Chapter -1

Introduction
1.1 Introduction to solar cells

The current world energy requirement is estimated to be ~13 terawatts (TW), which is expected to increase up to 25 TW by 2050[1]. So far the fossil fuels have been the major sources of energy. However, the reserves of fossil fuels are depleting. In addition, excessive use of fossil fuels have led to enhanced CO₂ level in the atmosphere that is responsible for the global warming. These issues have made researchers to exploit alternative sources of energy that are environmental friendly. Renewable energy (wind, solar, hydro, bio, etc.) which neither run out nor have any significant harmful effects on the environment has been one of the frontier alternative energy sources. Among various renewable energy sources, solar power has several advantages over other renewable resources. For example, wind, geothermal and hydroelectric power systems are limited to specific geographic regions and have limited potential, whereas solar power can be collected at almost any location on the earth surface and can easily meet world energy requirement.

1.1.1 Solar energy spectrum

Sunlight is an abundant energy resource freely available to everyone as the amount of solar energy reaching the surface of the earth is 1.7 x 10⁵ TW and a practical terrestrial global solar potential value is estimated to be about 600 TW. The spectrum of the solar light that reaches the earth is influenced by absorption of radiation in the earth’s atmosphere and therefore by the path length of the photons through the atmosphere. Fig. 1.1 shows the spectrum of solar radiation, which is close to that of a black body at
temperature of about 5800K. The AM0 spectrum corresponds to solar irradiance just outside atmosphere (1353 W/m²), whereas AM1.5G spectrum corresponds to an angle between the incident solar radiation and the zenith point of the measurements of 42° (1000 W/m²)[2]. The decrease in irradiance from 1353 W/m² to 1000 W/m² (or the dips in AM 1.5G spectrum) arise from atmospheric absorption by H₂O, O₃, and CO₂ gases (as shown in Fig. 1.1). Harvesting the energy directly from the sunlight using even low efficiency photovoltaic (PV) technology could supply the demand for huge energy consumptions.

![Figure 1.1: Solar irradiance at Sun, AM 0, and AM1.5G illumination.](image-url)
1.1.2 Basics of solar cells

Solar cells are semiconductor devices that convert sunlight into direct current electricity. Si-solar cells typically comprise of a thin wafer consisting of an ultra-thin layer of phosphorus-doped (n-type) silicon on top of a thicker layer of boron-doped (p-type) silicon. An electrical field is created near the top surface of the cell where these two materials are in contact, called the p-n junction. The p side contains holes as majority charge carriers, while n side contains electrons as majority charge carriers. In the region near the junction an electric field is formed. The electrons and holes, which are generated through light absorption in the bulk of Si, diffuse to this junction, where they are directed by the electric field towards the respective electrodes (as shown in Fig. 1.2). The amount of current or power generated from a solar cell along with some other characteristics are presented in next sections.

![Figure 1.2: A schematic depiction of p-n junction Si solar cell.](image-url)
1.1.3 Characteristics of solar cells

The most basic parameters of solar cells are the power conversion efficiency (PCE) usually measured under simulated AM1.5 G (1 Sun) standard conditions, and the spectral dependent external quantum efficiency (EQE), which is also called as incident photon to current collected efficiency (IPCE).

(a) I-V Characterization

The current density-voltage measurements of solar cells are usually performed under 1 sun AM 1.5G illumination of intensity 100 mW/cm². A typical I-V curve is shown in Fig. 1.3, from which following parameters are determined.

*Short-circuit current (I_{sc})*: The short-circuit current is the cell photocurrent measured at zero voltage. In general, it is presented in the form of the short circuit current density (J_{sc}) defined as the ratio of the short circuit photocurrent to the active cell area.

*Open-circuit voltage (V_{oc})*: The open-circuit voltage (V_{oc}) is the cell voltage measured when current within the cell is equal to zero. Maximum open circuit voltage is limited to difference in Fermi levels on p and n sides and may only be obtained at very high incident radiation intensity.

*Fill Factor (FF)*: The fill factor (FF) is defined as the ratio of the maximum power output (P_{max}) to the product of short circuit photocurrent and open circuit voltage, which is defined as:

\[
FF = \frac{P_{max}}{I_{sc}V_{oc}} = \frac{I_{max}V_{max}}{I_{sc}V_{oc}} \quad (1.1)
\]
where $I_{max}$ and $V_{max}$ represent the current and voltage corresponding to the maximal power point, respectively.

**Figure 1.3:** (a) Typical $J$-$V$ characteristics of solar cells under dark and 1Sun illumination, (b) Another way of representing the $J$-$V$ data, which is obtained after changing the sign of the photocurrent. This usually done as power generated by the device is positive.

*Power conversion efficiency:* The energy conversion efficiency is defined as the ratio of $P_{max}$ to the incident radiation power ($P_{in}$) illuminated on the solar cell surface.

$$\eta = \frac{P_{max}}{P_{in}} = \frac{J_{sc} \cdot V_{oc} \cdot FF}{P_{in}}$$  \hspace{1cm} (1.2)

As $\eta$ is a function of $I_{sc}$, $V_{oc}$ and $FF$, improvement of the solar cell performance is achieved by optimization of all the three parameters. $\eta$ is also dependent on the incident irradiation power $P_{in}$, a white light intensity of 5, 20 mW/cm$^2$ was used in some of solar cell measurements.
(b) Incident photon to current conversion efficiency

The IPCE is measured by illuminating the solar cell with monochromatic light with the power $P_{in}$ and recording the short circuit current $I_{sc}$ at different wavelengths $\lambda$. Thus, the IPCE can be calculated as follows:

$$IPCE \, (\%) = \frac{\text{number of collected electrons}}{\text{number of incident photons}} \times 100 = \frac{1240 \, \text{nm} \times f_{sc}}{\lambda \, \text{nm} \times P_{in} \times 100}$$

**Figure 1.4:** Equivalent circuit diagram of a solar cell. The blue shaded region represents the inside of the solar cell.

In order to understand the current voltage characteristics of a solar cell, the equivalent circuit diagram (ECD) of a solar cell can be drawn as shown in Fig. 1.4. From this, the external current is given as

$$I = I_{ph} - I_d - I_{sh} \quad (1.3)$$

Where diode current ($I_d$) and shunt current ($I_{sh}$) are written respectively as

$$I_d = I_0 \left\{ \exp \left( q \frac{V + IR_s}{nkT} \right) - 1 \right\} \quad (1.4)$$
\[ I_{sh} = \frac{V + IR_s}{R_{sh}} \]  

(1.5)

Therefore the circuit equation is rewritten in the form of

\[ I = I_{ph} - I_0 \left\{ \exp \left( \frac{q V + IR_s}{nkT} \right) - 1 \right\} - \frac{V + IR_s}{R_{sh}} \]  

(1.6)

Where \( I_{ph} \) is photo current, \( I_0 \) is saturation current, \( R_s \) is series resistance, \( R_{sh} \) is shunt (parallel) resistance, \( n \) ideality factor, \( q \) elementary electric charge, \( k \) Boltzmann constant, \( T \) is an absolute temperature.

In this equation:

i. The first term i.e. \( I_{ph} \) (photocurrent) is generated by the device upon illumination. This current results from the generation of excitons and their subsequent dissociation into free charges. The magnitude of the current will depend on the illumination intensity but it is assumed to be independent of the voltage in this model.

ii. The second term is the current due to recombination, which depends upon dark current \( (I_0) \), series resistance \( (R_s) \), and the ideality factor \( (n) \). Ideally the \( R_s \) should be as low as possible. The \( n \) describes how closely the \( J-V \) curve follows the theoretical model, and provides information on the recombination processes. The value of \( n=1 \) implies solar cell is close to an ideal diode. The values of \( n>1 \), indicates recombination from the localized states (traps) [3].

iii. The third term represents the shunt currents, which is governed by shunt resistance \( (R_{sh}) \), and represents losses due to any leakage in the device. Ideally the value of \( R_{sh} \) should be infinity.
With the help of the equivalent circuit diagram and the Eq.1.6, measured $J$-$V$ curves can be fitted to obtain characteristic parameters of the components. Even though this simplified model may not fully represent the physical reality, it helps to detect problems in the device limiting the device efficiency, from which improvements of the device structure can be deduced.

Figure 1.5: Efficiency improvement of various solar cell technologies.

1.2 Evolution of solar cell technology

The evolution of various solar cell technologies along with their efficiencies are summarized in Fig 1.5 (taken from NREL solar cell efficiency charts). It is clearly evident from this figure, many different solar technologies have emerged over a period of time, which can be broadly classified into three generations: (1) First generation solar cells based
on single crystal Si, GaAs, and multi-junctions; (2) Second generation solar cells based on thin films of chalcogenides and amorphous Si; and (3) Third generation solar cells based on organic semiconductors, inorganic quantum dots and hybrid materials.

1.2.1 First generation solar cells

The first crystalline silicon solar cell having an efficiency of 6% was developed at Bell Laboratories during 1950s, and today its efficiency has reached up to 24% [4, 5]. These crystalline Si solar cells currently account for more than 85% of the commercial market. Along with crystalline Si solar cells, technologies based on single-junction GaAs (current efficiency ~34.1%) and multi-junctions (current efficiency ~43%) are developed. Despite of such high efficiencies of these single and multi-junction solar cells, they could not find commercial market owing to high-cost and limitation in large-scale production.

1.2.2 Second generation solar cells

The second generation solar cells are based on thin film technology, where the material cost is believed to be reduced due to less quantity of the material used. In addition, thin film solar cell materials can be deposited onto large surfaces, which is beneficial for volume production (i.e. high throughput). The materials used in thin film solar cells include, amorphous silicon (a-Si), cadmium telluride (CdTe), copper indium gallium diselenide (CIGS) etc.[6-8]. Most of these materials have much higher absorption coefficient than silicon, and therefore, needed effective thickness of the film is < 1µm thick, which is ~300 times less than in single crystal Si solar cells.
Among various thin film solar cell technologies, the CIGS solar cells have reached an efficiency of ~20%. A typical device structure of CIGS solar cells with typical individual layer thicknesses is shown in Fig. 1.6. Soda lime glass or flexible substrates (polyimide or metal foils) coated with molybdenum layer (as back contact and for reflection of unabsorbed light back into the device) are used as substrates. A p-type CIGS absorber layer is then deposited followed by deposition of thin n-type buffer layer (typically CdS). The buffer is overlaid with a thin, intrinsic ZnO layer (i-ZnO) which is capped by a thicker, Al doped ZnO layer (serves as a transparent conducting oxide to collect and move electrons out of the cell while absorbing as little light as possible). The efficiencies of a-Si and CdTe solar cells have reached to 13 and 19.6%, respectively. The major problem with a-Si has been the degradation of efficiency with time. CdTe thin films solar cells may not be suitable for deployment at large scale due to the presence of poisonous cadmium content of the cells.

![Figure 1.6: Schematic view of the typical substrate structure of CIGS solar cells (with typical film thickness).](image-url)
1.2.3 Third generation solar cells

Though the first generation solar cells have demonstrated high efficiencies, they lack large area production and do not have possibility of using flexible surfaces. The second generation solar cells have overcome the limitation of the flexibility of first generation as well as large area production to certain extent. However, their efficiencies are moderately low and the employment of hazardous cadmium material has a bearing on environment. Therefore, the third generation solar cells have emerged which are largely based on organic materials, inorganic nanocrystals and hybrids (shown in Fig. 1.5, Inset box with no. 3).

Briefly, organic solar cells are typically fabricated by employment of organic semiconductors as absorber materials. Small molecule solar cells (introduced by C.W. Tang et.al.[9]) have shown efficiencies upto 12% (Heliatek), whereas polymer solar cells (introduced by Heeger et.al.) have reached efficiencies upto 10% (Toray). These solar cells with tandem structure comprising two or more sub cells (with complementary absorption) show improved efficiencies with their individual counterparts either resulting in increase of currents (connected in parallel) or voltages (connected in series). Dye-sensitized solar cells introduced by Grätzel and O’Regan in 1991[10] have emerged as low-cost solar cells, which have already demonstrated a potential market for portable electronics and Bi-PV. Gratzel’s group holds current world record efficiency of 12.6% with novel porphyrin based dyes and cobalt redox electrolytes [11]. The molecular engineering of dyes, novel catalyst materials and new electrolytes (quasi solid electrolytes) made this technology very near towards commercialization. Quantum dot solar cells employing semiconductor nanocrystals with tunable bandgaps (by changing the quantum dot size) have attained
efficiencies of ~10%. Perovskite solar cells, with organic-inorganic perovskites as absorber materials have shown efficiencies upto 15% [12]. Among the several emerging solar cells, polymer solar cells and dye-sensitized solar cells are of interest for thesis work and are discussed in detail in further sections.

Figure 1.7: Schematic depiction of polymer solar cells with corresponding energy diagram

1.3 Polymer solar cells

Device structure: A polymer solar cell is a solar cell made by sandwiching the photon absorber layer (typically called as photoactive layer) between two different electrodes (as shown in Fig. 1.7). The active layer consists of either a “mixture of conducting polymer (electron donor) and fullerene molecules (electron acceptor)” or “stacked layers of conducting polymer and fullerene”, a corresponding energy diagram is described in Fig.1.7. A 100-150nm thickness of active layer is sufficient to harvest all the incident light illuminated on solar cells. However, charge carriers generated in the active layer are bound
to form an electron-hole pair (termed as exciton), whereas in Si solar cells which leads to formation of free electrons and holes. The detailed working principle of these polymer solar cells are described as follows.

### 1.3.1 Working principles

**Working mechanism:** In a typical polymer solar cell operation, there are the four fundamental physical processes, which are described by schematic depiction (Fig. 1.8) and energetics of materials (Fig. 1.9)[13]:

![Figure 1.8](image-url) (a-d) Schematic depiction of various processes during the operation of polymer solar cells under 1Sun illumination
**Step 1: Light absorption**

When light is absorbed in the donor material (usually a conjugated polymer), strongly bound electron-hole pairs (so called excitons) are created (Fig. 1.8a, Fig. 1.9a).

**Step 2: Exciton diffusion**

The photogenerated excitons are strongly coulomb bound due to the low dielectric constant in organic materials, and the correspondingly low screening length. Thus, electrically neutral excitons can only move by diffusion in order to dissociate into an electron-hole pair at interface of donor-acceptor molecules (as shown in Fig. 1.8b & Fig.1.9b).

**Step 3: Exciton dissociation**

The excitons dissociate only at energetically favorable donor acceptor interfaces when the energy gain is larger than the exciton binding energy. An electron transfer (or charge transfer) takes place, dissociating the exciton into an electron on the fullerene acceptor, and a hole remaining on the polymer (shown in Fig. 1.8c and Fig. 1.9c). After dissociation, this electron-hole pair is still coulombically bounded, which is called geminate pair or polaron pair.

**Step 4: Charge transport**

The polaron pair are dissociated into free electron and hole with built-in electric field provided by two different electrodes. Finally the electrons and holes are transported to the respective electrodes, driven by the electric field. The carriers in respective phases are moved by a hopping transport process, which is a very slow charge transport with low carrier mobility (at least a factor of 1000 smaller) compared to crystalline silicon.
However, there are several loss mechanisms involved during the operation of solar cells (shown in Fig 1.9 e,f). Briefly, the loss mechanisms are an exciton decay, geminate recombination of bound electron-hole pairs, and bimolecular recombination of free charge carriers.

Figure 1.9: (a-f) various process involved in polymer solar cells.
1.3.2 Literature survey and issues

The concept of organic solar cells originates from conventional p-n junction silicon solar cells, where the former employ organic semiconductors and later inorganic semiconductors as the active materials. As schematically depicted in Fig. 1.10, light absorption in “Inorganic semiconductors” leads to free charge carriers owing to their perfectly ordered atomic structures, whereas in “Organic semiconductors” light absorption leads to formation of “Excitons” (coulombically bound electron-hole pair) due to high exciton binding energy in organic materials. Typically, Frenkel Excitons having binding energy ~ 0.1 - 0.4 eV, binding radius ~ 10 Å are observed in organic semiconductors. These localized neutral excitons which are bound to specific atoms or molecules move by hopping from one atom to another. Organic semiconductors can be widely classified into two groups on the basis of their molecular weight, conjugated polycyclic compounds of molecular weight less than 1000, and heterocyclic polymers with molecular weight greater than 1000. Solar cells fabricated with small molecules as active materials are termed as “Small molecule solar cells”, whereas solar cells employing high molecular weight conducting polymers as active materials are called as “Polymer solar cells”. Among this, polymer solar cells have attracted a great interest in research and industrial community due to their potential advantages over conventional Si solar cells, such as, low cost, light weight, flexibility, ease of fabrication, high throughput etc.[14-18].
The field of polymer solar cells (often called as polymer-fullerene solar cells) has taken a huge splurge with the discovery of conducting polymers [14]. Conducting polymers are highly conjugated polymers, having backbones of continuous $sp^2$ hybridized carbon centers which have a large overlap between $p_z$ orbitals providing large delocalized states. As described in above section, polymer solar cells employ conducting polymers as electron donor materials and fullerenes as electron acceptor materials. Since its inception, the power conversion efficiency of polymer solar cells has improved rapidly from below 1% to over 9%. This impressive achievement is mainly achieved by molecular engineering (synthesis) of novel low-bandgap polymers, introduction of various transport layers (hole & electron transport), tuning of active layer morphologies, employment of various device structures etc.[19]. In this regard, various conducting polymers were evolved, (i) firstly, poly(phenylene vinylene)s (PPV), poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-
phenylenevinylene) (MEH-PPV) and poly(2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene) (MDMO-PPV) were introduced. Power conversion efficiencies up to 3% were achieved by employing PPV based polymers as donors and Phenyl-C$_{61}$-butyric acid methyl ester (PC$_{61}$BM) as acceptors materials [20, 21]. (ii) Secondly, smaller-bandgap polymers (thiophenes) were investigated. Regioregular poly(3-hexylthiophene) (rr-P3HT) with PCBM as acceptor material demonstrated PCE up to 5% [22, 23]. (iii) Lately, polycarbazole based polymers and some patented absorber materials have demonstrated world record efficiencies over 9%. Although, many investigations were made during this period, no suitable materials were found to replace highly efficient fullerene derivatives (PC$_{61}$BM, PC$_{71}$BM, ICMA, ICBA) as acceptor materials in polymer solar cells. Some of the photovoltaic properties with various conducting polymers are presented from the literature in Table 1.1.

**Table 1.1**: Photovoltaic parameters of BHJ with different conducting polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Optical Bandgap (eV)</th>
<th>Acceptor</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDMO-PPV</td>
<td>2.3</td>
<td>[60]PCBM</td>
<td>5.25</td>
<td>0.82</td>
<td>0.61</td>
<td>2.5</td>
<td>[20]</td>
</tr>
<tr>
<td>P3HT</td>
<td>1.9</td>
<td>[60]PCBM</td>
<td>12</td>
<td>0.57</td>
<td>0.67</td>
<td>4.6</td>
<td>[24]</td>
</tr>
<tr>
<td>PFDTBT</td>
<td>1.9</td>
<td>[60]PCBM</td>
<td>4.66</td>
<td>1.04</td>
<td>0.46</td>
<td>2.2</td>
<td>[25]</td>
</tr>
<tr>
<td>PCDTBT</td>
<td>1.9</td>
<td>[70]PCBM</td>
<td>10.6</td>
<td>0.88</td>
<td>0.66</td>
<td>6.1</td>
<td>[26]</td>
</tr>
<tr>
<td>PCPDTBT</td>
<td>1.4</td>
<td>[70]PCBM</td>
<td>16.2</td>
<td>0.62</td>
<td>0.55</td>
<td>5.5</td>
<td>[27]</td>
</tr>
<tr>
<td>C-PCPDTBT</td>
<td>1.3</td>
<td>[70]PCBM</td>
<td>15.5</td>
<td>0.37</td>
<td>0.48</td>
<td>2.7</td>
<td>[28]</td>
</tr>
<tr>
<td>PBnDT-DTffBT</td>
<td>1.7</td>
<td>[60]PCBM</td>
<td>12.91</td>
<td>0.91</td>
<td>0.61</td>
<td>7.2</td>
<td>[29]</td>
</tr>
</tbody>
</table>
In the initial stages of research, the polymer solar cells were fabricated by sandwiching a thin film of conducting polymer (called homojunctions) between two different metal electrodes [19]. Since, the excitons generated in this homojunctions are so strongly bound, the field in a photovoltaic device, which arises from the work function difference between the electrodes, is much too weak to dissociate the excitons. Later, Tang et. al. [9] used two different materials (called donor and acceptor materials), which are stacked in layers, to efficiently dissociate the photogenerated excitons. This donor and acceptor materials are selected by carefully matching their energy levels, to prompt electron transfer from the donor to the acceptor (or hole transfer from the acceptor to the
donor)[19]. Since then, the various device structures evolved (as shown in Fig 1.11) in polymer solar cells are presented as follows.

(a) **Bilayer solar cells:** In bilayer heterojunction solar cells, donor and acceptor layers are sequentially stacked on top of each other (Fig. 1.11a) [30, 31]. In this devices, only excitons created within the distance of 10-20 nm (known as exciton diffusion length) from the interface can reach the heterojunction interface. Hence, the thickness of the individual films chosen typically ~20-30 nm. The thin films doesn’t absorb all the incident radiation, while the thicker films results in recombination of charge carriers generated away from the donor-acceptor interface. Thus the efficiency of bilayer solar cells are mostly limited by the thickness of the active materials.

(b) **Bulk-heterojunction solar cells:** The concept of bulk-heterojunction (BHJ) solar cells was introduced to overcome the limitations presented in the bilayer solar cells. In this solar cells, an active layer comprising a blend of both donor and acceptor materials, is sandwiched between two electrodes [32-34]. Unlike in bilayer solar cells, the interface is not planar but spatially distributed over the entire volume of the active layer. This results in a formation of three dimensional interpenetrating network with increased interfacial area between phase-separated donor and acceptor materials. As listed in Table 1.1., among the many conducting polymers employed in polymer solar cells, till date, the most successful BHJ polymer solar cells are based on P3HT and PCBM materials[35]. The efficiencies of this system is dependent mainly on film morphologies to provide high interfacial area between P3HT and PCBM phases and charge transport properties[13]. However, achieving
such morphology is difficult in reality as the structure and morphology depends upon interplay between various complex thermodynamic and kinetic factors [36]. Experimentally, the efficiencies of bulk heterojunction P3HT:PCBM based solar cells have been reported in the range of 2–5%[1], whereas the theoretically predicted value is as high as 8% [37, 38]. Thus there is a great experimental interest in the investigation of the structural and morphological evolution of P3HT:PCBM films so that the solar cells fabricated using them has high efficiencies. In order to control the structure and morphology of P3HT:PCBM films different approaches such as thermal annealing [39, 40], solvent annealing [41], electrical field annealing [42] and nano-patterning [43] have been employed. Among these, thermal annealing is widely employed owing to its simplicity and effectiveness in controlling the morphology via de-mixing of PCBM and stacking of P3HT in coplanar conjugated segments. Experimental results show that the highest efficiency is obtained when the active layer is annealed at a temperature in the range of 120-150°C [13, 44]. As of now it is not fully understood that how annealing processes affects the ordering of molecules, morphology and domain size of each component in the P3HT:PCBM films.

(c) **Hybrid solar cells:** To increase the interfacial area further between donor and acceptor phases, inorganic semiconductor nanoparticles were introduced as acceptor materials forming hybrid solar cells (Fig. 1.11 c). Although, efficiencies upto 5% were achieved, this technology still has poor control of morphologies with increased aggregates of nanoparticles[45].
(d) **Ideal solar cells:** Ideal solar cells are derived from ordered BHJ concept, where photogenerated excitons are within the exciton diffusion length of each phases. Also, this structure provides donor-acceptor phases a continuous straight pathways to the respective electrodes, to reduce carrier recombination and increase charge collection efficiency. Efforts were made to fabricate this ideal device structure by nano-patterning of conducting polymers [43]. Although, the efficiency of this solar cells are low, the ideal device architecture is among the most promising approach to obtain high efficiency in polymer solar cells.

(e) **Novel device architecture:** As ideal device structures with individual widths within exciton diffusion lengths are difficult to make, a new device architecture which are conceptually in between the bilayer and bulk-heterojunction configurations, so called “diffuse bilayer solar cells” are introduced. This device structure has the advantages of both device configurations, i.e., an increased donor-acceptor interface and spatially uninterrupted pathway for the opposite charge carriers to their respective electrodes. This device configuration has been achieved earlier in several ways. (i) Laminating two polymer thin films by applying moderate pressure and temperatures[46]. (ii) Spin-coating the second layer from a solvent that partially dissolves the underlying polymer layer[47, 48]. (iii) Annealing a bilayer device just over its melting point to cause inter-diffusion between donor and acceptor phases yielding intermixed interfacial regions [49]. All the above approaches have resulted in diffuse interface which improves their performance.

Briefly, from the above literature survey, the specific issues which limit the performance of polymer solar cells are as follows:
(1) Charge dissociation, extraction and collection.

(2) Low interfacial area between donor and acceptor phases etc.

(3) Low efficiencies and limited device architectures

All these issues play a vital role in determining the performances of polymer solar cells, and therefore, their roles need to be investigated in detail.

1.4 Dye-sensitized Solar Cells (DSSCs)

Dye-sensitized solar cells, also known as Grätzel cells, were invented by Grätzel and O’Regan at École Polytechnique Fédérale de Lausanne (EPFL) in 1991 [10]. The concept/mechanism for dye-sensitized solar cells was originated from nature’s photosynthesis principle. In photosynthesis, plant leaves are tiny factories in which sunlight absorbed by chlorophyll converts carbon dioxide gas and water into carbohydrates (glucose) and oxygen, thus providing for the energy requirements of the plant. Dye-sensitized solar cells (artificial photosynthesis) are based on the concept of a dye analogous to chlorophyll absorbing light and thus generating electrons which enter the conduction band of a high surface area semiconductor film and further move through an external circuit, thus converting light into "green" power (a schematic of DSSC is shown in Fig. 1.12).

A typical DSSC contains a fluorine-doped tin oxide (SnO₂:F, FTO) covered glass as transparent conducting substrate, a thin wide-bandgap oxide semiconductor, such as ZnO or TiO₂ film coated on FTO, a monolayer of dye attached to the surface of TiO₂ layer by self-assembly, an electrolyte (liquid-state dye-sensitized solar cell) or hole transport material (HTM) (solid-state dye sensitized solar cell) which fully covers the TiO₂/dye
surface and a counter electrode (such as platinum on glass used for electrolyte contained DSSCs, silver or gold electrode for hole transport materials contained solid-state dye-sensitized solar cells. Although DSSC have achieved excellent device performance, several limitations hinder their large scale applications.

1.4.1 Working principle

The schematic of the interior of a DSSC is shown in Fig. 1.12. Generally it comprises, the mesoporous oxide layer composed of a network of TiO$_2$ nanoparticles that have been sintered together to establish electronic conduction. Typically, the film thickness is say 10 $\mu$m and the nanoparticle size 10-30 nm in diameter. The mesoporous layer is deposited on FTO on a glass or plastic substrate. Attached to the surface of the nanocrystalline film is a monolayer of the charge-transfer dye (say Ruthenium polypyridyl complexes). Photoexcitation of the dye molecules results in the injection of an electron into the conduction band of the TiO$_2$, leaving the dye in its oxidized state. The dye is restored to its ground state by electron transfer from the electrolyte, usually an organic solvent containing the iodide/triiodide redox system. The regeneration of the sensitizer by iodide intercepts the recapture of the conduction band electron by the oxidized dye. The $I_3^-$ ions formed by oxidation of $I^-$ diffuse a short distance ($<50$ $\mu$m) through the electrolyte to the cathode, which is coated with a thin layer of platinum catalyst, where the regenerative cycle is completed by electron transfer to reduce $I_3^-$ to $I^-$. The voltage generated under illumination corresponds to the difference between electrochemical potential of the electron at the two contacts, which generally for DSSC is the difference between the Fermi level of the mesoporous TiO$_2$ layer and the redox potential of the electrolyte.
Figure 1.12: Schematic depiction of a dye-sensitized solar cell.

The basic electron transfer processes in a DSSC, comprising ruthenium based N₃ dye adsorbed on TiO₂ and I/I₃⁻ as redox couple in the electrolyte is shown in Fig. 1.13. Besides the desired pathway of the electron transfer processes (with black arrow 3, 4, 5, and 8) occurring in DSSC, the recombination processes (with red arrow 2, 6, and 7) are indicated. Reaction 2 is direct recombination of the excited dye, which is reflected by the excited state lifetime. Recombination of injected electrons in the TiO₂ with either oxidized dyes or acceptors in the electrolyte are shown in 6 and 7, respectively. In principle, electron transfer to I₃⁻ can occur either at the interface between the nanocrystalline oxide and the electrolyte or at areas of the anode contact (usually a fluorine-doped tin oxide layer
on glass) that are exposed to the electrolyte. In practice, the second route can be suppressed by using a compact blocking layer of oxide deposited on the anode by TiCl$_4$ treatment [50, 51].

**Figure 1.13:** Simple energy level diagram for a DSSC. The basic electron transfer processes are indicated by numbers (1-7). The potentials for a DSSC based on the N$_3$ dye, TiO$_2$, and the I/I$_3^-$ redox couple are shown.
1.4.2 Literature survey and issues

As described earlier, dye-sensitized solar cells compose many individual components that have to be optimized, both individually and then again as a whole device. The key components, affecting the performance of the DSSC are dye coated photoanodes, electrolyte, and counter electrodes. The progress made in each of these key areas with current major issues are discussed as follows.

a) **Photoanode:** Photoanodes typically comprise of dye molecules adsorbed on the surface of wide bandgap metal-oxide semiconductor films, which are deposited on TCO (Transparent conductive oxide) substrates. So far, ITO has been the most commonly employed substrates for photonic and optoelectronic devices. The employment of high temperature annealing conditions limits the usage of ITO as substrates for DSSC, because of poor thermal stability of ITO. Hence, fluorine-doped tin oxide (F:SnO\(_2\), FTO) with superior performance are employed as substrates for both electrodes, which accounts to half of total cost of the solar cell. Many wide bandgap metal-oxide semiconductors (such as TiO\(_2\), ZnO, SnO\(_2\), etc.) have been employed as photoanodes for DSSC. Among them, TiO\(_2\) (in its anatase form) mesoporous films and one dimensional (1D) ZnO nanostructures have turned out to be the most versatile materials delivering better efficiency.

**ZnO as photoanode:** ZnO had an advantage of high electron mobility as compared to that of TiO\(_2\)[52]. Unfortunately, ZnO suffers from several problems as listed below.

(i) The amount of dye loading onto ZnO is generally low, which to certain extent can be increased by prolonged sensitization.

(ii) Prolonged sensitization often leads to the formation of ZnO/dye complexes. This requires designing of new dyes which do not react with ZnO.
(iii) Formation of \( \text{Zn}^{2+}/\text{dye} \) complexes could block the injection of electrons from the dye molecules to the electrodes [53]. In addition, the interface can act as deep traps for the electron transfer resulting in enhanced dark current.

(iv) Desorption of dye into electrolyte takes place as the DSSC works for prolonged period.

**TiO\(_2\) as photoanode:** Although TiO\(_2\) has less electron mobility as compared to ZnO, it has been studied widely owing to its superior dye loading capacity with many organic and inorganic dyes. Although it has been widely been investigated, there are several issues pertaining to the TiO\(_2\) photoanode that remained yet unsolved. Some of these are:

(i) The recombination of photo-electrons from TiO\(_2\) to electrolyte is significant, which causes enhanced dark currents.

(ii) Mesoporous structures of TiO\(_2\) yields poor connectivity of nanoparticles, which leads to low electron mobility.

(iii) Desorption of dye into electrolyte takes place as the DSSC works for prolonged period for some specific dyes.

All the above three issues leads to poor efficiency of TiO\(_2\) photoanode based DSSC’s. In order to improve the power conversion efficiency of DSSCs, following three approaches have been normally employed:

(i) Fabrication of tandem device, i.e., a DSSC made by using different dyes being connected in series [54]

(ii) Use of single panchromatic sensitizers that are capable of absorbing light from visible to IR region [55] and
(iii) Usage of mixture or cocktail of dyes on TiO$_2$ electrode to achieve broad absorption range [56, 57].

While tandem cells require tuning of $J_{sc}$ and $V_{oc}$ along with adjustment of transmittance of the top cell; usage of single panchromatic sensitizers with wide absorption spectrum causes difficulty in injection of electrons from the dye to the TiO$_2$ electrode. This difficulty in single panchromatic sensitizer arises because the lowest unoccupied molecular orbital (LUMO) of the dye is at the same level as the conduction band (CB) of TiO$_2$ whereas a minimum gap of 0.2 eV is necessary to provide the thermodynamic force for efficient electron injection from the dye to TiO$_2$ CB [58]. Sensitization of TiO$_2$ electrode by a cocktail of dyes has been adopted widely for attaining higher levels of efficiency in DSSCs. However, this introduces problems in controlling the dye sensitization process on a TiO$_2$ electrode, as the adsorption kinetics of different dyes on TiO$_2$ electrode could be widely different. In addition, it becomes difficult to inject electrons from a mixture of dyes because of occurrence of unfavorable electron transfer between the dyes themselves, which consequently lowers the cell efficiency. This issue was addressed by either using step-by-step sensitization of TiO$_2$ electrode with dyes under pressurized CO$_2$ environment [59] or by introducing a blocking layer of Al$_2$O$_3$ between two dyes while fabricating the DSSC [60]. All these processes while improving the efficiency of DSSCs, involve an increase in the number of steps for device fabrication, and therefore, tend to be cumbersome at a commercial scale.

b) **Electrolyte:** Electrolytes typically consist of a redox couple and additives dissolved in a liquid solvent. The main function of the electrolyte is the dye regeneration and charge
transport between the TiO\textsubscript{2} photoanode and platinized counter electrodes. The photovoltaic performances of dye-sensitized solar cells mainly depend on the choice of redox couple and on the choice of electrolyte solvent employed. Generally, either organic solvents or ionic liquids have been used as liquid electrolyte solvents in DSSC. A huge number of organic solvents have been employed such as alcohols, ethylene carbonate, tetrahydrofuran, acetonitrile, propionitrile, valeronitrile, methoxyacetonitrile etc. Acetonitrile (ACN) has been the most successfully and efficient organic solvent used in electrolytes due to its low viscosity, good solubility to dissolve organic components and additives. However, owing to its high vapor pressure and liquid electrolyte, leakage and evaporation of solvent has become a critical issue in encapsulation of devices. In this regard, less volatile organic solvents such as 3-methoxypropionitrile (MPN) and butyronitrile got great attention owing to its high boiling point which showed a good stability performance, retaining over 90\% of their initial efficiencies under light soaking at 60°\textdegree C for 1000 hours [61]. However, the common problems of leakage and evaporation are still investigated by employing polymer matrix materials.

c) \textbf{Counter electrode:} The catalytic activity of counter electrodes is the main important step for the efficient reduction of triiodide ions into iodide ions at the surface of the electrode. So far platinum (Pt) coated on FTO glass substrates is the most common catalyst material used for reduction of I\textsubscript{3} to I\textsuperscript{-} ions in redox electrolyte due to its excellent electrochemical activity. In this regard, various methods have been used for the formation of Pt thin layer, such as sputtering, electro-deposition, and electrophoresis, in which sputtering is the most commonly employed method. However, sputtering requires ultra-
high vacuum environment and uses more amount of platinum to produce one flat surface while the amount of Pt necessary to obtain the desired catalytic effect is very small. The usage of platinum as a counter electrode in DSSCs has been limited (However, the commercial viability of platinum as CE has been limited) because of

i. High cost and limited flexibility,

ii. Corrosion of the platinum in presence of small traces of water in the electrolyte,

iii. High temperature processing (> 400°C),

iv. Platinum dissolution in corrosive electrolyte and formation of PtI₄ and H₂PtI₆ [62].

To address these issues, a great deal of research is oriented towards finding an alternative to platinum counter electrodes. In the pursuit, conducting polymers show the promise for enabling the replacement of platinum CEs in DSSC because of their unique properties, including low cost, ease of synthesis, good catalytic activity, and remarkable stability. Many conducting polymers such as, poly(3,4-ethylenedioxythiophene) (PEDOT) [63], poly(3,3-diethyl-3,4-dihydro-2H-thieno-[3,4-b][1,4]dioxepine) (PProDOT-Et₂) [64], polyaniline [65], and polypyrrole [66] were studied as alternative CEs for DSSCs. In most cases, the films of conducting polymers were prepared by spin casting on TCO substrates and annealed at high temperatures in order to improve film adhesion on TCO substrate. However, the conducting polymer films prepared in this manner have limited thickness. Additionally, the poor film adhesion on the substrate requires high temperature processing.

In order to avoid the use of high temperature processing, Xia et. al. [67] deposited conducting polymer films on TCO substrates by vapor phase polymerization in two steps: first an oxidant material was spin casted on TCO substrate and then the substrate was kept in monomer saturated vapor to polymerize the monomer on the substrate. However, the
conducting polymer films formed this way have low surface area owing to the limited thickness of the film. It is reported that conducting polymers based CEs require thicker and porous films for efficient charge transport properties. This issue was addressed by adopting template assisted electrochemical deposition of conducting polymer, which resulted in high surface area films [68]. However, the electrochemical deposition of conducting polymers requires TCO substrates, which adds to the cost of the DSSCs. Since the use of TCO substrate and platinum account for 50% of the total cost of DSSCs [69], a greater need for the development of cost effective (TCO-free and Pt-free) counter electrodes are required.

All these components play a vital role in determining the overall efficiencies of the DSSCs, and therefore, their roles need to be investigated in detail.

Figure 1.14: Various possible recombination processes (indicated with red solid line) occurring in (a) polymer solar cells, and (b) dye-sensitized solar cells.
1.5 Scope of thesis

Polymer solar cells as well as dye sensitized solar cells are promising candidates for the flexible and low-cost photovoltaic devices. In the case of polymer solar cells the efficiency depends on several factors, such as, molar extinction coefficient of donor and acceptor materials, energy gap, energy level alignment between donor-acceptor phases, exciton dissociation, interface between donor and acceptor phases, extraction and collection of carriers and selectivity of hole/electron transport layers etc. For dye sensitized solar cells the major factors that govern the efficiency are molar extinction coefficient of dyes, energy gap, energy level alignment between dye and TiO$_2$ semiconductor, charge injection, charge recombination, electrolyte leakage and evaporation, catalytic activity of counter-electrodes etc. However, in both polymer and dye sensitized solar cells, as shown in Fig. 1.14, recombination is a major factor that strongly influence the efficiency. In case of polymer solar cells, geminate and bimolecular recombinations are predominant, whereas in case of dye-sensitized solar cells recombinations at TiO$_2$-dye (recombination with the oxidized dye), and TiO$_2$-electrolyte (recombination with the oxidized redox mediator) interface are significant. In both devices, presence of disorders at the interfaces causes trapping of charge carries, which enhances the charge recombination. Therefore, in order to enhance the efficiency it is essential to minimize the disorders in the devices, which can be done by optimizing the materials parameters (i.e. morphology, structure, interfaces etc).

Both polymer and dye sensitized solar cells have been investigated because the primary aim of the thesis is to develop low cost and flexible technologies. Among such technologies, polymer and DSSC have been selected due to following similarities between them:
a. Fabrication uses similar contact materials and substrates i.e. Indium tin oxide (ITO) or Fluorine tin oxide (FTO) coated glass substrates.

b. Both type of devices have varying degree of sensitivity to environment and involve similar encapsulation techniques.

c. Conducting polymers are used in both type of solar cells (for example solid state DSSC also use polymer hole transport layers) and we have employed free-standing polypyrrole in DSSC and poly(3-hexylthiophene) and PEDOT:PSS etc. in polymer solar cells.

d. ZnO, TiO$_2$ and other inorganic semiconductor nanomaterials are employed in both type of solar cells: as photoanode in DSSC and electron transport layer in polymer solar cells.

e. Both devices require similar understanding of semiconductor organic molecules and use solution processes for fabrication. Similar techniques as electrochemistry, infrared absorption spectroscopy are used for characterization.

This thesis aims at fabrication of both polymer and dye sensitized solar cells with an emphasis to enhance their efficiency by tailoring the materials properties. We have measured the photovoltaic characteristics of the devices and estimated various device parameters by fitting to an equivalent circuit model. The correlations between materials parameters and device parameters have been established. The specific devices investigated during this thesis work are as follows:
(i) Polymer solar cells namely, bulk-heterojunction P3HT:PCBM, porphyrin/polyfullerene diffuse bilayer solar cells, and porphyrin-modified ZnO-NW/P3HT hybrid solar cells, have been investigated.

(ii) Dye-sensitized solar cells have been fabricated using: (a) different photoanodes e.g. ZnO or TiO$_2$; (b) photoanodes sensitized using single or two dyes; (c) different electrolytes, liquid or gel; and (d) different counter-electrodes, Pt or novel free-standing polypyrrole films.

The experiments and obtained results on above mentioned investigations have been organized into following chapters

In Chapter 2, we describe details of experimental procedure employed for the fabrication of diffuse bilayer solar cells and bulk-heterojunction polymer solar cells; growth of ZnO nanostructures by hydrothermal method; fabrication of dye-sensitized solar cell; synthesis of novel gel polymer electrolyte and free-standing polypyrrole films. The details of various characterization tools studied during the thesis work are presented.

In Chapter 3, results of various studies pertaining to bulk-heterojunction P3HT:PCBM, porphyrin/polyfullerene diffuse bilayer solar cells, and porphyrin-modified ZnO-NW/P3HT hybrid solar cells are discussed. The devices characteristics of P3HT:PCBM BHJ solar cells were found to depend upon annealing temperatures. Therefore, temperature dependent in-situ Raman spectroscopy of P3HT:PCBM films were investigated to gain insight into the structural and morphological changes. Diffuse bilayer solar cells, were fabricated by simultaneous deposition of porphyrin and fullerene films on ITO substrates yielding moderate photo-responses. In hybrid solar cells, the modification
of ZnO-NW surface with porphyrin yields better performance as compared to ZnO-NW/P3HT configuration.

In Chapter 4, the dye-sensitized solar cells were fabricated using different photoanodes, electrolytes and counter-electrodes. Briefly, we show that a proper selection of an organic dye with ZnO photoanodes results in better performances compared to ruthenium counterparts. In addition, the major recombination loss in TiO₂ photoanodes was restricted with an application of co-adsorbent (formic acid), which later used as an anchoring site for a co-sensitization of two dyes resulting in improved efficiencies. A gel polymer electrolyte was synthesized to prevent common leakage and evaporation problem of typical liquid based electrolytes. A novel free-standing polypyrrole films synthesized by interfacial polymerization were applied as substrate-free, TCO-free counter-electrodes for cost effective DSSC.

The summary of the present thesis work and the future scope of work are presented in Chapter 5.