. These hole conductors are made up of organic or inorganic framework and are much suitable for the roll to roll printing of the devices. In 1995, solution precipitated CuI was applied to DSSC as solid inorganic hole conducting materials since it acts as $p$-type semiconductor [110]. CuSCN was synthesized via precipitation from the acetonitrile solution as was utilized as hole conductor in DSSC; which showed the better charge transport properties as liquid cell but recombination reactions were faster [111,112]. The main problem concerned with such hole conductors is appears to be the large crystallite formation in the mesoporous film which is not fully counteracted by crystal growth inhibitor [113]. While Yanagida and co-workers were the first to utilize polypyrrole based conducting
polymer doped with LiClO₄ as solid organic hole conductor in DSSC by achieving 0.1% solar to electricity conversion efficiency [114]. Later on many conducting polymers like poly (3,4-ethylenedioxythiophene) [115], polyaniline [116], poly (3-hexylthiophene) [117] etc. were utilized in the DSSC as hole conducting materials. The most popular organic hole conductor for DSSC is found to be Spiro-OMeTAD (2,2′,7,7′-tetrakis(N,N-di-p-methoxyphenylamine)-9,9′-spirobifluorene). This was first introduced by Bach et al. in 1998 which were applied onto the photoelectrode by solution processed techniques [118]. Chung et al. have obtained ground breaking results in all solid state dye sensitized solar cell by using an p-type inorganic semiconducting material (CuSnI₃) as solid hole conductor [119]. They achieved more than 10% solar to electricity conversion efficiency.

1.4.5 Counter electrode

The counter electrode (CE) is an important component of the DSSCs, the roles of which are to collect electrons from external circuit and reduce I₃⁻ to I⁻ in electrolyte. Usually fluorine-doped tin oxide (FTO) glass is loaded with platinum to facilitate electron transfer from external circuit to I₃⁻/I⁻ redox electrolyte, due to the high catalytic activity and conductivity of platinum [120]. However, platinum is a noble metal and both of the two current methods, sputtering and electrochemical deposition [121,122], used for preparing Pt counter electrodes are high energy-consuming, which would limit the industrial applications. One of the widely used methods is, spin coating of the Pt precursor solution and the thermal decomposition of the same in order to get nanocrystalline Pt film. Therefore, many studies have been devoted to finding new alternative materials with low cost, high electronic conductivity, good chemical stability, and comparable catalytic effects for tri-iodide reduction to replace
platinum as counter electrodes for DSSCs. In this context, considerable efforts have been made to replace Pt with abundant low-cost alternatives, including carbon-based materials (for example, carbon nanotubes, carbon black, and graphite), [123-126] conjugated polymers, [127] and inorganic materials [128] as CEs. Lin et al. have shown the performance of polyaniline as a catalytic material in counter electrode by achieving 5.9% efficiency in the device [129]. While Peng et al. have reported a counter electrode fabricated from the composite of Platinum/polyaniline and achieved 5.4% electricity conversion efficiency [130]. Xia et al. have shown the polypyrrole based electrode with 3.4% efficiency in which polypyrrole was synthesized using vapor phase deposition method [131]. This electrode was prepared by spin coating method of precursor solution in which polyaniline reduces the K$_2$PtCl$_6$ to platinum leading to low temperature fabrication. But the carbon is a promising candidate. Sun et al. have shown the fabrication of low cost counter electrode based on Carbon/SnO$_2$/TiO$_2$ nanocomposite and achieved similar efficiency as Pt electrode [132]. Xin et al. have shown the catalytic activity of copper zinc tin sulfide nanocrystals which was synthesized using sol-gel method. They have achieved more than 7% efficiency in dye solar cell using selenized material (Cu$_{1.49}$Zn$_{1.00}$Sn$_{1.51}$S$_{0.85}$Se$_{4.78}$) [128]. Lin et al. have reported a tetragonal Neobium oxide as counter electrode material in DSSC and yielded more than 7% efficient device and also it supersedes the performance of Pt in the same fabrication process [133]. Thermally evaporated iridium (Ir) based counter electrode has also been employed in DSSC by M. J. Ko and coworkers. This group showed remarkable catalytic activity at 46 nm thin film of iridium (η=5.19%). They concluded that there are further rooms for the enhancement in the iridium based counter electrode [134].
Replacing noble metal with carbon materials is a good way to reduce its cost and achieving performance similar to Pt has been reported in the recent past [135]. Although carbonaceous materials are cost-efficient and resistant to corrosion and have good electrocatalytic activity, for the comparable high efficiency to Pt counter electrode systems, most of the carbonaceous materials have to have thickness of several µm and thus opaque [136]. Veerappan et al. have prepared amorphous carbon based flexible counter electrode using spray coating method and achieved more than 6% solar to electricity conversion efficiency [123]. Munkhbayar et al. have shown the electrocatalytic effect of various sample of multi walled carbon nanotubes (MWCNT’s) and reported more than 4% device performance using purified and grounded MWCNT’s [125]. Liu et al. have synthesized a new class of catalyst based on carbon supported transition metal-nitrogen catalyst for the counter electrode in DSSC and have found that electrocatalytic activity of Co and Ni based complexes is more than that of Fe [137]. Wang and coworkers have demonstrated a low cost counter electrode composed of doped mesoporous carbon [138]. Their results showed that the crucial factor for the enhanced catalytic activity is due to enhanced surface area of nitrogen doped mesoporous carbon. DSSC output from this electrode is quite comparable with that of Pt based electrode. The nitrogen donor moiety in this was polypyrrole in order to entrap the metal ions onto the carbon surface; they have achieved more than 7% efficient device using this new class of Co based catalyst. Rhee and co-workers have demonstrated the performance of carbon nanofibre (CNF) based counter electrode in dye solar cell [139]. They have shown three types of carbon nanofibres hollow CNF, CNF with herringbone structure and CNF with antler structure and results shows that the CNF with antler structure is better catalyst by giving 7% solar to electricity conversion efficiency. MoN has good electrocatalytic
activity for the triiodide ion but large impedance for the diffusion hinders its use as counter electrode in DSSC hence MoN-CNT hybrid was synthesized via hydrothermal route and found to be a good catalyst in DSSC by achieving 6.7% efficiency [140]. A MoS-C hybrid material synthesized via hydrothermal route has recently been reported by Yue et al. and was utilized as counter electrode material in DSSC [141]. They have achieved 7.7% electricity conversion efficiency by using MoS doped with 3.3 wt% carbon atoms. Recently, two-dimensional graphene, with a single layer of $sp^2$ network of carbon arranged in a flat honeycomb structure, has attracted considerable attention as potential counter electrode due to its single-atom-thick layer structure, excellent electrical properties, large specific surface area, and inertness against oxygen and water vapor [142]. Jang et al. have prepared moderately reduced graphene oxide using modified hummer’s method and the same was utilized as electrocatalytic material in dye solar cell [126]. They have shown a transparent counter electrode with electricity conversion efficiency 3.6%. Das et al. have shown that graphene-CoS composite can be better catalyst for the counter electrode material in dye solar cell than plain graphene by achieving almost doubly enhanced performance [124]. Recently, Zheng et. al. have demonstrated a unique method for the preparation of counter electrode based on C and Ni NP’s. This electrode showed remarkable power conversion efficiency (~6.5%) thereby being a potential candidate to the Pt based catalyst [143].

1.5 Charge Transfer in Dye Sensitized Solar Cell

Unlike traditional photovoltaic devices such as crystalline Silicon and thin films (e.g. CdTe and CIGS) devices where light absorption, charge separation and collection occurs within a single material, all charge transfer processes in DSSCs occur between
physically distinct components like dye, titania, electrolyte and counter electrode. Most interesting scientific aspects of DSSC are, (1) almost all of these charge transfer processes can be directly measured and (2) the rates of these processes can vary depending upon the dye, photoanode, and hole conducting medium chosen [144].

The charge transfer processes and recombination reactions play crucial role in the determination of internal quantum efficiency and the open circuit potential of dye solar cell. There are two most important processes in efficient DSSC; electron injection ($k_{inj}$) by dye molecule to semiconductor and regeneration of oxidized dye ($k_{reg}$) by electrolyte components. Following Figure 1.2 shows the various charge transfer processes in the DSSC. Once the sensitized dye molecules absorb a photon, electron excites to a higher energy state from which both radiative as well as non-radiative decay can occur. Electron in semiconductor matrix may recombine with the holes in dye ($k_{rec}$) or with the electrolyte components ($k_{br}$) and these reactions are known as back electron transfer.

![Jablonski plot of the charge transfer processes in DSSC](image)

**Figure 1.2** Jablonski plot of the charge transfer processes in DSSC
Lifetime of the all these processes are depicted in the Table 1.4. The competition between various charge transfer processes are determined by dye, semiconductor, composition of electrolyte and counter electrode and determine the propertied of final device. These processes occur in the finite time domain; following Table 1.4 shows the lifetime for each processes occurring during the working of dye sensitized solar cell. Electron injection and regeneration of the dye are studied using the laser spectroscopy since the life time of these processes are quite low while recombination processes are studied using AC impedance techniques [145,146].

<table>
<thead>
<tr>
<th>Process</th>
<th>Notation</th>
<th>Lifetime</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron Injection</td>
<td>$k_{inj}$</td>
<td>20fs to 500 ps</td>
</tr>
<tr>
<td>Hole regeneration</td>
<td>$k_{reg}$</td>
<td>1-10 µs</td>
</tr>
<tr>
<td>Electron recombination by dye</td>
<td>$k_{rec}$</td>
<td>200 µs to 8 ms</td>
</tr>
<tr>
<td>Electron recombination by electrolyte</td>
<td>$k_{br}$</td>
<td>1 ms to 1s</td>
</tr>
</tbody>
</table>

fs: femtosecond; ps: picosecond; µs: microsecond; ms: millisecond

1.6 p-type Dye Sensitized Solar Cell

1.6.1 What is p-type DSSC..??

TiO$_2$ is an $n$-type semiconducting material and the DSSC fabricated using this material is known as the $n$-type dye solar cell. But if we replace $n$-type material by $p$-type in DSSC the functioning of the device is reversed and known as the $p$-type dye sensitized solar cell. It is customary to note that the electron flow in the $p$-type DSSC is reversed in which dye is an acceptor one as compared to $n$-type DSSC in which dye donates electron to semiconductor. The molecular design of sensitizer is also reversed in case of $p$-type DSSC in which pendant groups are electron acceptor which pulls the electron density from semiconducting material upon excitation by light. NiO is widely
studied as the semiconductor in the \( p \)-type dye solar cell; following schematic represents the functioning of the same [147]. **Scheme 1.2** shows that sensitizer excites upon absorption of quanta and accept an electron from the NiO while excited electron is transferred to electrolyte which is again catalytically given to the Pt counter electrode and sent to external circuit.

![Diagram of NiO based \( p \)-type DSSC](image)

**Scheme 1.2** Schematic representation of NiO based \( p \)-type DSSC

Electron from the external circuit reached to the working electrode and reached back to NiO. It can be seen from this mechanism that the direction of the electron flow is reversed as compared to \( n \)-type DSSC. Renaud et al. have shown that the CuGaO\(_2\) is a promising new alternative for the NiO in the \( p \)-type DSSC by achieving enhanced photovoltage [148]. Morandeira et al. reported the charge transfer dynamics of coumarin 343-sensitized NiO and showed that hole injection from the dye to the VB is ultrafast and occurred in around 200 fs [149].
1.6.2 Design of dye for p-type DSSC

The dye is a crucial component for the p-type DSSC since it deviates from the normal design. Following schematic diagram (Scheme 1.3) shows the design of the organic sensitizer for p-type DSSC and shows the direction for the electron flow.

![Scheme 1.3 Schematic representation of dye for p-type DSSC](image)

In this design electron flow occurs from acceptor to donor hence the pendant groups in this case will be donor moieties. As the molecule will excite, electron density will be moved toward the pendant groups while vacancy at the acceptor side will be fulfilled by semiconductor.

1.7 Plasmonic Dye Sensitized Solar Cell

1.7.1 Plasmonics

Plasmonic is in general sense defined as the *optics at nanoscale* which utilizes the nanoscale properties of metallic particles. In the miniaturization of photonics circuits, it is now realized that metallic structures can confer unique ways to manipulating light at length scales smaller than the wavelength [150]. This is a promising new approach...
to enhance the light trapping in the photovoltaic devices thereby leading to enhanced performance. Metallic nanoparticles support surface plasmons that are the collective oscillation of excited free electrons and characterized by a resonant frequency [151]. They can be either localized as for metal nanoparticles or propagating as in the case of planar metal surfaces [152]. The surface plasmon resonance is affected by the size, shape and the dielectric properties of the surrounding medium. Silver and gold have dominated experimental research in this area although other metals also support surface plasmons. Three different mechanisms that could be utilized for photovoltaic applications are (a) the scattering from the metal particles that also act as dipoles (far-field effect), (b) the near field enhancement and (c) direct generation of charge carriers in the semiconductor substrate. Most reported photocurrent enhancement results for inorganic devices are explained by the first mechanism of scattering and for organic devices by near field enhancement.

When excited, surface plasmon excitation can result in scattering and giant enhancement of the electric field. Metal particles in the order of wavelength of light act as miniature dipoles scattering the incident radiation, which is coupled to the modes of the underlying semiconductor. Metals show this behavior because of the presence of free charge carriers. Highly doped semiconductors and metal oxides can also show plasmon effects but because of the lower number of free charge carriers; their resonance is mostly in the infrared. For small particles in the quasi-static limit, the scattering and absorption cross-sections are given by following equation 1.1 and 1.2 respectively [153].

\[ C_{Abs} = \frac{2\pi}{\lambda} \text{Im}[\alpha] \]  
(1.1)

\[ C_{Scat} = \frac{1}{6\pi} \left( \frac{2\pi}{\lambda} \right)^4 |\alpha|^2 \]  
(1.2)
Where $\alpha$ is the polarizability of the particle for a small spherical particle in vacuum, given by,

$$\alpha = 3V \left[ \frac{\varepsilon - 1}{\varepsilon + 2} \right]$$

(1.3)

Where $V$ is the volume of the particle, $\varepsilon$ the permittivity of the metal and $\varepsilon_m$ the permittivity of the surrounding medium. The scattering efficiency $Q_{sca}$ is given by $Q_{sca} = C_{sca}/(C_{sca}+C_{abs})$. For frequencies near their resonance, these nanoparticles can have a scattering or absorption cross-section much larger than their geometric cross-section [154]. For example the scattering cross-section of a 100nm silver nanoparticle can be ten times more than the geometric cross-section at the Plasmon frequency. The relative importance of absorption and scattering is size dependant. Therefore for photovoltaic applications the size of the particles needs to be optimized to ensure maximum scattering. Scattering for particles around 100 nm is more relevant to solar cell applications. However the particle sizes cannot be too large as this leads to multipole oscillations which tend to decrease the scattering efficiency of the nanoparticles.

### 1.7.2 Plasmonics in DSSC

Generally Ag and Au nanostructures are used in order to enhance light trapping in the TiO$_2$ photoelectrode by Plasmon resonance of metallic nanoparticles. The Plasmonic nanoparticles are directly incorporated into the TiO$_2$ matrix in form of thin film or particles in order to enhance the light absorption. This approach was a bit specious since the metallic particle can corrode the electrolyte or may lead to charge recombination. In order to overcome this problem, community has moved toward the core-shell nanostructure made up of metal@insulator and metal@semiconductor. In this case, nanoparticles are surrounded by a shell of insulating material like SiO$_2$ or
semiconductor material like TiO$_2$ in order to passivate the chemistry of nanoparticles by electrolyte components. The thickness of outer shell is generally controlled in the range of few nanometers. The core shell nanoparticles are directly incorporated into the TiO$_2$ paste and a thin film is made therefrom. The Plasmonic can confer the efficient solar to electricity conversion efficiency even at thin film photovoltaic.

Brown et al. have reported a successful strategy for incorporating metal nanoparticles with strong surface plasmon resonance into DSSC that overcomes four main issues of introducing metal into the bulk of a solar cell: charge recombination within the metal, thermal stability during processing, chemical stability, and control of metal nanoparticles dye chromophore separation to inhibit non-radiative quenching [155]. Using optical spectroscopy, they have identified that for this system, plasmon-enhanced photogeneration of charge carriers can only occur when the electron transfer from the photoexcited dye to the TiO$_2$ is faster than around 10 fs. They have shown that the performance of Plasmonic DSSC is almost twice than that of normal device with enhancement in photocurrent as well as slight enhancement in photovoltage. Qi et al. have shown the synthesis of Ag@TiO$_2$ core shell nanoparticles for DSSC application and have shown that a small amount of Ag@TiO$_2$ nanoparticles (0.1 wt%) can enhance the performance of DSSC from 7.8% to 9.0% while decreasing the photoanode thickness by 25%. In addition, they have showed that the incorporation of Plasmonic components into DSSC would require 62% less material than normal device [156]. TiO$_2$-Au based nanocomposite photoelectrode has also been examined in DSSC by attaining almost 25% enhancement in overall performance of photon to electricity conversion efficiency [157]. Naphade et al. have shown the perfect utilization of scattering effect and near field plasmonic effect by using Au nanoparticles loaded with TiO$_2$ nanofibres. They have achieved more than 25%
enhancement in the performance using Au loaded TiO$_2$ nanofibre based electrode [158]. Sheehan et al. have synthesized core-shell-shell type nanostructure consisting of Au nanoparticles surrounded by SiO$_2$ and TiO$_2$ shell. They have shown the efficiency enhancement from 2.8% to 5.5% using this type of nanostructure [159]. Chen and co-workers have reported Ag$_2$S encapsulated gold nanorods as Plasmonic material in dye solar cell [160]. They have precluded that the longitudinal Plasmon resonance in rod like geometry would help to enhance the absorption in longer wavelength. They have shown more than 37% absorption enhancement in the range of 600-720 nm by achieving 7.1% performance at 11µm thick film. Lin and coworkers have designed two types of photoelectrode i.e. FTO/TiO$_2$/Ag NP’s and FTO/Ag NP’s/TiO$_2$ for the dye solar cell application. They have showed remarkable enhancement in performance using FTO/TiO$_2$/Ag NP’s architecture in which Ag was deposited onto the top of the photoelectrode using sputtering technique [161].

1.8. FRET based Dye Sensitized Solar Cell

FRET stands for Foster type Resonance Energy Transfer which is a non-radiative energy transfer from a molecule to another one. Förster resonant energy transfer involves dipole-dipole coupling of two chromophores known as the donor and acceptor through an electric field. The FRET radius ($R_0$), the distance at which Förster energy transfer is 50% probable between individual chromophores, is the primary figure of merit used to evaluate the strength of resonant energy transfer from donor to acceptor dye. The rate of Förster resonant energy transfer ($k_{FRET}$), is a function of the separation distance between the donor molecule to nearby acceptor molecules. The rate of Förster energy transfer between isolated chromophores, known as point-to-point transfer, is given by $k_{FRET} = k_0 \frac{(R_0)^6}{r^6}$, where $r$ is the separation distance and $k_0$
is the natural fluorescence decay rate. When multiple acceptor molecules are present, the FRET rate is equal to the sum of the transfer rates to each of the acceptors [162]. This technology has been pioneered by McGehee group at Stanford University [163-165]

DSSCs have morphology that is uniquely suited for the energy transfer because mesostructured titania films have relatively small pore sizes ranging from 5 nm to 45 nm diameter and sensitizing dyes packed tightly on titania effectively acting as 2D array on the surface. It is possible for highly luminescent donor chromophores inside the liquid electrolyte to absorb high energy photon and efficiently transfer the energy to sensitizing acceptor dye, increasing the absorption bandwidth of DSSC. In typical DSSC, light is absorbed by sensitizing dyes and transfer electrons to the TiO₂ and hole to the electrolyte. In FRET based DSSC, the unattached energy relay dye (ERD) is excited by high energy photons that undergoes foster type resonance energy transfer to sensitizing dye molecules. This design is analogous to photosynthesis in purple bacteria where an aggregate of light-harvesting pigments transfer their energy to the reaction center initiating charge separation [166].

1.9 Perovskite and quantum dot sensitized solar cells

There are certain miscellaneous sensitizers which were utilized in DSSC and performed well. Researchers have used quantum dots, metal halide perovskites, natural dye extracts etc. as sensitizers in dye solar cell. Inorganic semiconductor quantum dots like CdS, CdSe etc were utilized owing to their excellent properties such as tunable energy band gaps via varied and controlled size as well as shape of nanocrystals, large optical absorption coefficient, and large dipole moment for charge separation [167-169]. Moreover, quantum dots have unique characteristics to generate
multiple exciton from a single photon with energy higher than its band gap thereby opening up possibility of exceeding the schottky-quassier limit [170]. While Pb based metal halide perovskite like CH$_3$NH$_4$PbI$_3$ and CH$_3$NH$_4$PbBr$_3$ [171] were tested as sensitizers in DSSC with liquid electrolyte by Miyasaka and coworkers in 2009. They have achieved remarkable light harvesting properties of these materials in DSSC with adorable open circuit voltage. Major breakthrough in the perovskite sensitized solar cell was achieved by Gratzel and Park in 2012 [172]. They have shown 9.7% photo to electricity conversion efficiencies using submicron thick TiO$_2$ film sensitized with CH$_3$NH$_3$PbI$_3$. In 2013, the performance of TiO$_2$ based solar cell with lead halide perovskite was optimized further to attain an overall power conversion efficiency ~15% setting up a new milestone in this technology [11]. The interfaces of the particles play a vital role in the case of quantum dot based DSSC since the maximum recombination sites are available on the interface leading to poor charge collection.

1.10 Objectives of Thesis

Looking to above mentioned literature review, we have planned our study according to the short falls in this technology. It has been now clear that there are many issues related with DSSC which are needed to be solved before going to commercialization. We have identified three major issues in dye solar cell hampering its development to commercial level i.e. rare metal based dye molecules, liquid electrolyte and loss of light through photoelectrode. Our study focuses on the development of new strategies in order to answer these major issues in DSSC. This thesis would discuss about the purely organic dye based sensitizer for DSSC, polymer gel based redox electrolyte, Plasmonic DSSC and Synthesis and application of TiO$_2$ nanoparticles by sol-gel route. Chapter 2A deals with the design and synthesis of various potential dye
molecules for the sensitizing application in DSSC. This chapter also incorporates the characterizations of these dye molecules using NMR, IR, Mass spectroscopy, Cyclic voltammetry and UV-Vis spectroscopy. Chapter 2B demonstrates the fabrication and characterization of DSSC using these organic dyes as sensitizers. Chapter 3 discusses the synthesis of TiO₂ nanoparticles using sol-gel methods and their application as semiconductor in dye solar cell. Chapter 4 deals with the fabrication of plasmonic photoelectrode by incorporating Ag nanoparticles in it. It also elaborates the synthesis of appropriate molecular organic sensitizer in order to harness light efficiently. Chapter 5 gives the preparation of polymer gel electrolytes and their application to dye solar cell. Chapter 6 gives experimental brief about the series and parallel connections of dye solar cells along with cost estimation and market survey of the DSSC. While chapter 7 gives the concluding remark of the whole study.
1.11 References


Introduction


Chapter 1


Chapter 1

2015

Introduction


Chapter 1 | 2015

Introduction


Introduction


