ENGINEERING OF BINARY METAL OXIDE NANOSTRUCTURES FOR HIGHLY EFFICIENT AND STABLE EXCITONIC SOLAR CELLS

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A THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
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NATIONAL UNIVERSITY OF SINGAPORE
2013
DECLARATION

I hereby declare that the thesis is my original work and it has been written by me in its entirety. I have duly acknowledged all the sources of information which have been used in the thesis. This thesis has also not been submitted for any degree in any university previously.

____________________________
Naveen Kumar Elumalai

12 August 2013
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Dedicating this thesis to God’s Lotus feet.
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SUMMARY

Excitonic solar cells (ESCs) such as Dye Sensitized Solar Cells (DSCs) and Organic Solar Cells (OSCs) are promising candidates of third generation photovoltaics owing to their higher performance efficiency, ease of fabrication, and low cost. Immense research has been carried out in these areas for the last two decades, focusing on improving the device performance and stability in order to make it economically viable. Nanostructured binary metal oxide semiconductors (n-MOS) form an inevitable part in ESCs serving as an interfacial buffer layer in OSCs or an electron transporting layer (photoelectrode) in DSCs.

One of the unresolved problems in OSCs despite large investments in this technology, is to unite high efficiency and operational stability. In general selective charge collection at the respective electrodes in OSCs is achieved by using hole- and electron-transporting buffer layers at the collecting electrode – photoactive layer interface. In this thesis, Molybdenum Oxide (MoO₃) and Zinc Oxide (ZnO) is used as hole and electron transporting interfacial layers respectively. This doctoral research identifies that the depth of trap states in the band gaps of these n-MOS which originates as a result of structural disorders, plays a dominant role in determining the efficiency and stability of OSCs. By engineering the buffer layers to have a reduced trap depth, this research work shows the possibilities to combine high efficiency and operational stability in OSCs. Furthermore, ZnO nanowires were planted in the electron buffer layer to enhance charge collection efficiency and charge carrier lifetime. The study is further extended to DSCs, in which an n-MOS,
Tin Oxide (SnO$_2$) serves as a charge separation and electron transport medium (photoelectrode). Optimization of the SnO$_2$ photoelectrode with reduced trap states significantly improved the photovoltaic performance parameters. The DSCs with the optimized SnO$_2$ photoelectrode exhibited record open circuit voltage. The underlying device physics of this SnO$_2$ based DSCs was studied in detail.
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<tr>
<td>Ag</td>
<td>Silver</td>
</tr>
<tr>
<td>Al</td>
<td>Aluminium</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Aluminium Oxide</td>
</tr>
<tr>
<td>BHJ</td>
<td>Bulk Heterojunction</td>
</tr>
<tr>
<td>Ca</td>
<td>Calcium</td>
</tr>
<tr>
<td>CeO₂</td>
<td>Cerium Oxide</td>
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<td>CN-MEH-PPV</td>
<td>(poly-[2-methoxy-5-(2’-ethylhexyloxy)-1,4-(1-cyanovinylene)-phenylene)</td>
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<td>DSCs</td>
<td>Dye Sensitized Solar Cells</td>
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<tr>
<td>EQE</td>
<td>External Quantum Efficiency</td>
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<td>F8TB</td>
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<td>Fe₂O₃</td>
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<td>FF</td>
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<td>Ge</td>
<td>Germanium</td>
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<td>Indium Phosphide</td>
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<tr>
<td>ITO</td>
<td>Indium doped Tin Oxide</td>
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<tr>
<td>Jsc</td>
<td>Short Circuit Current Density</td>
</tr>
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<td>MoO₃</td>
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<td>NREL</td>
<td>National Renewable Energy Laboratory</td>
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<tr>
<td>OECD</td>
<td>Office of Economic Cooperation and Development</td>
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<td>OSCs</td>
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<tr>
<td>P3HT</td>
<td>poly(3-hexylthiophene)</td>
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<td>Silicon</td>
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<tr>
<td>SnO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Tin Oxide</td>
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<tr>
<td>SrTiO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Strontium Titanate</td>
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<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Titanium di-Oxide</td>
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<td>V&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>Vanadium Pentoxide</td>
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<td>Voc</td>
<td>Open Circuit Voltage</td>
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<td>WO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Tungsten Oxide</td>
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<tr>
<td>ZnO</td>
<td>Zinc Oxide</td>
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LIST OF PUBLICATIONS


11. Effect of trap depth and interfacial energy barrier on charge transport in inverted organic solar cells employing nanostructured ZnO as an electron buffer layer. **Naveen K. Elumalai**, C.Vijila, R. Jose, Zhang Jie and
Seeram Ramakrishna. In communication - International Journal of Nanotechnology.

12. Influence on Trap Depth on Charge Transport in Inverted Bulk Heterojunction Solar Cells employing ZnO as electron transport layer. 


Introduction

1.1 Solar energy – the ultimate renewable resource

Growing economies and increasing population will demand more energy in the coming years. Primary supply of sustainable and eco-friendly energy is one of the major challenges of the 21st century. A recent report on 2030 Energy Outlook by BP points that that an additional 1.3 billion people will become new energy consumers by 2030.[1] Exxon’s 2040 Energy Outlook projects 85% increase in global electricity demand during 2010–2040.[2] Developing non-OECD countries alone will experience a 150% surge in electricity demand. However, to have such quanta of energy, current energy growth of 1.6% per year would require at least 35 years; therefore, a crisis is inevitable. This increased energy demand is one part of the story; the other part is depleting natural resources, increased production cost, high environmental concerns such as global warming due to excessive use of fossil fuels. Over 85% of the primary supply in the present-day energy mix is contributed by the fossil fuels; thereby putting the life sustenance in the planet at an increased risk.[3] To point out a consequence of increased energy production cost, many gas wells produce 80–95% less gas after just 3 years contrary to the predictions that their lifetime to be 40 years. Given this rapid decline in natural gas production from newly drilled wells, it would be necessary to drill 7200 wells per year at a cost of 42 billion dollars so that the current level of natural gas production could be sustained.[4] All these concerns point out to turn our attention to clean, sustainable, and zero cost
sources of energy; i.e., the solar energy and its conversion into electrical energy as the most convenient to use in the modern life.

A total of 36,000 TW solar energy strikes the Earth. Assuming an efficiency of 25%, a solar cell farm of area \(\sim 367 \text{ km} \times 367 \text{ km}\) in the Sahara desert would meet the projected energy demand. Just for comparison: this area is only 0.3% of 9.4 million km\(^2\) of the Sahara desert. Therefore, the sun could be a single solution to all our future energy needs.[5, 6] However, the existing solar cell technology put severe limitations to deploy them primarily because solar electricity is \(\sim 3-6\) times more expensive than the energy derived from the fossil fuels.[7] In fact, solar photovoltaic energy is presently the most expensive of all renewable sources.

1.2 Solar cell classification

Solar cells are classified into different schemes based either on the historical evolution or on their principles of operation. The class of solar cells based on a p–n junction is the first of its evolution; and therefore, are typically called first generation solar cells. Semiconductors, either elemental such as Si or Ge or compound such as GaAs or InP, are materials of choice to build p–n junction solar cells. Photoexcited carriers in the p–n junction are separated into mobile carriers by the built-in-electric field, or band bending, at the junction between the p– and the n–type semiconductors. The photovoltage in the p–n junction is the difference in quasi-Fermi levels (i.e. the band bending) of n-type and p–type regions. A typical device consists of a 5 \(\mu\text{m}\) long n–type semiconductor and 300 \(\mu\text{m}\) long p–type ones. i.e., the minority carriers in the p–n junction are expected to travel \(\sim 300 \mu\text{m}\) for efficient charge collection,
which requires rigorous control on their chemical purity. Requirement of such extreme purity of the semiconductors is one of the major cost limiters of the first generation solar cells. The p–n junctions are typically built on single crystalline and polycrystalline platforms. The latter polycrystalline overcomes the cost limitations on chemical purity; however, at the expense of the photovoltaic conversion efficiency (PCE). Whether or not a p–n junction is made from single or poly crystals, inherent limitations between the absorption and electron emission in those crystals put a theoretical limit on the photovoltaic conversion efficiency in p–n junction solar cells, known as a Schokely-Queisser limit.

![Figure 1.1 Best Research-Cell efficiencies, NREL. (source: http://www.nrel.gov/ncpv/)](image-url)
The Schokely-Queisser limit predicts a theoretical upper limit of 34% PCE for p–n junction solar cells for unconcentrated light under standard AM 1.5.

The second generation solar cells are based on the charge separation at an interface either between two conjugated polymers or a fluorophore molecule conjugated with a metal oxide semiconductor. The National Renewable Energy Laboratory (NREL) at Colorado, US categorize them as “emerging solar cells” (Figure 1.1). In the third generation, a semiconducting nanocrystals of size in the quantum confinement region, known as quantum dots, is used as the light harvester. The quantum dot offers possibility of many photoelectrons per single absorbed photon of sufficient energy; and thereby, uplifting the theoretical conversion efficiency over 60%. The third generation solar cells especially Dye-sensitised solar cells (DSCs), Organic and hybrid photovoltaics (OPVs and HPVs) are collectively called ‘excitonic solar cells (ESCs).

In the ESCs, light absorption results in the generation of a transiently localized excited state, known as exciton–usually a Frenkel type is formed. These Frenkel excitons cannot thermally dissociate into free carriers in the material in which it was formed. Excitons are the characteristics of semiconductors analogues to Fermi fluids in metals and are often characterized as a mobile excited state. An exciton can be considered as a quasi-particle with an electron in the conduction band (or lowest unoccupied molecular orbital, LUMO, in the case of molecules and nanoclusters) and a hole in the valence band (or highest occupied molecular orbital, HOMO). When a semiconductor (molecule, crystals, or clusters) is anchored with another material whose
conduction band (LUMO) lies at lower energy, then the exciton dissociates into mobile carriers (or free carriers) at the interface of the materials system (Figure 1.2). This process is the basis of ESCs. Examples of this type of ESCs include organic solar cells (OSCs), dye-sensitized solar cells (DSCs), and quantum dot solar cells. Conjugated polymers and/or organic materials such as PCBM, P3HT etc. are the materials of choice in OSCs. In the DSCs, a wide band gap metal oxide semiconductor, such as TiO₂, is anchored to a dye. In the third generation quantum dot solar cells, quantum dots are used as light harvesters.

![Energy-level diagram for an excitonic solar cell.](image)

Although an inferior energy technology when compared to other renewable energy technology such as wind and hydro-electricity, photovoltaics—the science and technology of solar cells have steadily progressed. Figure 1.1 shows the state-of-the-art performance of various types of solar cells published by NREL. One may note that the p–n junction solar cells made from single crystals have reached a stage of performing in their theoretical conversion
efficiency. On the other hand, performance of “emerging solar cells” in the second and third generation is relatively inferior. Compared to the first generation solar cells, these emerging sol Although an inferior technology ar cells offer ease of fabrication, flexibility, lower cost, and higher performance efficiency1. Although p–n junction solar cells have the advantage of high PCE (>20%) and long lifetime (25 years), ESCs have improved enormously in the past few years demonstrating PCEs as high as 12% and lifetimes of 10 000 h. Next section of this chapter describe the device structure and materials embodied in OSCs and DSCs in detail.

1.3 Organic solar cells

1.3.1 Organic semiconducting materials

Organic and polymeric semiconductors are macro molecular structures consisting of a backbone along which the carbon atoms (or nitrogen, sulfur, oxygen) are sp² hybridized and possess a π-atomic orbital. The π-orbitals are conjugated (overlapped) along the backbone resulting in the formation of delocalized π-molecular orbitals. The π-π* transitions between the bonding and anti-bonding p<sup>z</sup> orbitals provide two energy states for the electrons as shown in Figure 1.3.[8-11] These π-molecular orbitals determines the HOMO and LUMO electronic levels and also the optical and electronic properties of these molecules.

---

1 Performance efficiency is defined as the ratio of energy output from the solar cell to input energy from the sun.
The HOMO and LUMO electronic levels are analogous to valence and conduction bands in inorganic semiconductors. In an organic semiconductor, when an electron is excited from the HOMO to the LUMO, the molecule itself is excited into a higher energy state in contrast to the excitation of free electron from the valence band to the conduction band in inorganic semiconductors. The carrier mobilities in these materials are governed by the overlap of the \( \pi \)-molecular orbitals between the adjacent polymer chains which defines the intensity of the intermolecular electronic couplings. Hence in organic semiconductors, the weakness of the electronic couplings (a function of their intermolecular characteristics) combined with the electron-vibration couplings and disorder effects leads to lower carrier mobilities owing to charge-carrier localization and formation of polarons. Therefore, the carrier transport in these molecular structures relies on polarons hoping from one polymer chain segment to another. As a result, the charge carrier mobilities are characterized by the structural morphology of the polymers, with mobility values ranging from \( 10^{-6} \) to \( 10^{-3} \) cm\(^2\) V\(^{-1}\)s\(^{-1}\) in disordered amorphous films to \( >1 \) cm\(^2\) V\(^{-1}\)s\(^{-1}\) in highly ordered crystalline materials. \cite{12, 13} Some of the

Figure 1.3 Schematic representation of the bonding–antibonding interactions between the HOMO and LUMO levels of an organic semiconductor. Modified / redrawn from [17]
widely used organic semiconductors in OSCs—conjugated polymers and fullerene derivatives are listed in Figure 1.4. These materials are solution processible due to their side-chain solubilization, and the polymers exhibit photo- and electroluminescence.[14, 15]

Figure 1.4 Representatives of conjugated polymers and fullerene derivative used in organic solar cells. Modified / redrawn from [40]

1.4 Device structure of OSCs

1.4.1 Bilayer organic solar cells

The structure of an organic photovoltaic device similar to that reported by Tang in 1986 is shown in Figure 1.5.[16] It consists of a transparent electrode, typically a conducting oxide such as indium-tin oxide (ITO), two organic light-absorbing layers, and a second electrode. The two organic layers are made of different organic semiconductors, one an electron-donor and the other an electron-acceptor. Electron-donor molecules (D) exhibit a low ionization potential (and thus a high-lying HOMO energy), while electron-acceptor
molecules (A) possess a high electron affinity (and thus a low-lying LUMO energy). The electrodes are chosen with appropriate work function such that the holes and electrons are collected efficiently.

A significant drawback for bilayer solar cell is that the short exciton diffusion length of organic materials limits the thickness of the donor and acceptor layers. If the donor or acceptor layer is too thick, the excitons generated far away from the heterojunction may recombine before reaching the heterojunction where the charge separation occurs. Also, the donor and acceptor layers are limited to tens of nanometers which lead to weak absorption. These factors lead to low EQE and impose challenges in the design of bilayer OSCs.[17]

### 1.4.2 Bulk heterojunction solar cells

One of the most important breakthroughs in the field of OSCs is the discovery of the bulk heterojunction solar cells (BHJ) in the 1990s.[18] The BHJ structure is shown in Figure 1.6 in which the heterojunction is formed by...
intermixing of donor and acceptor materials in a solution and then depositing them onto the substrate. The resulting blend film is an interpenetrating nanoscale network of donor and acceptor materials. The phase separation within the film is commonly 10–20 nm, which is within the exciton diffusion length of many organic semiconductors. Consequently, nearly unity internal quantum efficiency has been achieved for BHJ solar cell denoting that nearly all photogenerated excitons are dissociated.[19] Carriers are then transported through percolating pathways within the active layer toward the respective contacts for collection. Focussing on the active layer blend in BHJs, a thicker active layer could be fabricated in these cells due to the small nanoscale phase separation within them. The efficiency of solar cells is strongly dependent on the morphology of the BHJ and various methods such as thermal annealing [20], solvent annealing [21], and modifying polymer functional groups have been studied to optimize the performance of OSCs.[22]

Figure 1.6 Schematic representation of the bulk heterojunction solar cells (left) and blend morphology with interpenetration network of the donor and acceptor (right). Modified / redrawn from [32]
Amongst various active layer materials, P3HT:PCBM BHJ is the well-optimized and most commonly used active layer in OSCs. In 2002, using these blend materials, Schilinsky et al. demonstrated a short-circuit current density of 8.7 mA/cm² with an efficiency of 2.8%, which was the highest current at that time.[23] Within a year, the efficiency of P3HT:PCBM solar cells were pushed up to 3.5 % efficiency and the P3HT:PCBM has become a popular material combination in organic solar cell research.[24] Thermal annealing of P3HT:PCBM BHJ was found to improve carrier mobility and cause the crystallization of P3HT in the BHJ.[25] Furthermore, the regio-regularity in P3HT chains offer improved performance.[26] The weight ratio of P3HT:PCBM and secondary additives in the blend solution were also optimized for high performance.[27, 28] Eventually, ~4.5 % efficiency was reported by Yang et al. using a solvent annealing approach which improved the percolation in the nanoscale morphology of the P3HT: PCBM layer.[29] Due to consistency in the device performance and simplicity in material processing for the device fabrication, P3HT:PCBM BHJ has become a benchmark for investigating various device mechanisms in organic solar cells.

1.5 Working principle of OSCs

1.5.1 Exciton generation

Upon photon absorption, electrons in the organic semiconductor are excited from the occupied to the unoccupied molecular orbitals as shown in Figure 1.7A.
However, due to low dielectric constant (3-4) and localized electron and hole wavefunctions in organic semiconductors, strong Coulombic attraction exists between the electron–hole pair.[30-32] The resulting bound electron–hole pair is called an exciton, with a binding energy of 0.1–1.4 eV [31], as opposed to a much lower binding energy of a few meV in inorganic semiconductors. The absorption coefficient of organic materials is commonly high at ~10^5 cm\(^{-1}\).[33]
Hence, although the thicknesses of the active layer of OSCs are limited by electrical conduction, a few hundreds of nanometers of the active layer are thick enough to absorb an adequate amount of light and show significant photovoltage and current.[34] A main concern for organic materials in general is the large band gap which leads to low absorption efficiency of photons in the long wavelength region >700 nm as shown in Figure 1.8. P3HT has a band gap of ~1.9 eV, while most organic materials have band gaps of ~2 eV.[35] The absorption efficiency can be enhanced by developing low band gap organic semiconductors.[36]

### 1.5.2 Exciton diffusion and dissociation

After exciton generation, the next step is to diffuse the excitons to the nearest heterojunction interface for dissociation (refer Figure 1.7B). The distance that excitons can diffuse before recombination is called the exciton diffusion length ($L_n$) defined as:

$$L_n = \sqrt{D\tau}$$  \hspace{1cm} (1.1)
where D is the exciton diffusivity and \( \tau \) is the natural lifetime of the exciton. The \( L_n \) in organic semiconductors is typically \( \sim 20 \) nm; within this distance the excitons should find a heterojunction interface for dissociation into free carriers.\([37, 38]\) The rationale of using BHJ is to solve this issue; i.e., the blend layer ensures the donor-acceptor interface to be within \( L_n \).\([35]\) To enable efficient charge dissociation at the donor-acceptor interface, two organic materials with band alignment as shown in the Figure 1.5 is needed. The difference between the HOMO of donor (D) and the LUMO of acceptor (A) has to be lower than the potential difference between the bound electron–hole pair. This difference energetically favours the transfer of an electron from the LUMO of the donor to the LUMO of the acceptor. The competing process of luminescence, which involves the radiative recombination of excitons, occurs at a timescale of \( \sim 1 \) ns.\([39]\) In contrast, the charge transfer process occurs at a much faster timescale of \( \sim 45 \) fs, allowing efficient exciton dissociation at the heterojunction.\([40]\) After dissociation, excitons form a charge pair called a geminate pair (shown in Figure 1.7C and Figure 1.9B), in which charges are still coulombically bound i.e. an electron and hole may form an intermolecular CT complex at the interface that may eventually recombine or get separated depending on the local electric field.\([11, 40, 41]\) During the charge separation process, the constituents (electrons and holes) of the geminate pair (e\(^-\) & h\(^+\)) formed after exciton dissociation at the heterojunction interface gets separated into free carriers when the electron affinity (EA) of the acceptor is higher than the exciton binding energy (\( \text{Ext}_B \)). A simplified schematic representation of the excitons during the formation and diffusion stage is shown in Figure 1.9A. The geminate pair formed after exciton dissociation at the donor-acceptor (D-
1.5.3 Charge carrier transport and recombination

After charge separation i.e. formation of free carriers, the main driving forces for the transport of holes to the anode and electrons to the cathode are drift and diffusion currents.\cite{42, 43} The drift current corresponds to carrier movement along the potential gradient or electrochemical potential within the solar cell. This potential gradient is determined by the choice of collecting electrodes in the solar cell. When an external bias is applied, the internal electric field is modified and the drift current changes. The carriers drift along the resultant internal electric field of the solar cell toward the respective electrodes for collection. Another mechanism of carrier transport is the diffusion current, which is the diffusion of carriers along the carrier concentration gradient within a solar cell. As the geminate pairs are generated around the solar cell heterojunction, the concentration of electrons and holes are commonly higher around the heterojunction. Carriers hence diffuse along the concentration gradient away from the heterojunction, leading to the diffusion current. The diffusion current mainly dominates when the applied bias modifies the internal
electric field to nearly zero, while drift current dominates when the internal electric field is large.[17] The drift distance \((L_d)\) of the photo-generated carriers within the active layer is given as

\[
L_d = \mu \times \tau \times E
\]  

(1.2)

where \(\mu\) is the mobility, \(\tau\) is charge carrier lifetime and \(E\) is the electric field, which limits the maximum thickness of the active layer \((d_{\text{max}} < L_d)\).

Monomolecular recombination commonly refers to either Shockley-Read-Hall (SRH) recombination or geminate recombination in organic solar cells.[44]

Shockley-Read-Hall recombination is defined as a first-order recombination process in which one electron and one hole recombine through a trap state or recombination center. Impurities in the polymer materials and fullerene, incomplete phase separation, and interfacial defects act as traps and contribute to recombination. The fundamental assumption which makes SRH first order recombination is the time delay (or interval) between the capture of the first
charge and the second charge. The rapid initial capture of electrons \( n_{e,\text{trap}} \) creates a reservoir of stationary trapped electron charge with which mobile holes \( n_h \) would recombine. [44]

\[
R_{SRH} \propto n_{e,\text{trap}} \cdot n_h(I) \tag{1.3}
\]

where \( I \) is the incident light intensity upon illumination.

**Geminate Recombination:** After exciton dissociation, electron–hole pairs form a charge pair called a geminate pair, in which charges are still coulombically bound and have to be separated by an internal field. When this pair recombines back to its original state, then it is called as geminate recombination. The concept of geminate recombination is shown in Figure 1.10.

**Bimolecular recombination:** involves non-geminate (free carriers) electrons that recombine with holes as the carriers travelling through the device to their respective electrodes. Usually in organic materials with electron density \( n \) and hole density \( \rho \), the recombination rate \( R \) is given by [45]

\[
R = -\beta n\rho \tag{1.4}
\]

where \( \beta \) is the fitting parameter. The bimolecular recombination in most organic solar cells appears to follow Langevin-like kinetics.[45] In this case, \( \beta \) is given as:

\[
\beta = (\mu_e + \mu_h)/e\varepsilon_o\varepsilon \tag{1.5}
\]

Here the Langevin recombination is limited by the rate at which the electrons and holes meet because the carriers are confined to their own phases, i.e.,
electrons in fullerene and holes in the polymer. In other words, the fastest carrier determines recombination rate. Recently it has been discerned that the recombination rate is limited by the slowest carrier thereby deviating from the Langevin-type.[46] It has been shown that the Langevin-type recombination exists in low-efficiency (unannealed) P3HT/PCBM solar cells whereas non-Langevin recombination has been observed in high-efficiency (annealed) P3HT/PCBM based solar cells. The product of a given carrier mobility multiplied by the recombination coefficient determines a maximum PCE value.[46] Therefore, to improve the PCE in the OSCs either the slower charge carrier mobility must be improved or carrier recombination must be reduced.

*Space-charge Recombination:* As discussed earlier, the main limitation of carrier transport is the carrier mobility in OSCs. The difference between hole and electron mobilities is also a critical factor in determining charge transport characteristics; a difference of more than a factor of 10 will lead to space charge limited current (SCLC).[42] In short, SCLC arises when one type of carrier, say electrons (electron commonly has higher mobility in OSC materials) is transported much more efficiently to the cathode. As the rate of electrons reaching the cathode is higher than that of holes to the anode, electrons may accumulate in the active layer near the cathode interface thereby creating the space charge effect, which modifies the charge transport characteristics of the active layer and creates an upper limit for the current output of a solar cell. The space-charge limited photocurrent for a bulk heterojunction is given by [45]

\[
J_{SCL} = e\left(9\varepsilon_0\varepsilon_r/8e\right)^{3/4} G^{3/4} V^{1/2}
\]  

(1.6)
where $\mu_l$ is the lower of the two carrier mobilities, $\varepsilon_o$ is the permittivity of free space, $\varepsilon$ is the dielectric constant of the medium, $G$ is the generation rate of charge pairs, $e$ is the electron charge, and $V$ is the internal voltage of the cell. Generally in polymer: PCBM based BHJs; the performance is limited by the space charge limited current owing to $\sim2–3$ orders of magnitude difference between electron and hole mobilities. Therefore, a balanced hole and electron mobilities is required to achieve efficient carrier transport in the active layer of solar cell.[42]

### 1.5.4 Charge collection at electrodes

The separated charge carriers (electrons and holes) are extracted from the active layer to the respective electrodes. To achieve high efficiency in charge extraction, the potential barrier at the active layer/electrode interfaces have to be minimized. Commonly, a high work function anode and low work function cathode are used. In ohmic contacts, the work function of the anode is ideally expected to match the donor HOMO, while the work function of the cathode is expected to match the acceptor LUMO. In this case for ohmic contacts the $V_{OC}$ is governed by the LUMO and HOMO levels of the acceptor and donor, respectively, which pins the fermi levels of the cathode and anode.[47] On the other hand, if the work functions of anode and cathode materials are not near the donor HOMO or acceptor LUMO, correspondingly an ohmic contact cannot be formed. In this case, the carrier extraction behavior is governed by the metal-insulator-metal (MIM) model.[47, 48] The schematic representation of the concept is shown in Figure 1.11.
A method to improve efficient charge extraction at the electrodes via work function matching is to utilize different types of interfacial materials.

In summary the External Quantum Efficiency (EQE) in OSCS is defined as

$$\eta_{EQE} = \eta_A \cdot \eta_{Diff} \cdot \eta_{CT} \cdot \eta_C$$

(1.7)

i.e. the product of efficiencies - photon absorption ($\eta_A$), exciton diffusion ($\eta_{Diff}$), exciton dissociation/charge separation ($\eta_{CT}$) and charge collection ($\eta_C$).[49] The three parameters ($\eta_A \cdot \eta_{Diff} \cdot \eta_{CT}$) are primarily the functions of the active layer material (blend) whereas the charge collection ($\eta_C$) is the function of the electrode. Even if the active layer materials with high absorption coefficient and charge transport properties are chosen, its complete efficacy cannot be realized without suitable charge collection materials/electrodes. Therefore the rationale of choosing right electrode materials and interfacial buffer layers is crucial for optimal device
performance. This thesis primarily focuses on improving the charge collection parameters while keeping the active layer material as P3HT:PCBM.

1.6 Normal and Inverted OSCs

Normal or conventional OSCs are illuminated through the anode electrode i.e. via the electrode that collects the positive carriers (refer Figure 1.12A). Usually, indium-doped tin oxide (ITO), a transparent conducting oxide coated onto the transparent substrate is used for this purpose. The top electrode serving as cathode, is usually a low work function metal like Aluminum (Al). Though this device structure was quite successful in terms of performance efficiency, it is susceptible to degradation. The low work function metal cathode (Al) oxidizes faster leading to reduction in device operational stability.[50] In an inverted OSCs (IOSCs), the bottom transparent electrode/substrate i.e. ITO serves as cathode whereas the top electrode is the high work function metal (Ag, Au) serving as anode (refer Figure 1.12B). IOSCs provide the following advantage (i) they offer high environmental stability compared to normal structure; (ii) they provide greater flexibility in the processing/fabrication of tandem OSCs.[51] In these devices, the quality of the collecting electrodes and its corresponding energy level alignment with the photoactive layer is crucial as it contributes substantially to the overall performance efficiency.[52] Therefore interfacial buffer layers i.e hole transporting layer (HTL) and electron transporting layer (ETL) are used between the photoactive layer and the collecting electrodes of the OSCs as shown in Figure 1.12B.
1.7 Role of metal oxide nanostructures in OSCs

Metal oxides can be p-type and n-type materials, contingent on the position of the conduction band and valence band. For an n-type material, electron transfer from the LUMO of the acceptor to the conduction band (CB) of the metal oxide is the requisite. For a p-type contact material, the valence band (VB) of the metal oxide is required to match the HOMO of the polymer. The wide band gap of the interface materials also serves as a barrier for carriers of the other sort thus improving the carrier selectivity of the contacts.\cite{50, 53-56}
The main functions of interface materials are:

(1) To align/adjust the energetic barrier height between the photo-active layer and the electrodes

(2) To form a selective contact for carriers of one sort (either holes or electrons)

(3) To determine the polarity of the device (to make normal or inverted device structure)

(4) To prohibit a physical or chemical reaction between the polymer and electrode

(5) To serve as an optical spacer.

Figure 1.13 Schematic view of the energy levels of metal oxides and orbital energies of some of the organic components used in OSCs. Modified / redrawn from [52,53]

P-type transition metal oxides have been successfully incorporated in OSCs. Metal oxides such as WO\(_3\), NiO, V\(_2\)O\(_5\) and MoO\(_3\) are widely used p-type or
hole transporting buffer layers with respect to P3HT. Energy levels of some of the widely used metal oxides and organic components of OSCs are shown in Figure 1.13. It has been demonstrated that thermally evaporated transition metal oxides have the potential to replace PEDOT:PSS, which is susceptible to faster degradation owing to its hygroscopic nature.[41, 50, 55] Similarly, metal oxide materials like TiOx and ZnOx are widely used n-type interfacial layers for OPV devices. These wide band gap metal oxide materials are transparent to visible light but absorb ultraviolet (UV) light. The thickness of these wide band gap interfacial layers is also tunable without absorption losses in the visible (VIS) spectrum and thus it can additionally serve as an optical spacer.[50, 55, 57, 58]

1.8 Stability of the OSCs

This section mainly presents the degradation processes occurring in the OPVs, and the methods to enhance the stability. The chemical degradation of OPVs is mainly caused by the oxygen, water and electrode material reacting with the organic materials. During the fabrication process of OPVs, it is difficult to avoid introduction of some oxygen and water and their absorption in the different layers. Furthermore, oxygen and moisture can also diffuse into the finished device when exposed to air.[59, 60] By using $^{18}\text{O}_2$ and $\text{H}_2^{18}\text{O}$ to map the reaction products into OPV devices, oxygen/water diffusion process can be detected.[59, 60] Reports have shown that the oxygen and water molecules diffuse through the outer electrode (counter electrode to ITO) more than through the lateral sides of the device. Apart from that, ITO could also etch the active layers indirectly by means of indium diffusion into the OPV device.[61]
P3HT is one of the widely used polymers with superior stability, presumably due to the lack of easily oxidizable vinylene groups. On the other hand, the degradation of the electrodes is induced by the reactions between the ITO or unstable metal and oxygen or water respectively. For example, it is well known that aluminum (Al) as a top contact can react with oxygen to form Al₂O₃ within several minutes exposed in air. The moisture and impurities within the polymer further enhance ionic conduction and hence accelerate corrosion. This problem can be solved by using a noble metal with a high work-function as top contact, while a metal oxide is introduced in the hybrid solar cells as a charge carrier selective layer and deposited on the other unstable electrode made of ITO.[61-64]

Organic solar cells employing inorganic semiconductor oxides such as TiO₂, ZnO, SnO₂, Nb₂O₅, and CeO₂, the lifetime of devices depends on the presence of oxygen and UV-irradiation in a complicated way. For example, the photocatalytic properties of TiO₂ can lead to the oxidation of organic materials adsorbed to the surface.[65] In addition, TiO₂ can be excited by UV light to photogenerate electron–hole pairs in which the electron is efficiently transferred to bound oxygen (O₂) to generate the superoxide radical anion O²⁻, which can de-acidize numerous organic compounds including polymers. Moreover, the photogenerated holes can react with surface hydroxyl groups to produce TiOH⁺ that could react and degrade adsorbed organic compounds.[65] Since the UV-irradiation results in degradation of organic materials, a band-structure engineered wide gap metal oxide like ZnO can serve as a UV-filter, improving the stability of organic solar cells. However, UV induced interaction of oxygen in IOSCs is still a topic of intense research. Taking the
ZnO-based inverted cells for example, some results were reported that modifications in processing conditions led to a better device performance.[66-68] This thesis will be exploring few aspects in improving device stability along this direction.

1.9 Basics of dye sensitized solar cells (DSCs)

O’Regan and Graetzel reported the dye sensitized solar cell (DSCs) based on the mechanism of a first regenerative photoelectrochemical processes with an efficiency of ~7.9 % (1991).[69] Following its success, extensive research have been carried out in this field to increase the power conversion efficiency (PCE) of DSCs by incorporating n-type metal oxide semiconductors such as TiO2, ZnO, SnO2, Nb2O5, SrTiO3 etc. and their composites as photoelectrode materials. The wide band gap metal oxide semiconductors (Eg> 3eV) having suitable band position relative to dye (or photosensitizer) has been employed for the fabrication of DSCs. Owing to wide band gap, The metal oxides employed for the fabrication of DSCs have absorption at ultraviolet region. Therefore, photosensitizer/dye is responsible for the absorption of light at visible and near-infrared region. Furthermore, the high surface area of nanoporous metal oxides increases dye loading; thereby enhancing light absorption leading to improved performance of DSCs. In addition to the above mentioned physical characteristics, lower cost, natural abundance and facile synthesis methods of metal oxides is another key advantage for the application in DSCs.[70-72]
1.9.1 Key components of a dye-sensitized solar cell

Dye-sensitized solar cells consist of a variety of components that have to be optimized both individually and as a component of the whole assembly. This includes the glass substrate with the transparent conducting oxide (TCO) layer, a mesoporous titanium dioxide (TiO$_2$) layer, dye, electrolyte (organic) solvent, redox couple, and a counter electrode.[70-72]

1.9.2 Photoelectrode

Among the many wide-bandgap oxide semiconductors (TiO$_2$, ZnO, and TiO2) that have been examined as potential electron acceptors for DSCs, TiO$_2$ is the most versatile. It delivers the highest efficiencies, is chemically stable, non-toxic, and available in large quantities. TiO$_2$ has many crystalline forms, with anatase, rutile, and brookite being the most important ones. The crystal structure of anatase and rutile are based on a tetragonal symmetry, in which the Ti$^{4+}$ atoms are 6-fold coordinated to oxygen atoms. The main difference between both structures is the position of the oxygen atoms. In contrast to rutile, anatase has the smaller average distance between the Ti$^{4+}$ atoms; thus, anatase is thermodynamically metastable. The phase transformation from anatase to rutile occurs in the temperature range of 700 – 1000°C, depending on the crystallite size and impurities.[73-75]
Rutile has slightly lower indirect band gap (3.0 eV) as compared to anatase (3.2 eV), which is attributed to a negative shift of the conduction band in anatase by 0.2 eV. The bonding within TiO$_2$ is partly covalent and partly ionic. Therefore, stoichiometric crystals are insulating.[71, 72] However, a significant amount of trap states are induced during most synthesis routes, which are due to oxygen vacancies. These vacancies can also be formed reversibly under reduced pressure and/or elevated temperature, which can lead to a variation in conductivity by several orders of magnitude. The oxygen vacancies cause the formation of Ti$^{3+}$ state, which dope the crystal negatively (n-type). In contrast to other semiconductors of similar band gaps (e.g. ZnO), it does not photo-degrade upon excitation. On the other hand, TiO$_2$ is less stable to UV degradation compared to tin oxide (TiO$_2$) owing to its high band
gap and high work function. However, low electron mobility ($\mu_n$) through mesoporous TiO$_2$ (~0.1 cm$^2$ V$^{-1}$ s$^{-1}$) is a crucial issue and imposes severe limitations in enhancing the $\eta$ of DSCs closer to the theoretical limits. The energy levels of the conduction and valence bands of the metal oxides used in DSCs is shown in Figure 1.14. In the standard version of DSCs, the typical film thickness is 2 - 15 µm, and the films are deposited using nanosized particles of 10 - 30 nm. A double-layer structure can be fabricated, where an underlayer of thickness 2 - 4 µm is first deposited using larger (200 - 300 nm) size particles that acts as a light-scattering layer to induce a photo-trapping effect.[71, 73, 74, 76]

1.9.3 Sensitizers for dye-sensitized solar cells

The photosensitizer ("dye") is a fundamental component of the DSC since its main function is to absorb the solar radiation and inject electrons into the conduction band of the oxide substrate. The desirable properties for an efficient photosensitizer are the following: strong light absorption in the visible and near-IR region (for efficient light harvesting); high solubility in organic solvents (to improve the deposition from stock solutions); the availability of suitable anchoring ligands such as carboxylic or phosphonic acid groups (to promote the effective interaction with the oxide surface and thus the coupling of donor and acceptor levels); the LUMO of the dye must be sufficiently high in energy for an efficient charge injection into the TiO$_2$, and the HOMO must be sufficiently low in energy for an efficient regeneration of the oxidized dye by the redox pair; high thermal and chemical stability (to assure a high turnover number and a corresponding lifetime of the device).
Moreover, electron transfer from the dye to the TiO$_2$ must also be rapid in comparison with decay to the ground state of the dye.

Up to now, the best performing dyes are the polypyridine complexes of Ru (II) with one or more anchoring groups (carboxylic or phosphonic acid) as a peripheral substituent. The highest conversion efficiencies have been reached using the tetra-protonated cis-bis (isothiocyanato)bis(2,2’-bipyridyl-4,4’-dicarboxylate)ruthenium(II) complex ("N3"). Generally, metal complex photosensitizers consist of a central metal ion with ancillary ligands having at least one anchoring group. Light absorption in the visible part of the solar spectrum is due to a metal-to-ligand charge transfer (MLCT), which promotes an electron from the metal d orbitals to the ligand π* orbitals, d(π)→π*.[63]

Charge injection occurs from the π* orbitals of the anchoring group to the titanium 3d orbitals.

1.9.4 Electrolytes for dye-sensitized solar cells

Generally, the electrolyte for DSC consists of a solvent based solution containing the redox couple and various additives, such as a lithium salt and tert-butylpyridine. The function of the redox couple is to reduce the dye cation, following charge injection, and to work as a shuttle, carrying the charge back and forth between the two electrodes. The crucial aspects is that the dye cation should be reduced faster than the back reaction with the injected electron, and that the electrolyte should be reduced slowly by the conduction band electrons in the TiO$_2$, and fast at the counter electrode. Among many redox couples examined, the iodide/tri-iodide couple has been found to have the best performance.
1.9.5 Counter electrode

To complete the regenerative cycle in a DSC, the oxidized form of the redox couple has to be reduced at the counter electrode by the electrons flowing through the external circuit. In the case of the iodide/iodine redox couple, the oxidized form corresponds to tri-iodide and its reduction involves two electrons:

$$I_3^- + 2e^- \rightarrow 3I^-$$ (1.8)

The counter electrode must be catalytically active to ensure rapid reaction and low over-potential. Platinum has been the material of choice; deposited as Pt-metal clusters in low quantities (~ 5 µg/cm²) on TCO glass.[71, 76]

1.9.6 Working mechanism of DSCs

Dye-sensitized solar cells are based on a non-toxic semiconductor that is sensitized with a ruthenium containing dye molecule. A redox electrolyte and two conducting glass substrates provide the connector to the external circuit. The functional principle is similar to photosynthesis: Upon photoexcitation, the dye molecules inject an electron into the conduction band (E_c) of TiO₂, leaving the dye in its oxidized state (D⁺, also referred to as dye cation). The dye is restored to its ground state by electron transfer from the redox pair.[77] The mechanism of operation of the DSCs is illustrated in Figure 1.15.
The regeneration of the sensitizer by iodide intercepts the recombination of the conduction band electron with the oxidized dye. Diffusion of $e^-$ through the nano-crystalline TiO$_2$ film to the substrate electrode and diffusion of the oxidized redox species ($I_5^-$ ions formed by oxidation of $I^-$) through the solution to the counter electrode allow both charge carriers to be transferred to the external circuit, where useful work is performed and the regenerative cycle is completed by electron transfer to reduce $I_3^-$ to $I^-$. It is of critical importance for the functioning of the cell that the injection of electrons into the TiO$_2$ is
many orders of magnitude faster than any recombination (loss) of charge carriers. Moreover, the most important recombination process is the direct electron-transfer from the conduction band of TiO$_2$ to the redox electrolyte without passing the external circuit.

### 1.9.7 Photochemical processes and recombination in DSCs

Photovoltaic performance is predominantly influenced by the events at the interfaces between the metal oxide semiconductor, the dye, and the electrolyte. In general, the metal oxide/dye interface is maintained such that the oxidation potential of the excited dye (LUMO) is sufficiently negative to initiate the effective electron injection to the conduction band of metal oxide.

![Figure 1.16 Schematic showing photochemical processes and rate limiting steps in DSCs.][68]

Upon photo-irradiation, dye molecule undergoes a $\pi \rightarrow \pi^*$ transition thereby exciting an electron form the HOMO to the LUMO due to the relatively weak lateral overlapping of atomic orbital’s ($\pi$ bonds) with loosely bound electrons.
(π electrons) in HOMO. Moreover, a built in energy gradient (ΔE) exists between the dye/metal oxide interface due to the energy difference between the LUMO state of dye and the CB of metal oxide (E_{CB}). Hence, the electrons in the LUMO of photoexcited dye undergo a non-radiative transition to the conduction band of metal oxide within a time scale of few picoseconds and thereby oxidized. The oxidized dye is then reduced to its ground state by means of a redox couple together with platinum as catalyst at cathode.[70, 71, 76] Figure 1.16 shows the photochemical and recombination processes involved in DSCs

The fundamental processes of photoconversion and rate limiting steps involved in DSCs are listed below: [71, 76, 78, 79]

I. The rate of excitation of dye is determined by the quantity of photons absorbed at the absorption wavelength of dye, intensity of solar radiation or photon flux, and the absorption cross-section of the dye.

II. The relaxation/radiative recombination of the excited electron of the dye from LUMO to HOMO, and the corresponding rate constant $k_1$:
Relaxation processes occur typically in a time scale of nanoseconds.
The typical rate of decay from the excited state to the ground state of dye is in the range $\sim 10^7$- $10^{10}$ s$^{-1}$. This process reduces the excited state free energy by $\sim$ 400 meV.

III. Exciton diffusion length $D_{\text{EXT}}$.

IV. Interfacial electron transfer, i.e., the excited electron from the LUMO of dye is injected into the conduction band of metal oxide with the rate constant $k_2$: The kinetics of the interfacial electron transfer at the
interface strongly depends on the energetics of the metal oxide/dye/electrolyte interface and the density of electrons in metal oxide (i.e. Fermi level of metal-oxide). The interfacial electron transfer occurs typically in a time scale of several picoseconds. Electron injection rate of \( > 10^{12} \text{ s}^{-1} \) have been reported for a range of sensitizers and metal oxide films.

V. Injected electron transport through the mesoporous layer of metal oxide to the transparent conducting oxide (TCO). The efficacy of this process is mainly determined by the diffusion coefficient of electrons \( (D_e) \), and the electron lifetime \( (\tau_e) \).

VI. Phonon relaxation process, i.e. an electron loses its energy by electron-phonon recombination. In general in solar cells, upon illumination, the energy used is the energy gained over the energy bandgap, the rest of the energy is lost to kinetic energy, phonons (vibrational energy of the lattice) etc., generally called thermalization or cooling. This results in Non-radiative recombination.

VII. Interfacial charge recombination, i.e., the oxidized dye captures electrons from the conduction band (CB) of metal oxide with the rate constant \( k_3 \) which is typically in the time scale few \( \mu \text{s-ms} \). The recombination rate of this process is determined by the electron density of states in the photoelectrode, light intensity, and cell voltage.

VIII. Back electron transfer, i.e., the electrons from the conduction band (CB) of metal oxides recombines with the oxidized mediator in the electrolyte \( (I_3^-) \) with the rate constant \( k_d \); back electron transfer is typically very slow with the rate constant in the range of ms-s and it is
strongly dependent on the concentration and viscosity of the electrolytes as well as the structure of dye.

IX. Regeneration of dye, i.e., the transfer of electron from the redox mediator in the electrolyte to the oxidized dye with the rate constant $k_5$: The restoration of the oxidized dye occurs in the timescale of nanoseconds. It is typically 100 times faster than any recombination process and about 108 times faster than the inherent lifetime of the oxidized dye.

In case of N3 dye, the interfacial charge recombination and the regeneration rate constants are $k_3 = 1.4 \times 10^3$ s$^{-1}$ and $k_5 = 1.1 \times 10^5$ s$^{-1}$, respectively. This implies that high electron injection yield can be achieved in the DSC systems employing metal oxides, since the regeneration step is ~100 times faster than recombination. Moreover, the rate of the electron injection ($k_2 > 1.4 \times 10^{11}$ s$^{-1}$) is three order of magnitude faster than the radiative recombination.

From the above discussion, it can be assumed that the two rate limiting processes i.e. the radiative recombination and interfacial charge recombination, do not limit the photoconversion of DSCs significantly. In addition, the exciton diffusion could also be neglected since the exciton is highly localized on dyes because the particle radius is significantly smaller than the Bohr radius. Thus, the rate limiting processes that mainly contribute to the photoconversion efficiency are (I), (IV), (V), (VI), (VIII) and (IX). The rate limiting steps, (I) and (IX) are highly dependent on the dyes and electrolyte, respectively. Steps (IV) and (VIII) depends on the metal oxide/dye interface and metal oxide/electrolyte interface respectively. Steps (V) and (VI) are completely dependent on photoelectrode.[70] Thus the metal oxides
serving as photoelectrode, play a significant role in determining the performance of DSCs.

1.10 Role of metal oxide nanostructures in DSCs

The metal oxides as discussed earlier form the most prominent part of the device – the photoanodes. The excitons generated in the dye are separated into free carriers at the dye/photoanode interface. Two basic driving forces for this charge separation are: (i) the charge separation is energetically favoured at the interface because the conduction band (CB) of the metal oxide is at lower energies than the LUMO of the dye; (ii) the charge separation process is entropically favoured because there is larger density of electronic energy states (DOS) in the conduction band of the nanocrystalline metal oxide than molecular orbital of a dye.[70] Moreover, the photoconversion efficiency of DSCs is significantly influenced by the nanostructured metal oxide semiconductors with particle size greater than their exciton Bohr radius. The factors that affect the DSCs performance are (i) its mesoporosity and large surface area allows large amount of dye anchoring which enhances the absorption cross-section, (ii) larger amount of density of states (DOS) in metal oxides than the molecular orbital of dye enables faster injection of electrons from the dye to the metal oxide. Inefficient charge transport in the nanostructured metal oxide semiconductors originate from the trapping and detrapping of electrons at the surface atomic states in the electronic band. The surface atoms form a large fraction in nanostructured materials, so as the trap density. Trapping and detrapping process lowers the kinetic energy of the mobile electrons ultimately leading to inferior cell performance.
Quantification of the traps and their subsequent removal could improve the photovoltaic conversion efficiency of DSCs beyond the present record of 11-15%.[73-75, 80] Furthermore, optimization of the photoanode morphology is required to enhance the photon to electron conversion efficiency and the charge collection efficiency. Metal oxides such as TiO$_2$, SnO$_2$, ZnO, Nb$_2$O$_5$, Fe$_2$O$_3$, ZrO$_2$, Al$_2$O$_3$, and CeO$_2$ have been tested for their use as photoelectrodes in DSCs. Other approaches, such as doping, composites, core/shell structures, have also been explored to enhance the electrical transport properties and PCE.[74, 81]

1.11 **Scope and structure of the thesis**

Metal oxides play a dominant role in excitonic solar cells serving as interfacial buffer layers in OSCs and as photoelectrodes in DSCs. The discussion embodied earlier in this chapter show how the properties of metal oxides influence the final PCE and stability of the two types of solar cells. In particular, nanostructured metal oxide semiconductors typically affect the charge transport, which is fundamentally different than the transport through corresponding bulk materials. Figure 1.17 shows a schematic on the difference in charge transport mechanisms in metal oxides between the bulk and their nanostructured analogue.\(^2\) Periodic array of atoms in bulk crystalline materials depicts that the band gap is completely forbidden to have any energy states; whereas in the nanostructured materials the band gap is characterized by a

broad distribution of localized energy states that arise as a result of deviation of equilibrium atomic coordinates. Density of those localized states is higher at the bottom of the conduction band and exponentially decreases in the energy scale towards the Fermi level. The photogenerated electrons in the nanocrystalline materials are trapped by the localized states and subsequent thermal activation leads the electrons to de-trap. The injected carriers thus move via a trap-detrap mechanism, otherwise called multiple trapping (MT), through the band gap in nanocrystalline material. On the other hand, the charges are transported through the conduction band in the case of bulk material by thermally activated hopping from one transport state to another.

Figure 1.17 Schematic showing the difference in charge transport mechanisms between the (A) bulk and their (B) nanostructured analogue in metal oxide semiconductors.

Therefore, depending on the density of traps in the band gap of nanocrystalline materials, the injected electrons first undergo trap filling which may or may not be collected depending on the lifetime of those trap states. This trap filling
does not occur in the perfect crystalline bulk material as there are no traps. In addition, bulk materials could support an electric field on account of a space charge region which would further accelerate the electrons; whereas the space charge is completely depleted in the case of nanomaterials (≤ 25 nm) and could not support a macroscopic electric field. Therefore, the electron diffusion coefficient ($D_n$) and hence electron mobility ($\mu$) in nanomaterials are typically less by several orders of magnitude in nanostructured materials than the corresponding bulk material.

The implications of such inferior charge transport properties in the nanostructured metal oxides serving as interfacial layers in OSCs are straightforward i.e. the charge collection efficiency reduces significantly if it has a higher density of trap states. Therefore, improving the transport parameters by reducing the density of trap states is one of the promising ways to enhance the PCE and operational stability of the OSCs. Similarly, in the case of DSCs, the inferior $D_n$ and $\mu$ of the nanostructured photoelectrodes affects the PCE significantly. For instance, typical electron (MOS) – hole (electrolyte) recombination time in DSCs is $\sim 10^{-6}$ s, which requires faster electron mobility for efficient charge collection. Moreover, the distance travelled by electrons before recombining with the electrolyte - known as the diffusion length, $L_n = (D_n \tau)^{1/2}$, where $\tau$ is the electron lifetime, is a crucial device parameter. Thus, owing to the inferior $\mu$ and limited $L_n$ in the nanostructured materials, photoelectrons only from a small thickness of the film (12 – 15 μm) are collected in the state of the art DSCs. Therefore, its PCE
can be enhanced only if a metal oxide nanostructure with large specific surface area and \( \mu \) is used as photoelectrode.

The research embodied in this thesis aims to develop innovative materials so as to solve the above mentioned issues in charge transport through the interfacial layers (OSCs) and photoelectrodes (DSCs). Materials with improved charge transport properties were developed during the course of this research that not only yielded highly efficient solar cells but significantly enhanced their operational stability.

The thesis is structured as follows:

In **Chapter 1**, the basics of the two types of excitonic solar cells, viz. OSCs and DSCs are discussed in detail. First, the working principle of the organic solar cells and the most prominent materials used in OSCs are elaborated. The charge carrier transport in organic devices is discussed. The normal and inverted device architecture is explained. Similarly, the working principle and device physics of DSCs are elaborated. The role of metal-oxide nanostructures in these devices is discussed.

In **Chapter 2**, the techniques used for synthesis of materials, physico-chemical methods for the characterization of synthesized materials and details of device fabrication are discussed. In addition, the methods to evaluate and validate the physical properties of the devices are also discussed in detail.

**Chapter 3** elaborates the fabrication of metal oxide - electron and hole transporting layers in OSCs, and their effects on the PCE and stability of the devices in detail.
In **Chapter 4**, a thorough device characterization has been undertaken to unveil the sources of enhanced PCE and operational stability in the devices studied in chapter 3.

In **Chapter 5**, an alternate method to improve the charge collection efficiency that outlined in Chapter 3 is described. The method is to plant electron conducting nanowires in the electron transport layers (ETL) of the OSCs that enhances the collection of electrons from the photoactive layer.

**Chapter 6** refers the synthesis of metal oxide semiconductors with high crystallinity, specific surface area, high charge mobility and fabrication of DSCs with record performance parameters. The underlying reasons for the record performance are also investigated in detail in this chapter.

In **Chapter 7**, future prospects for the improvement in device performance and stability of OSCs and DSCs are discussed.
2 Materials and methods

Material selection and optimization lie at the heart of device engineering. Photovoltaic industry requires well characterized materials using which reproducible high quality devices could be produced. This chapter deals with synthesis of various materials for both OSCs and DSCs. It also describes briefly the characterization techniques used to analyze them. Table 2.1 shows the materials employed in this work, source, and device that employed it.

Table 2.1 List of major materials used in the present work

<table>
<thead>
<tr>
<th>Materials</th>
<th>Source</th>
<th>Device</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indium doped tin oxide coated glass substrate (ITO)</td>
<td>Asahi Glass (~12-15 Ω/square)</td>
<td>OSCs</td>
</tr>
<tr>
<td>ZnO nanoparticles and nanowires</td>
<td>Nanoparticles were prepared by sol-gel method using zinc acetate dehydrate purchased from Aldrich and nanowires were prepared by electrospinning technique.</td>
<td>OSCs</td>
</tr>
<tr>
<td>MoO₃</td>
<td>Sigma Aldrich</td>
<td>OSCs</td>
</tr>
<tr>
<td>P3HT</td>
<td>Rieke Metals</td>
<td>OSCs</td>
</tr>
<tr>
<td>PCBM</td>
<td>Nano-C</td>
<td>OSCs</td>
</tr>
<tr>
<td>Al</td>
<td>Sigma Aldrich</td>
<td>OSCs</td>
</tr>
<tr>
<td>Ag</td>
<td>Sigma Aldrich</td>
<td>OSCs</td>
</tr>
<tr>
<td>Ca</td>
<td>Sigma Aldrich</td>
<td>OSCs</td>
</tr>
<tr>
<td>Fluorin doped tin oxide coated glass substrate (FTO)</td>
<td>Asahi Glass (~15-18 Ω/square)</td>
<td>DSCs</td>
</tr>
<tr>
<td>SnO₂ nanowires and nanoflowers</td>
<td>Electrospinning technique</td>
<td>DSCs</td>
</tr>
<tr>
<td>RuL₂(NCS)₂·2H₂O; L = 2, 2’–bipyridyl-4,4’-dicarboxylic acid</td>
<td>Solaronix</td>
<td>DSCs</td>
</tr>
<tr>
<td>Lithium iodide</td>
<td>Sigma Aldrich</td>
<td>DSCs</td>
</tr>
<tr>
<td>Iodine</td>
<td>Sigma Aldrich</td>
<td>DSCs</td>
</tr>
<tr>
<td>Pt</td>
<td>Sigma Aldrich</td>
<td>DSCs</td>
</tr>
</tbody>
</table>
As shown in the Table 2.1 most of the materials in this work were as-purchased except the ZnO and the SnO$_2$ nanostructures, which were produced by the electrospinning technique. This chapter is organized in three sections: the first section deals with the material synthesis by electrospinning process and the characterization techniques used for nanostructures; the second section deals with device fabrication process of all the steps involved; and the third section deals with analytical characterisation techniques used to study the devices.

2.1 Material synthesis and characterization techniques

2.1.1 Electrospinning technique

Electrospinning technique works under the principle of asymmetric bending of a charged liquid jet when accelerated by a longitudinal electric field. It is a technique that allows fabrication of continuous nanofibers of polymers and advanced functional materials with high aspect ratio. In the electrospinning process, a polymer solution is injected from a needle in the presence of an electric field. When the strength of the applied electric field is sufficient enough to overcome the surface tension of the liquid, a continuous jet is ejected which upon subsequent solvent evaporation and bending; produces nanofibers on a collector surface.[84] Figure 2.1 shows a schematic of the processes during electrospinning. Various fiber morphologies could be produced by electrospinning such as random, core-shell, aligned, and mats etc. and these are produced by merely changing the collection and/or injection strategy.[85-88] If the polymer solution contains respective metal ions for
forming an inorganic solid, appropriate post-electrospinning heat treatment yields continuous inorganic nanofibers.[89, 90]

Figure 2.1 Schematics of the electrospinning process. The experimental set-up consists of a high voltage power supply, a spinneret, and a collector. The three processes, viz. formation of tailor cone (1), bending due to various instabilities (2), and collection of solid samples (3) are shown. The qE is the electrostatic force, η is the viscosity and T is the surface tension. Conventionally electrospinning produce a fiber cloth consists of randomly oriented nano/microfibers, a typical SEM image of which is also shown.

2.1.2 Scanning Electron Microscope (SEM)

The scanning electron microscope (SEM) employs a focused beam of high-energy electrons with significant amounts of kinetic energy, and this energy is dissipated as a range of signals on interaction with the surface of specimens. The signals that obtained from the electron-sample interactions reveal information about the sample’s surface topography and composition. These signals include (i) secondary electrons (SE) from which the SEM images are obtained, (ii) backscattered electrons (BSE) which are used to determine crystal structures and orientations of minerals), (iii) photons i.e. the characteristic X-rays basically used for elemental analysis, (iv) visible
light (cathodoluminescence--CL), and (v) heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most important for producing morphology and topography of samples while backscattered electrons are most essential for illustrating contrasts in composition of multiphase samples. It is important to note that a vacuum environment is needed to operate the SEM efficiently for the following reasons. First, if gases are present in the column, they can react with the electron source, results in producing random discharges that destabilize the beam. Secondly, other molecules present in the mean free path of the electrons might hinder the transmission of the electron beam. This interaction forms compounds, which condense on the sample and compromise the detail and resolution of the image. In a typical SEM, an electron beam is thermionically emitted from an electron gun coupled with a tungsten filament cathode. Tungsten is normally used because it has the highest melting point and lowest vapour pressure of all metals, thereby making it suitable for electron emission. The electron beam is focused on the sample through the condenser lens to a spot size of about 0.4nm to 5nm diameter. The emitted electrons emitted back as a function of electron-sample interactions are collected by a detector, and then converted to voltage and amplified which is used for generating images in output devices (CRT). The present study employed a field emission scanning electron microscope (JEOL, FEG JSM 6700 F) with secondary electron imaging operating at 10 kV.

2.1.3 Transmission Electron Microscope (TEM)

Transmission Electron Microscope (TEM) uses a microscopy technique similar to that of a scanning electron microscope. The short wavelength of
electrons makes TEM capable of high-resolution imaging (up to a few order of Armstrong) and hence a very useful tool in material characterization. TEM is composed of a vacuum system, which can build a pressure of the order of $10^{-4}$ to $10^{-8}$ Pa, to allow uninterrupted passage of electrons. It has an electron emission source, a series of intermediate and projector lenses and electrostatic plates. In TEM, a coherent beam of electrons, directed at the specimen, interacts and transmits electrons as it penetrates through the specimen. The transmitted electrons are then focused by the objective lens into an image, which is then magnified and focused by intermediate and projector lenses onto a phosphor image screen. An image of dark and light contrast is formed due to different concentration of electrons transmitting through the specimen. Both surface topography and crystallographic information can be obtained. It is important to note that for TEM, the specimen needs to be ultra-thin in order for electrons to be able to penetrate through the sample. Hence, sample preparation is an important aspect in TEM imaging. For the present work, all the samples were dispersed in ethanol and dropped onto the carbon grid. The measurements were performed on a JEOL-2100 high-resolution transmission electron microscope (HRTEM) at an accelerating voltage of 300 kV with a Lorentz lens. The JEOL-2100 features a high-stability goniometer stage specifically tuned for large angle tilt applications.

### 2.1.4 X-Ray Diffraction (XRD)

XRD is a common technique used to determine the crystallographic structures of solids, including lattice constants, orientation of single crystals, defects, stresses and the chemical composition. A beam of x-rays with wavelengths
ranging between 0.7 and 2 Å is projected on the specimen, which is diffracted by the crystalline phases present in the specimen by Bragg’s law, given by:

\[ n\lambda = 2dsin\theta \] (2.1)

Here \( d \) is the spacing between atomic planes in the crystalline phase, \( \lambda \) is the wavelength of the x-ray and \( \theta \) is the angle between the incident ray and scattering planes. The planes vary in orientation from material to material each with its own unique d-spacing. In XRD, a monochromatic x-ray beam is projected onto a crystalline material at an angle of \( \theta \). Diffraction phenomenon only occurs when the distance traveled by the rays reflected from successive planes differ by a whole number \( n \) of wavelengths. The XRD pattern is obtained by plotting the angular positions and intensities of the resultant diffracted peaks. Philips Analytical X-Ray Diffractometer (PW1820/00) with Cu K\( \alpha \) radiation was used in this work.

2.1.5 X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) is a surface chemical analysis technique that measures the elemental composition of a material. The material to be analyzed is irradiated by a beam of monochromatic and low energy x-rays. The resulting energy of the photoelectrons that have escaped from the surface is measured. The analysis and detection of photoelectrons require that the sample be placed in a high-vacuum chamber. XPS has to be performed under ultra-high vacuum (UHV) conditions at pressures lower than \( 10^{-7} \) Pa. An electrostatic analyzer analyzes the energy of the photoelectrons, and an electron multiplier tube or a multichannel detector, such as a microchannel
plate, detects the photoelectrons. A spectrum with a series of photoelectron peaks is thus obtained. As the binding energy of the peaks is characteristic of each element, these peaks can be used to identify the elements that exist within the material surface. In addition, XPS also provides information on the existing chemical bonding in the specimen since the chemical state of the photoelectron emitted can alter the binding energy. X-Ray Photoelectron Spectrometer (XPS) with a spatial resolution of 30 µm is used in this work.

2.1.6 Brunauer–Emmett–Teller (BET) measurement

BET measurements on samples were conducted using Quantachrome Nova 1200 with N₂ as the adsorbate at liquid nitrogen temperature. BET method is used to measure the surface area of a material. The physical adsorption of gas molecules onto a solid surface serve as the basis for analysis of the specific surface area of that material. Surface area and pore size distribution are evaluated by the use of nitrogen adsorption/desorption isotherms at liquid nitrogen temperature ~70K and relative pressures \((P/P₀)\) ranging from 0.05-1.0. Brunauer-Emmett-Teller (Autosorb-1) Quanta-chrome equipment used to analyze the specific surface areas of samples in this work.

2.1.7 UV-Vis Spectroscopy

Electromagnetic radiation (light) interacts with matter during which various processes can occur such as reflection, scattering, absorbance, transmittance and fluorescence/phosphorescence. Photon absorption by matter causes its energy content of the molecules (or atoms) to increase. In general, the total potential energy of a molecule can be represented as the sum of its electronic, rotational and vibrational energies. The wavelength of light absorbed is equal
to the energy required to excite an electron from a lower energy level to a level of higher energy.

When the light is irradiated on a sample, it passes through or gets reflected, therefore the amount of light absorbed is the difference between the incident radiation ($I_o$) and the transmitted radiation ($I$). The amount of light absorbed is expressed as either transmittance ($T$) or absorbance ($A$), and they are defined as follows:[91]

\[ T = \frac{I}{I_o} \quad (2.2) \]

\[ A = -\log T \quad (2.3) \]

In general a UV-VIS spectrophotometer comprises of a tungsten-halogen or deuterium lamp to generate the radiation, a dispersion device and a detector, which converts visible light into electrical signal. Shimadzu UV-1800 UV/Visible scanning spectrophotometer is used for this work.

2.2 Fabrication of OSCs

Two sets of inverted devices were considered in the present study with the device structure;

Device 1: ITO/Ca/P3HT:PCBM/MoO$_3$/Ag

Device 2: ITO/ZnO/P3HT:PCBM/MoO$_3$/Ag

Major methods/ instrumentations used for the fabrication of the devices are described in the following sections.
2.2.1 Substrate design

OSC are fabricated on a pre-patterned ITO coated glass substrates with a size of ~25×25 mm$^2$ purchased from Asahi Glass Co. The design of the patterned ITO is shown in the Figure 2.2. Four devices each with area of 0.09 cm$^2$ were developed on the pre-patterned ITO. Thickness of the ITO layer was ~150 nm and has a sheet resistance ~15 Ω/sq. The ITO substrates were cleaned using acetone, isopropanol, and deionized water via ultrasonication.

![Patterned ITO substrate used to fabricate organic solar cells.](image)

2.2.2 Spin-coating

A typical spin coating process involves depositing a small quantity of precursor solution or resin (fluid) onto the center of a substrate and then spinning the substrate at high speed. During rotation the centripetal acceleration will cause the fluid to spread, and eventually off, the edge of the substrate leaving a thin film of the material on the surface of the substrate. Factors such as rotational speed, acceleration, and fume exhaust contribute to final thickness and properties of the deposited film. Apart from this other factors such as viscosity, drying rate, surface tension, etc. also determines the properties of the film. In our study, the deposition of ZnO layer (ETL) onto ITO and the
subsequent photoactive layer are carried out by spin coating the respective solutions. The thickness of the layers was controlled by the spin speed (500-5000 rpm). The exact rpm and the corresponding film thickness obtained in each case are discussed in the respective chapters under device fabrication section. CEE 100 spin coater (Brewer Science) is used in this work.

2.2.3 Thermal vacuum deposition

Thermal vacuum deposition is a commonly used method for depositing metallic, metal oxide, and low molecular weight organic films on various substrates. The process is based on the sublimation of a compound from a resistively heated boat or crucible at high vacuum $\sim 10^{-6} - 10^{-10}$ mbar.[44, 51] The metallic vapor is then deposited on the substrate mounted inside the chamber. The mean free path of the vapour in the vacuum chamber is usually longer than the size of the chamber. Thus, the vapour could travel from the source to the substrate without colliding with foreign material or gases present in the chamber. In our experiment, typical deposition rates used are $\sim 1$ Å/s to 100 Å/s which are controlled by changing the source temperature. Additionally, the use of substrate and source shutters can provide Å -level control of the evaporated film thicknesses. The counter electrode (Silver $\sim 100$nm) of the organic solar cells was deposited using this method. Calcium (10-20 Å) as ETL was also deposited using this technique. MBraun ProVap vacuum deposition equipment (4 source) integrated within the glovebox was used for this process.
2.2.4 Preparation of photoactive blend layer

P3HT and PCBM are purchased from Merck and Nano-C, respectively. The blend solution is prepared as follows. P3HT and PCBM are dissolved in 1,2 di-chlorobenzene (DCB) with concentrations of 40 mg/ml and 32 mg/ml, respectively. The two solutions were mixed in the volume ratio of 1:0.8 and the blend solution is stirred in the dark for 12 hours. Then blend layers were spin coated on cleaned ITO substrates (with any interlayers) at a spin speed of 500 rpm for 120 s. Followed by a slow dry process after taking out samples of spin coater, they were covered with a petri dish for 2 hours. Then annealing is carried out via heating the samples on a hotplate before and after the deposition of top contact. The annealing temperature is determined depending on the type of device fabrication, which will be discussed in detail in the following chapters.

2.2.5 Fabrication of inverted OSCs

The inverted solar cells are built with a following structure: ITO/ ETL/ P3HT: PCBM/ HTL/ Ag as shown in Figure 1.12B. A metal oxide film (via solution processing) or low work function metal (via thermal vapor deposition) is deposited on cleaned ITO serving as electron buffer layer (ETL). The synthesis and deposition techniques of the buffer layers varied according to the material used (Ca or ZnO), the details of which are discussed in respective chapters. A P3HT: PCBM blend layer was then spin-coated (500 rpm for 120s) on top of the ETL layer. It is followed by the deposition of a thin hole transporting buffer layer (~5-10 nm) of MoO₃ via thermal evaporation. Then, a 100 nm Ag layer is deposited as the top contact.
2.3 Fabrication of DSCs

Fabrication of DSCs include (i) deposition of a nanoporous n-type metal oxide (TiO$_2$, SnO$_2$ or ZnO) layer on a conducting glass substrate (FTO) by doctor blading or screen-printing techniques; (ii) sensitization of the nanoparticles with a dye; (iii) placing a spacer of ~10 µm thickness to fill in an electrolyte; and (iv) sealing the device using a counter electrode coated with platinum. The platinum coating in this work was carried out using thermal evaporation.

2.3.1 Substrate preparation

Transparent conductive glass (fluorine-doped tin oxide, FTO) (1.5 cm × 1 cm) with a sheet resistance of 25 Ω/square was purchase from Asahi Glass Co. Ltd., Japan. The FTO was cleaned with detergent, ethanol, isopropyl alcohol and de-ionized (DI) water by using an ultrasonic bath for 15 min. FTO was then dried at room temperature.

2.3.2 Deposition of metal oxide nanostructures (photoanodes)

The photoanodes in this work were developed by the electrospinning technique. The polymeric solutions containing Sn precursor were electrospun separately onto FTO glass substrates. Thickness of the electrode was controlled by placing the FTO substrates under the spinneret for different durations of time. The samples were wrapped in aluminium foil and hot-pressed (Stahls’ Hotronix 6×6 press, USA) at ~200 ºC with a pressure of 0.4 MPa for 15 min to improve the adhesion of the fibers and the flowers to the FTO substrate. The hot-pressed films were then subjected to annealing at 500 ºC for 3h to completely remove polymer and allow nucleation and growth of SnO$_2$. 
2.3.3 Sensitization of the metal oxide nanostructure electrodes

The DSCs were fabricated by soaking a 0.28 cm² SnO₂ electrode in a photosensitizer/dye solution containing in a 1:1 volume mixture of acetonitrile and tert-butanol of a ruthenium-based dye [Ru₂L₂(NCS)₂₂H₂O; \( L = 2, 2' - bipyridyl-4,4'-dicarboxylic \) acid (0.5 mM), N3 Solaronix)] for 24 h at room temperature. The dye-sensitized samples were then washed in ethanol to remove unanchored dye and dried in air.

2.3.4 Deposition of the electrolyte

The dye-anchored electrodes were then sealed using a 50 µm spacer. Acetonitrile containing 0.1M lithium iodide, 0.03M iodine, 0.5M 4-tert-butylpyridine and 0.6M 1-propyl-2,3-dimethyl imidazolium iodide was used as the electrolyte.

2.3.5 Counter electrode

A 20 nm thick Platinum (Pt) layer was sputtered on the FTO. The dye anchored photoanode and Pt-counter electrode were assembled into a sandwich type cell. The edge of the FTO outside of the cell was cleaned with ethanol and acetone in order to have a good electrical contact for the measurements.

2.4 Device characterization

2.4.1 I-V characterization

The directly measurable parameters of a photovoltaic cell are short-circuit current (\( I_{sc} \)), open circuit voltage (\( V_{oc} \)), fill factor (FF) and power conversion efficiency (PCE). Typical I-V curves with and without illumination are shown
in Figure 2.3. The dark curve shows a typical diode characteristic. Under illumination the I-V curve is shifted towards negative currents because of the photo generated current. $I_{sc}$ is the short-circuit current, $V_{oc}$ is the open circuit voltage, MPP is the maximum power point and $P_{max}$ is the maximum power output of the solar cell.

Photocurrent measurements were carried out using a XES-151 S solar simulator (San Ei, Japan) under AM1.5G conditions. The level of standard irradiance (100 mW cm$^{-2}$) was set with a calibrated c-Si reference solar cell. Data acquisition was facilitated by a source meter – Keithley 2400.

The open circuit voltage ($V_{oc}$) is defined as the voltage at which no current flows through a solar cell. The fill factor (FF) - The maximum electric power $P_{max}$ of a photovoltaic cell is determined by the maximum power point in the I-V Curve. Therefore, the fill factor is defined as
The fill factor is significantly determined by the serial electrical resistance of the cell and therefore by the mobilities of charge carriers in the organic layers of the cell.

Power conversion efficiency (PCE) or $\eta_p$: The efficiency $\eta_p$ is the maximum electrical power $P_{\text{max}}$ per light input $P_I$. For an efficient device a large fill factor, a large short-circuits current and a large open circuit voltage is needed. It is not sufficient to optimize only one of these parameters for efficient photovoltaic cells. Since the electrical response of the solar cell on the incident light is strongly dependent on its spectrum, standardized solar simulators which simulate an AM 1.5 spectrums are used for device characterizations.[41]

$$ \eta_p = \frac{P_{\text{max}}}{P_I} = \frac{I_{sc}V_{oc}}{P_I} FF $$  \hspace{1cm} (2.5)

A specific theory describing the current-voltage dependence in excitonic solar cells i.e. both organic solar cells (OSCs) and dye sensitized solar cells (DSCs) is still missing, one has to use equations describing inorganic devices. Despite the fact that the photo current in organic solar cells is generated in a significantly different way compared to inorganic cells, the inorganic equations describe the current-voltage characteristics in the these cells effectively. [92-94]
The current-voltage characteristic of an ideal solar cell can be described as the sum of the dark current of a diode \[ I(V) = I_{sat}\left(\exp\frac{eV}{n k_B T} - 1\right) \] \hspace{1cm} (2.6)

and the photocurrent contributing equation is

\[ I(V) = -I_{ph} \] \hspace{1cm} (2.7)

\( I_{sat} \) is the diode saturation current and \( n \) is the diode ideality factor. The ideality factor is derived to 1 by semiconductor theory. However, from empirical measurements it has been found that the real diodes deviate from the ideal diode relation \((n = 1)\). Adding up the equation (2.6) and (2.7) results in equation (2.8) \[ I(V) = I_{sat}\left(\exp\frac{eV}{n k_B T} - 1\right) - I_{ph} \] \hspace{1cm} (2.8)

Figure 2.4 Ideal solar cell consisting of a current source \( I_{ph} \) shunted by a diode.

The equivalent circuit of an ideal solar cell can be drawn from the standard equation as shown in Figure 2.4 which consists of an ideal diode and a current source in parallel.
The simplest extension of the ideal circuit to a real device incorporating the actual losses via a series resistance $R_s$ and a parallel resistance $R_p$ is shown in Figure 2.5. $R_s$ represents contact resistances such as ohmic losses in the front and rear contact. $R_p$ includes any current bypassing the DA- interface as well as shunt currents through shorts. The solar cell equation considering the series resistance $R_s$ and a parallel resistance $R_p$ becomes equation (2.9).[92, 94]

$$I(V) = -I_{ph} + I_{sat} \left( \exp \left( \frac{e(V - IR_s)}{n k_B T} \right) - 1 \right) + \frac{V - IR_s}{R_p}$$  \hspace{1cm} (2.9)$$

The I-V curve is substantially modified by these two resistors, since the voltage $V (R_s) = IR_s$ drops over the serial resistance, whereas the shunt adds the current $I_p = (V - IR_s)/R_p$ to the output current. The operation mode $V (I = 0) = V_{oc}$ defines the open circuit voltage of a solar cell; $V (I = I_{sc}) = 0$ the short circuit current.
2.4.2 Incident Photon-to-Current Conversion Efficiency (IPCE)

The external quantum efficiency (EQE) or IPCE gives insight to the spectral response of a photovoltaic device. It is defined as the number of electrons delivered to an external circuit divided by the number of incident photons at a specific wavelength:[41]

\[
EQE(\lambda) = \frac{I(\lambda) \cdot hc}{qP_0(\lambda) \cdot \lambda} \tag{2.10}
\]

Where \( I(\lambda) \) is the current density, \( q \) the electronic charge, \( P_0(\lambda) \) the incident power, \( h \) Planck’s constant, \( c \) the speed of light in a vacuum.

\[
I_{sc} = \int \lambda EQE(\lambda)P(\lambda)d(\lambda) \tag{2.11}
\]

The theoretical short circuit current ISC can be obtained from the measured EQE, which is convolved with the AM 1.5G solar spectrum and integrated over all wavelengths.

EQE characterization is obtained by recording the photocurrent responding to illumination with monochromatic light at different wavelengths. A 150 W Xe lamp is focused onto a LOT-Oriel Omni 150 monochromator. The illumination wavelength is swept from 280 nm to 800 nm in steps of 2 nm. Devices are kept in an opaque metal box during the measurements. The light intensity at different wavelengths is calibrated with a Fraunhofer Institute certified silicon reference solar cell equipped with a KG5 filter.
2.4.3 Temperature and photon flux dependence measurement

The temperature (T) and photon-flux (Φ) dependent I-V measurements are carried out in a continuous helium flow cryostat maintained at a pressure of \( \sim 10^{-5} \) mbar. White light intensity calibrated to a maximum of \( \sim 100 \) mW/cm\(^2\) inside the cryostat was used as the illumination source. The vacuum pressure \( \sim 10^{-5} \) mbar has to be maintained in the cryostat chamber during the measurement for obtaining the correct values. The current – voltage characteristics of the two types of devices were measured by varying the light intensities between 5 and 100 mW/cm\(^2\) in the temperature range 143–323 K. The measurements are made with Janis cryostat and the illumination is provided by the white light source via fiber illuminator (Nikon).

2.4.4 CELIV and Photo-CELIV measurements

Charge carrier mobility techniques in organic materials can be classified according to e.g., the mode of charge generation (photogenerated, doping induced, electrostatic, or injected by electrical contacts) or as transient or (quasi-) steady state. CELIV technique is used to determine charge carrier mobility and recombination in bulk heterojunction solar cells. The measurement principles and the schematic responses of these transient conductivity techniques are illustrated in Figure 2.6.
In the CELIV technique the equilibrium charge carriers are extracted from a dielectric under a reverse bias voltage ramp ($A=dU_{\text{max}}/dt_{\text{pulse}}$). The mobility of extracted charge carriers is calculated from the CELIV transients i.e. from the time when the extraction current reaches its maximum ($t_{\text{max}}$). The CELIV technique measures the equilibrium charge carriers that are generated by traps or dopants due to oxygen or moisture. In general, due to the wide band gap of most organic materials, the amount of equilibrium charge carriers extracted by CELIV technique is very low, but it can be increased by chemical doping. Alternatively, charge carriers can also be photogenerated by a short laser pulse. The photogenerated charge carriers then undergo recombination or extracted under the built-in field through the external circuit (short circuit condition). The built-in field can be compensated by applying a DC offset bias ($U_{\text{offset}}$) resulting in flat band condition, in which case the photogenerated

Figure 2.6 The pulse sequence and schematic response of the CELIV and photo-CELIV technique.

\[
\mu = \frac{2d^2}{3A t_{\text{max}}^2 \left[ 1 + 0.36 \frac{\Delta j}{j(0)} \right]}
\]
charge carriers are forced to meet and recombine. The remaining charge carriers which does not undergo recombination can be extracted by applying a reverse bias voltage ramp after an adjustable delay time (\( t_{del} \)) determining their lifetime (Photo-CELV). The photo-CELIV measurement is most conveniently carried out when the current due to the capacitance displacement (\( j(0) = A \times \varepsilon \varepsilon_0 / d \)) equals to the extraction current at its maximum \( \Delta j \). This experimental condition is achieved by selecting the proper thickness of the sample or by selecting a suitable ramp rate. The calculation of the mobility in the Photo-CELIV technique is shown in Figure 2.6. The Photo-CELIV technique offers the possibility to study charge relaxation phenomena (density relaxation) by varying \( t_{del} \), the determination of the concentration dependence of the mobility by changing the incoming light intensity, and the voltage (electric field) dependence of the mobility by changing the maximum of the applied voltage pulse (\( U_{max} \)).[95-97]

![Schematic representation of the Transient Photovoltage measurement (TPV) technique.](image-url)
2.4.5 Transient Photovoltage measurements

Transient Photovoltage (TPV) measurements were performed by connecting the devices to high input impedance (1 MΩ) of the oscilloscope as shown in Figure 2.7. The device was illuminated with various white light intensities in order to change the V_{oc} condition of the device. A pulsed laser (wavelength: 532 nm, pulse width<5 ns, pulse repetition rate 1 Hz) was used to generate a small perturbation on Voc (λV_{oc}< 20 mV), since the system is in open-circuit conditions, Voc decay is proportional to the photogenerated excess carriers relaxation (dλV_{oc}/dt ∼ dλn/dt) that allows measuring the carrier lifetime directly.[98, 99]

2.4.6 Electrochemical Impedance Spectroscopy (EIS)

EIS is one of the most powerful tools for understanding the electron transport kinetics in DSCs. EIS is a steady state measurement technique used for evaluating the current response of the device to the applied AC voltage as function of frequency. EIS has been widely employed to investigate the kinetics of photoelectrochemical and electrochemical processes including the various ionic and electronic processes occurring in the DSCs. Typical characteristic impedance spectrum (Nyquist plot) along with the electrical transmission line model of equivalent circuit for DSCs is shown in Figure 2.8. The transmission line model is basically a combination of resistance (R) and capacitance (C). The series resistance, along with the sheet resistance of fluorine-doped tin oxide (FTO) glass and the contact resistance of the cell is denoted by R_s. The series resistance and the capacitance of the FTO/metal oxide interface are denoted by R_{CO} and C_{CO} respectively. The charge transfer
resistance and subsequent double layer capacitance of the FTO/electrolyte interface are denoted by $R_{\text{TCO}}$ and $C_{\text{TCO}}$ respectively. The transport resistance of the metal oxide film (photoanode) is represented by $r_t$. The charge transfer resistance and the charge recombination processes between electrons in the metal oxide photoelectrode and electrolyte is determined by $r_{\text{CT}}$. The chemical capacitance of the metal oxide film is denoted as $C_{\mu}$. The Warburg diffusion of ions in the electrolyte is represented as $Z_d$. Finally, the charge transfer resistance and the double layer capacitance of the platinized FTO counter electrode are denoted as $R_{\text{Pt}}$ and $C_{\text{Pt}}$ respectively. Therefore, EIS serves to be a valuable tool for evaluating (i) electron transport resistance through metal oxide film, (ii) ion diffusion through electrolyte, (iii) chemical capacitance at the metal oxide/electrolyte interface, (iv) double layer charge transfer capacitance at the FTO/electrolyte interface, and (v) double layer charge transfer capacitance at the platinized FTO counter electrode.[100] [101]

![Diagram of equivalent circuit](image)

Figure 2.8 Typical impedance spectra of DSCs (Nyquist plot) and its electrical transmission line model of equivalent circuit.
3 Band structure engineered interfacial layers for highly efficient and stable organic solar cells

3.1 Introduction

As detailed in the Chapter 1, charge transport across the interfacial layers play a dominant role in the final PCE and stability of OSCs. This chapter deals with engineering of metal oxide semiconductors used as interfacial layers, both hole and electron conducting, for efficient charge extraction. We chose the inverted geometry because it offers the advantage of combining high PCE and stability. Firstly, we studied the effect of hole transport layer (MoO₃) in an inverted geometry on its PCE and stability while keeping Ca as electron transport layer. The rationale of selecting Ca as ETL is to reduce the number of variables in the given experiment thereby focusing on the effect of only one metal oxide interlayer - MoO₃ (HTL). Secondly, the optimized hole transport layer is used for further optimization of the electron transporting layer (ZnO).

3.2 Functions of MoO₃ as hole transport layer

A number of hole transport materials are proposed for the OSCs, a brief account of which are given in the Chapter 1. Among the various transitional metal oxides used as HTL, MoO₃ has gained significant attention for improving device performance and stability in OSCs.[102-105] The MoO₃ HTL reduces the charge recombination by suppressing the exciton quenching as well as the resistance at the photoactive layer/anode interface.[106] Besides, MoO₃ HTL also serves as an optical spacer for improving the light absorption thereby enhancing the photocurrent.[107-109] However, MoO₃ is highly sensitive to oxygen and moisture; trace amounts of oxygen in nitrogen-filled
glove box, where the device is fabricated, are shown to have detrimental effects on its electronic levels thereby imposing severe drawbacks in the device stability.[110] Generally, the hole transport in nanostructured MoO3 layer occurs via the shallow defect states present in its band gap formed as a result of oxygen vacancies.[111-113] These oxygen vacancies serve as n-type dopants and lead to Fermi-level pinning at the photoactive layer–MoO3 interface.[114] The mechanism of the charge transfer process across MoO3 interlayer is represented in Figure 3.1, which shows that the holes are extracted by injecting electrons into the HOMO of the donor (P3HT). Subsequently, the holes transferred to MoO3, hop to the Ag electrode through the shallow defect states generated by the oxygen vacancies.

Figure 3.1 Schematic showing the mechanism of hole transport across the Molybdenum trioxide (MoO3) interlayer.
On the other hand, the defect states are depleted for a more ordered MoO$_3$ lattice with lesser density of oxygen vacancies thereby decreasing its hole-conductivity. Stability studies performed by Girotto and Voroshazi et al [115] have shown that solution processed MoO$_3$ improves the device stability ~1000 h under dark (shelf conditions) in normal geometry devices. In the case of inverted geometry such solution processing technique may not be suitable for long term stability because the precursor solution has to be spin coated on top of P3HT: PCBM blend layer, in which the solvents from the precursor may have detrimental effect on the adjacent blend layer affecting the performance and long term device stability. Though some reports have shown improved device stability using MoO$_3$ interlayer as HTL and ZnO as ETL in inverted device geometry, the mechanism behind the processes of improving the stability is not well explored.[116, 117]

3.3 Fabrication of inverted device with Ca and MoO$_3$

Solar cells with device architecture of ITO/Ca/P3HT: PCBM/MoO$_3$/Ag as shown in Figure 3.2 was fabricated by vacuum depositing a thin Ca layer (1 nm) with a base pressure of ~10$^{-7}$mbar onto pre-cleaned, pre-patterned indium tin oxide (ITO) glass substrates. Subsequently, a mixture of P3HT and PCBM dissolved in the ratio of 1:0.8 in 1, 2-dichlorobenzene solution was spin coated on the ITO/Ca layer. The thickness of the blend layer was ~200 nm. The film was then annealed at 120 °C for 10 minutes. The MoO$_3$ layer of different thicknesses ~3.5 to 10 nm was then thermally evaporated on to the above film in a vacuum chamber with a base pressure of ~10$^{-7}$ mbar. The rationale of fabricating device with different MoO$_3$ interlayer thickness is to identify the
optimum thickness to maximize the performance. Finally, Silver (~100nm) electrode was deposited onto the MoO₃ layer at a pressure \( \sim 10^{-5} \) mbar. Area of the devices was \( \sim 0.09 \) cm². The devices were annealed at 120 °C for 10 minutes using a hotplate in nitrogen filled glove box (< 1 ppm O₂ and H₂O).

3.4 **Photovoltaic performance and IPCE of the device (ITO/Ca/P3HT:PCBM/MoO₃/Ag)**

The photovoltaic parameters of the devices with different MoO₃ interlayer thicknesses (3-20 nm) were studied and the corresponding J-V spectra are shown in Figure 3.3. The highest PCE of 3.2% was observed for the device with MoO₃ interlayer thickness of 5 nm with Jsc of 9.6 mA cm⁻², Voc of 576 mV with a fill factor of 59%. The Voc is higher in 5nm device compared to that of 3 nm because the 5 nm thick MoO₃ forms a continuous interlayer on top of the photo-active layer, thereby forming an effective interface for hole transport. It also protects the active layer from the migration of the electrode materials.
With further increase in MoO$_3$ thickness (10 and 20 nm), the Jsc drops slightly along with the Voc as shown in Table 3.1. It has also been reported that high MoO$_3$ interlayer thickness could increase the series resistance of the device which affects the PCE.[118]

Table 3.1 Effect of MoO$_3$ thickness on the photovoltaic parameters

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Jsc (mA/cm$^2$)</th>
<th>Voc (mV)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 nm</td>
<td>9.3</td>
<td>564</td>
<td>57.7</td>
<td>3.0</td>
</tr>
<tr>
<td>5 nm</td>
<td>9.6</td>
<td>576</td>
<td>59</td>
<td>3.2</td>
</tr>
<tr>
<td>10 nm</td>
<td>9.2</td>
<td>537</td>
<td>61.1</td>
<td>3.0</td>
</tr>
<tr>
<td>20 nm</td>
<td>9.1</td>
<td>528</td>
<td>59.1</td>
<td>2.8</td>
</tr>
</tbody>
</table>

The device with the optimized thickness is then subjected to further optimization by varying the annealing conditions. One set of the optimized device was annealed at 120 °C for 10 minutes using a hotplate placed in a cryostat chamber at the pressure of ~10$^{-5}$ mbar (device V) and the other set in
nitrogen filled glove box (< 1 ppm O₂ and H₂O) (device N). Many such devices/samples are prepared in each set (device V and N).

Figure 3.4 Current density - Voltage characteristics of the device ITO/Ca/P3HT: PCBM/MoO₃/Ag annealed in nitrogen and vacuum.

Current density - Voltage (J-V) measurements to evaluate the photovoltaic parameters of the freshly prepared devices are carried out at room temperature under simulated illumination (AM 1.5G) in glove box conditions. J-V spectra of the devices with vacuum and nitrogen annealed MoO₃ interlayer is shown in Figure 3.4. The device V showed slightly better PCE of 3.5% compared to that of the device N of 3.2%. It can be observed that the freshly prepared devices (both V and N) do not show any significant change in the photovoltaic parameters. The photovoltaic parameters between the two devices annealed in nitrogen and vacuum conditions are listed in Table 3.2.
Table 3.2 Photovoltaic parameters of the devices annealed in nitrogen (N) and vacuum (V)

<table>
<thead>
<tr>
<th>Device</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen annealed (N)</td>
<td>0.572</td>
<td>9.59</td>
<td>59</td>
<td>3.2</td>
</tr>
<tr>
<td>Vacuum annealed (V)</td>
<td>0.577</td>
<td>9.44</td>
<td>63.7</td>
<td>3.5</td>
</tr>
</tbody>
</table>

The IPCE spectra of the two devices (V and N) are shown in Figure 3.5. The maximum quantum efficiency of ~65% and ~63% at 550 nm was recorded for the devices V and N respectively. Both devices followed similar IPCE trend suggesting that the annealing conditions do not alter the light harvesting properties of the device. The role of MoO$_3$ as optical spacer does not vary much with the annealing conditions.

Figure 3.5 IPCE spectra of the device - ITO/Ca/P3HT:PCBM/MoO$_3$/Ag for device V and N.
3.4.1 Dark stability of the device with Ca and MoO₃

The stability studies (ISOS-D-1-shelf) performed on device annealed in Vacuum condition is able to retain ~80% of their original efficiency even after 30 days (~700h) as shown in Figure 3.6. This is the first report to show such high stability for the inverted device structure of ITO/Ca/P3HT: PCBM/MoO₃/Ag with thermally deposited MoO₃ interlayer.

![Figure 3.6 Stability of the inverted devices with Ca (ETL) and MoO₃ (ETL) in dark conditions tested under Protocol ISOS-D-1.](image)

The stability obtained in vacuum annealed device is comparable to the stability studies under dark conditions (ISOS-D-1-shelf) reported by Voroshazi et al [119] with the normal geometry employing evaporated MoO₃ and Ca as buffer layers. Moreover the dark stability (ISOS-D-1-shelf) of the device V is even slightly better compared to the reports of stability studies using thermally evaporated MoO₃ interlayer in device structure of ITO/ZnO/P3HT: PCBM/MoO₃/Ag.[117] Those devices maintained ~70% of their original efficiency under dark storage conditions after 700h (~30 days). Exact comparison may not be possible since the device area used by them is
0.134 cm\(^2\) and our device is 0.09 cm\(^2\). On the other hand, the device N showed commendable decay of its photovoltaic parameters over a period of thirty days. Therefore, the vacuum annealed MoO\(_3\) improves the dark stability of the device while maintaining high PCE.

### 3.4.2 Photo-stability of the device with Ca and MoO\(_3\)

The photo-stability of both devices (V and N) was evaluated using the Protocol ISOS-L-1 (under continuous illumination). However, its stability under light conditions as shown in Figure 3.7 is rather poor because of the Ca layer used as the ETL, which transmit all wavelengths including UV. Both devices retain only \(\sim50\%\) of their original efficiency upon constant illumination (1 Sun at ambient conditions) for 420 hrs.

![Figure 3.7 Stability of the inverted devices with Ca (ETL) and MoO\(_3\) (ETL) under constant illumination tested under Protocol ISOS-L-1.](image)

The UV induced degradation of the photoactive layer is expected to be responsible for the observed poor stability of the device in its real operating
conditions. Such degradation could be avoided by using wide band gap metal oxide semiconductors with their band gap in the UV region.

3.5 **Function of ZnO as electron transport layer**

Among the various ETL materials proposed, Zinc Oxide has promising prospects because of its optical transmittance in visible range, relatively high electron mobility (0.066 cm²/Vs), large exciton binding energy (60 meV) and wide direct band gap (~3.4 eV).[120] Additionally, ZnO thin films can be readily fabricated by solution processing techniques followed by subsequent thermal annealing treatment.[11,27,28] Air stable devices employing ZnO ETLs have been reported to retain near 80% of their original efficiency even after 30 days in dark (shelf) conditions.[120, 121] On the other hand, ZnO functionality as an efficient ETL reduces photo-degradation considerably when exposed to UV containing light for a prolonged time.[117, 122] Stability studies performed by inter-laboratory collaboration (ISOS-3) [117] showed that even minor difference in the processing conditions of ZnO is found to be critical for device lifetime. Though some reports show that this UV induced photo-degradation of the ZnO layer can be reversed by simple reverse-biasing, [123] the stability of the device is not fully recovered, especially from the degradation of the active layer under such circumstances. It is better to have a proactive approach to decrease the UV induced degradation by means of optimizing the fabrication conditions of ZnO thin films. UV-ozone treatment of freshly prepared ZnO thin films before device fabrication was found to have a beneficial effect in improving the device stability.[122, 124] Increase in annealing temperature of the ZnO layer has been found to decrease the series
resistance significantly, owing to the increase in improved crystallinity.[121]
Though reports have shown that the annealing temperature determines the
functionality of ZnO layer when exposed to simulated sunlight with UV and
without UV significantly,[122] the mechanism behind the processes affecting
the stability of ZnO based devices still remains an open debate.[60, 121, 123,
125] Numerous research were carried out to improve the functionality of ZnO
layer to enhance device performance, but very few reports exploits the reason
or mechanism that affects the long term dark and photo-stability of ZnO
interlayers employed in inverted device architecture.[117, 123, 126]

3.6 Preparation of the solution processed ZnO interlayer

The ZnO precursor solution for spin coating was prepared by dissolving zinc
acetate di-hydrate \([\text{Zn} \ \text{(CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}, \ \text{Alfa Aesar, 99.9\%}, \ 0.6 \ \text{g}]\) and
ethanolamine \((\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}, \ \text{Sigma Aldrich, 99.5\%}, \ 0.15 \ \text{g})\) in 2-
methoxyethanol \((\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}, \ \text{Aldrich, 99.8\%}, \ 5 \ \text{mL})\) under vigorous
stirring for 24 h in air. One millilitre of ammonia \((\text{NH}_3)\) was then added to the
above solution and stirred for 2 h. The solution was then filtered with 0.25 \(\mu\text{m}\)
PVDF filter to remove any insoluble impurities. The ZnO thin films with
optimized thickness (~25-30 nm) were produced by spin coating the prepared
precursor solution onto the cleaned ITO substrates at 3500 rpm for 90 s. The
substrates with spin casted ZnO films are then annealed at 240\(^\circ\)C (A) or 160\(^\circ\)C
(B) in air for 3 h. The ZnO thin films thus formed were washed mildly with
isopropyl alcohol and blow dried in air. The annealed ZnO thin films were
subjected to UV-Ozone treatment for 10 min in a glove box.
3.6.1 ZnO film morphology

The SEM images of the films annealed at the two temperatures are shown in Figure 3.8A. The films were homogeneous and without any cracks. The particles of the films annealed at 160 °C were of size 7 – 10 nm, whereas the film annealed at 240°C were in the 15 – 20 nm range. Figure 3.8B shows the micrographs of the B NPs. The dimensions of the nanoparticles is quite larger compared to A NPs with the size of about 15-20 nm. Moreover the distribution is not as uniform as the A NPs and intermittent regions of compacted surface is also observed (dark patches). This compaction or surface agglomeration reduces the percolation propensity of the active layer and reduces the effective charge transport pathways across the active layer and the ZnO (ETL).

![Figure 3.8 SEM images of a) ZnO nanoparticles annealed at 240°C (A) b) ZnO nanoparticles annealed at 160°C (B).](image)

The AFM images (3D View) of the ZnO NP films annealed at annealed at 240 °C and 160 °C are shown in Figure 3.9A and B respectively. The root mean square roughness is ~ 15nm and ~40 nm for the ZnO films A and B respectively.
Figure 3.9 AFM images (3D View) of the ZnO interlayers (A) annealed at 240 °C (B) annealed at 160 °C.

The top view (2D images) portraying the surface morphology of the ZnO films (A and B) is shown in Figure 3.10. The ZnO-A films have uniformly distributed ZnO particulates than the ZnO-B films owing to higher annealing temperature (240°C).

Figure 3.10 AFM - 2D images (Top View) of the ZnO interlayers (A) annealed at 240°C (B) annealed at 160 °C.

3.6.2 XRD characteristics of the ZnO interlayer

The XRD patterns of the ZnO nanostructures annealed at the two temperatures 160 and 240 °C is shown in Figure 3.11, all the peaks of which are indexed for the ZnO hexagonal phase with Wurtzite crystal structure [space group C6V
(P6_{3}mc)] having lattice parameters \( a = b = 3.25 \, \text{Å} \) and \( c = 5.2 \, \text{Å} \) (JCPDS card no.0-3-0888). The XRD peaks of the sample annealed at 240 \(^{\circ}\)C were more intense and sharper than that annealed at 160 \(^{\circ}\)C thereby indicating higher crystallinity for the former as expected.

![XRD spectra](image)

Figure 3.11 XRD spectra of both the ZnO nanostructures.

3.7 **Fabrication of inverted device with ZnO and MoO\(_3\)**

Inverted OSCs (IOSCs) of device architecture ITO/ZnO/P3HT:PCBM/MoO\(_3\)/Ag was fabricated by spin coating solution processed ZnO onto pre-cleaned, pre-patterned ITO coated glass substrates. The substrates incorporating spin casted ZnO films annealed at 240\(^{\circ}\)C is used as ETL for fabricating device A and that annealed at 160\(^{\circ}\)C is used for device B.
A mixture of P3HT and PCBM dissolved in the ratio of 1:0.8 in 1, 2-
dichlorobenzene solution was spin coated on the prepared ITO/ZnO layer. The
thickness of the blend layer was ~200 nm. The films were then annealed at
120 °C for 10 min. The hole transporting MoO₃ layer of thickness ~5 nm was
then thermally evaporated on to the above films in a vacuum chamber with a
base pressure of ~10⁻⁷ mbar. Finally, silver (~100 nm) electrode was deposited
onto the MoO₃ layer at a pressure ~10⁻⁵ mbar. Both devices were annealed at
~70 °C for 10 min in a cryostat chamber at the pressure of ~10⁻⁵ mbar. The
device structure of the IOSCs incorporating ZnO films as ETL is shown in
Figure 3.12.

3.8 Photovoltaic performance and IPCE of the device (ITO/ZnO/P3HT:
PCBM/MoO₃/Ag)

Current density-Voltage (J-V) characteristics for the devices using ZnO NP
interlayers annealed at 240°C (device A) and 160°C (device B) are shown in
The device A showed best performance of 3.8% with ~30% higher short circuit current density ($J_{SC} \sim 10.9 \text{ mA/cm}^2$) compared to the device B (~8.4 mA/cm$^2$).

![Figure 3.13](image)

**Figure 3.13 Current density-Voltage (J-V) characteristics of the devices with A and B nanoparticles.**

**Table 3.3 Photovoltaic parameters of the devices annealed at 240 °C (ZnO-A) and 160 °C (ZnO-B)**

<table>
<thead>
<tr>
<th>Device</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO-A</td>
<td>0.57</td>
<td>10.9</td>
<td>61.6</td>
<td>3.8</td>
</tr>
<tr>
<td>ZnO-B</td>
<td>0.53</td>
<td>8.43</td>
<td>60</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Device B exhibited lower Open circuit voltage ($V_{OC}$) than device A, however, the fill factor of both devices remind practically similar ~60% (refer Table 3.3). Following the above enhancements in $J_{SC}$ and $V_{OC}$, the photovoltaic conversion efficiency (PCE) of the device A was ~40% higher (3.8 %).
compared with that of the device B (2.70%). To substantiate the observation of J – V measurements, quantum efficiency of the two devices were evaluated.

The IPCE spectra of the two devices are shown in Figure 3.14. The device A recorded a maximum quantum efficiency of ~78% at 550 nm against ~58% by the other device. Both devices followed similar IPCE pattern except for a 20% increase in IPCE for the device A. Thus, the device A shows enhanced photovoltaic performance in which the only variant is the degree of crystallinity in its ETL compared with the other. The increase in the IPCE can be attributed to the improvement in light absorption in the blend layer through efficient light transmission and scattering of light by the A interlayer. The fine distribution of NPs enables this re-scattering of light which improves the conversion efficiency effectively.

Figure 3.14 IPCE spectra of the device employing ZnO A and B nanoparticles.
3.8.1 Dark stability of the device with ZnO and MoO₃

The results of the dark device stability are summarized in Figure 3.15. The normalized PCE of the devices measured under ISOS-D-1(shelf) protocol as a function of time that shows that the devices A and B are air-stable retaining ~81% and ~78% of their original efficiency even after 30 days of exposure to ambient conditions.

![Figure 3.15 Stability of the inverted devices with ZnO (ETL) and MoO₃ (ETL) under dark conditions tested under Protocol ISOS-D-1.](image)

3.8.2 Photo-stability of the device with ZnO and MoO₃

The normalized PCE of the devices as a function of time under ISOS-L-1 (laboratory simulations) conditions is shown in Figure 3.16.
The devices A and B retained ~64% and ~48% of their original efficiency after 400 h of constant illumination, respectively. The reason behind improved photo-stability and the underlying mechanisms are discussed in chapter 4.

3.9 Conclusions

To summarize, the IOSCs with MoO$_3$ as hole transporting interlayer (HTL) were fabricated and the optimum film (MoO$_3$) thickness was determined. The optimized device was then subjected to different annealing conditions i.e. nitrogen and vacuum in order to improve the efficacy of MoO$_3$ interlayer on PCE and lifetime. The freshly prepared devices did not exhibit any significant difference in terms of PCE and other photovoltaic parameters, whereas it had an immense impact on the long term operational stability. The stability studies performed under dark (shelf) conditions showed that the device annealed in
vacuum has better lifetime when compared to the device annealed in nitrogen. On the contrary, both devices exhibited moderate photo-stability under continuous illumination. In order to overcome this issue, Ca interlayer is replaced by ZnO as a UV absorbing ETL. ZnO films of varying morphology and crystallinity are synthesized, which is then incorporated in the IOSCs. The IOSCs employing highly crystalline ZnO films exhibited improved PCE and lifetime. Next chapter deals with the in-depth analysis of the devices in order to ascertain the mechanism behind improved efficiency and stability in these devices.
4 Charge transport in the IOSCs employing the modified interfacial layers

4.1 Introduction

The previous chapter demonstrated that vacuum annealed MoO$_3$ as HTL and the solution processed ZnO (annealed at a temperature of $\sim$240 °C) as ETL improve the stability and PCE of inverted solar cells. This chapter deeply investigates the underlying mechanism for those enhancements. The methodology involves (i) quantification of trap depth, i.e., the extent to which the localized energy states occurs in the band gap of the material, from current – voltage measurements of the device under conditions of varying photon flux ($\Phi$) and temperature (T), and (ii) estimation of charge mobility and carrier concentration in the device through charge extraction by linearly increasing photovoltage measurements. First, the characteristics of the ITO/Ca/P3HT: PCBM/MoO$_3$/Ag device is presented to isolate the effect of the HTL in consistent with the previous chapter and subsequently similar studies are extended to the complete device ITO/ZnO/P3HT: PCBM/ MoO$_3$/Ag.

4.2 Photon flux and temperature dependent current-voltage characteristics of the device (ITO/Ca/P3HT: PCBM/ MoO$_3$/Ag)

The encapsulated devices V (vacuum annealed) and N (nitrogen annealed) were subjected to temperature and photon-flux ($\Phi$) dependent studies for evaluating trap depth and recombination. The temperature (T) and photon-flux ($\Phi$) dependent I-V measurements were carried out in a continuous helium flow cryostat maintained at a pressure of $\sim$10$^{-5}$ mbar. White light intensity calibrated to a maximum of $\sim$100 mW/cm$^2$ inside the cryostat was used as the
illumination source. The current–voltage characteristics of the two types of devices were measured by varying the light intensities between 5 and 100 mW/cm² in the temperature range of 143–323 K.

Figure 4.1 I-V characteristics of device V (A) and device N (B) as a function of illumination intensity ($\Phi$) at constant $T$ (323K). Variation of efficiency (C), short circuit current (D), as a function of $\Phi$ at $T = 323K$ is shown for both devices.

I–V curves and the corresponding photovoltaic parameters (Jsc and PCE) measured as a function of $\Phi$ at constant $T$ (323 K) for the freshly prepared devices annealed in vacuum and nitrogen conditions is shown in Figure 4.1 (A-D). The PCE and Jsc increased monotonously with illumination intensity for both devices which is attributed to the increased generation rate of bound
electron-hole pairs with the incident illumination intensity. It also indicates that the photogenerated excitons are effectively dissociated depicting the similarity in integrity of the photo-active layer in both devices (Riedel 2004). The observed difference in PCE and Jsc values (magnitude not the trend) at their corresponding incident illumination intensity is due to the difference in the charge collection efficiency at the respective electrodes, depending on the transport across the interfacial layers.

Figure 4.2 Open circuit voltage ($V_{oc}$) as a function of illumination intensity ($F$) at constant $T$ (323K).

The increase in $V_{oc}$ with increase in illumination intensity as shown in Figure 4.2 indicates that the quasi-Fermi levels are constant throughout the entire active layer, including both drift and diffusion of charge carriers.[127] Therefore, the observed results from the illumination intensity dependent measurements indicate that the change in processing conditions i.e. annealing in vacuum and nitrogen conditions did not have any effect on the active layers of the device (V) and (N) respectively.
I – V curves measured as a function of temperature (T) at constant illumination intensity (100 mW/cm²) for the devices annealed in vacuum (V) and nitrogen (N) and their corresponding photovoltaic parameters is shown in Figure 4.3 (A–F). At constant Φ, the PCE, JSC, and FF increase monotonously with increase in temperature whereas Voc follows a decreasing trend in both cases. In order to understand the effect
of temperature on the photovoltaic parameters in OSCs, a brief picture of the phonon assisted transport mechanism is described as follows.

In OSCs, the carrier mobility is thermally activated; charge transport occurs via localized states assisted by the phonons i.e. the carrier mobility increases with increase in temperature via phonon activated hopping mechanism. The charge conductivity and carrier mobility is related to temperature as per the equations [128]

$$\sigma \propto e^{\frac{-\Delta E}{2kT}}$$

and

$$\mu = \frac{\sigma}{en}$$

where $\sigma$ is conductivity ($\Omega^{-1}$ cm$^{-1}$), $e$ is the charge of carriers, $n$ is the charge carrier concentration, $k$ is the Boltzmann constant, $T$ is temperature and $\Delta E$ is the activation energy or trap depth.

In general in excitonic solar cells, including OSCs, one of the main sources of recombination is the difference in two characteristic times involved in the device, viz., the electron lifetime and the charge transport time or charge mobility. The mobile charges having exceedingly higher transport time for their collection than their lifetime undergo recombination. In semiconducting nanostructures, charge transport occurs via thermally activated hopping through the localized states or trap states at the bottom of its conduction band, the density of these trap states is distributed exponentially within the band gap. Photogenerated carriers falling in the trap states are thermally energized by phonons thereby detrapping them to enable the charge transport.[129, 130]
The depth of this trap distribution is a function of a number of parameters including Fermi energy, electron density of states, and phonon dispersion in the material.[58, 131] Therefore, quantification of trap depth is required to understand the charge transport properties in these devices.

4.2.1 Evaluation of trap depth

The variation of $J_{SC}$ as a function of temperature for the devices V and N is shown in Figure 4.4 (A and B) respectively. The $J_{SC}$ increases with temperature in both types of devices; however, slope of the $J_{SC}$–$T$ curve is relatively smaller in the device V than the other device N.

![Figure 4.4 Variation of Jsc as a function of temperature for the devices V (A) and N (B) respectively.](image)

In general, the charge mobility in semiconductors is thermally modified; i.e., as the temperature increases, the thermal phonons increase the charge mobility by providing the activation energy required for hopping from one localized state to another.[129, 130] Under steady state, i.e., with similar trapping and detrapping frequencies, the temperature does not alter the photocurrent generation for the same light intensity whereas it assists in increasing the carrier mobility by moving the charges across the band gap.[128] However, if
the distribution of the trap states is deep such that transport time exceeds the lifetime, the charges recombine thereby lowering the $J_{SC}$. In other words, the capture of charge carriers by the trap states leads to subsequent recombination with opposite charges, resulting in variation of the current with temperature. The recombination probability therefore depends on the dwell time on trap states and will be higher at low temperatures.\[128\] $J_{sc}$ and the trap depth ($\Delta$) in OSCs is related as per the equation[128]

$$J_{sc} (T, \Phi) = J_o (\Phi) \exp \left(-\frac{\Delta}{k_B T} \right)$$  \hspace{1cm} (4.3)

where $J_o (\Phi)$ is a pre-exponential factor comprising of photogenerated charge-carrier density, its mobility and the electric field, $\Delta$ is the trap depth, $k_B$ is the Boltzmann constant and $T$ is the temperature.

Figure 4.5 Trap depth ($\Delta$) in devices V and N calculated from ln $J_{sc}$ vs 1/T curves at $\Phi = 100$ mW/cm$^2$. Inset shows the variation of trap depth ($\Delta$) as a function of $\Phi$. 
The magnitude of $\Delta$ evaluated from the dependence of $J_{sc}$ on $T$ and $\Phi$ using the equation (4.3). Trap depth ($\Delta$) in devices V and N calculated from $\ln (J_{sc})$ Vs $1/T$ curves at $\Phi=100$ mW/cm$^2$ is shown in Figure 4.5. The $\Delta$ value thus obtained is $\sim8$ and $\sim21$ meV for the devices V and N respectively. The device V presents $\Delta$ lower by a factor of nearly three than the device N. In other words, traps are shallow in the device V and deep in the device N. Figure 4.5 (inset) shows the variation of $\Delta$ calculated from the $\ln J$ vs $1/T$ curves as a function of $\Phi$. The $\Delta$ values does not vary with illumination intensity indicating that the distribution of the trap states is independent of the concentration of the photogenerated carriers. It is noteworthy to indicate that the trap depth values obtained from these devices is a resultant sum of the traps in active layer and interfacial layers. As the active layers are same in both devices, the origin of the difference in the trap depth ($\Delta$) in the device V and N is expected to arise from the MoO$_3$ interlayer, which is subjected to different processing conditions i.e. annealed in vacuum and nitrogen.

Figure 4.6 Variation of Series resistance ($R_s$) as a function of temperature in vacuum and nitrogen annealed devices.
A direct influence of the difference in $\Delta$ on the device performance could be observed from the changes in their series resistances ($R_S$) as a function of temperature. A plot of $R_S$ vs temperature (Figure 4.6) shows that the device $V$ presents nearly 4-fold lower $R_S$ at $\sim$140 K than the other device, the origin of this difference will be discussed in the following section.

### 4.2.2 Effect of trap depth on the open circuit voltage

To further confirm the role of MoO$_3$ on the $\Delta$ and subsequently the operational stability of the OSCs, we have examined the dependence of $V_{OC}$ on temperature for varying $\Phi$. The $V_{OC}$ of the OSCs is related to temperature as per the relation [133, 134]

$$V_{OC} = \frac{E_g}{e} - \frac{k_B T}{e} \ln \left( \frac{N_C^2}{n. p} \right)$$  \hspace{1cm} (4.4)

where $E_g$ is the effective band gap, i.e., $E_g = E_{g, \text{LUMO (Acceptor)}} - E_{g, \text{HOMO (Donor)}}$, $N_C$ is the effective density of states, $e$ is elementary electronic charge, and $n$ and $p$ are the electron and hole densities, respectively. The $V_{OC}$ in BHJ OSCs approaches the $E_g$ when the contacts are perfectly ohmic; i.e., when the contact allows carriers of one type to pass through and blocks the other (refer Figure 1.11). On the other hand, i.e., if the contacts are not ohmic, the $V_{OC}$ approaches the difference in the work function between the electrodes, which for the active layer combination chosen here is $\sim$0.6 – 0.65 V.[135]
For non-ohmic contacts, charge accumulation occurs at the photoactive layer–HTL interface. Figure 4.7 (A and B) shows the dependence of $V_{OC}$ on temperature as a function of $\Phi$ for both devices V and N. The $V_{OC}$ decreases linearly with increasing temperature for entire $\Phi$ for the device V although a small step was observed at ~200 K. The $V_{OC}$ of the device V obtained by extrapolating the $V_{OC} – T$ graph at $T = 0$ K, following Eq. (4.4), is ~0.7 – 0.75 V, which is much higher than the difference in work functions between the electrodes (0.6 – 0.6 V). Therefore, the $V_{OC}$ of the device V is determined by $E_g$ thereby clearly establishing that the contact is perfectly ohmic in this device. On the other hand, for the device N, the $V_{OC}$ increases linearly until 173 K after which it drastically drops. The maximum $V_{OC}$ observed was $\leq$ 0.65 V for entire $\Phi$; thereby clearly indicating that the HTL employing the MoO$_3$ is no longer ohmic in the device N. This non-ohmicity is attributed to the interfacial barrier built up at the photoactive layer – HTL interface due to
the deep trap states in the MoO$_3$ film in the device N. As noted before, this non-ohmicity made the $R_S$ of the device N to be higher at lower temperature. The Ca layer employed ETL when used in normal architecture could be oxidized to CaO on exposure to air, but in the case of inverted architecture it is protected from air exposure since it is sandwiched between ITO and the active layer. We note that the Ca layer would also create a small barrier at the interface. The electron injection barrier at the Ca/PCBM interface is shown to be $\sim$0.05–0.1 eV [136] at low temperature ($\sim$150 K), which is much lower than the $V_{OC}$ drop observed in the present case; thereby corroborating that majority of the loss comes from MoO$_3$/Ag side.

Thus the differences in the $V_{OC}$ and $R_S$ between these devices clearly demonstrate that the observed variation in the $\Delta$ between the devices originate from the hole conducting MoO$_3$ layer. As stated in the introduction section, efficient hole conductivity in the MoO$_3$ is determined from the oxygen vacancies, which in this case is produced by annealing the device in the vacuum. The shallow traps in the device V lead to efficient hole transport at the photoactive layer – HTL (P3HT/MoO$_3$) interface whereas the deep trap states in the device V lead to charge accumulation at the interface thereby creating a dipole. The interfacial dipole and the corresponding accumulated charges lead to an increase in the barrier height, and therefore, non-ohmic contact for holes is formed. These inherent anomalies existing at the interface have direct consequences on the device performance over a period of time leading to device degradation.[110] To substantiate the effect of charge accumulation on charge transport properties, the charge carrier mobility and equilibrium carrier concentration in these devices are evaluated.
4.2.3 Determination of charge mobility and carrier concentration

The difference in the charge transport mechanism in these two devices annealed at vacuum (V) and nitrogen (N) was studied by the CELIV technique. The CELIV has emerged as a powerful technique in organic electronics for its efficacy in measuring the mobility (µ) in thin film devices. In this technique, a linearly increasing voltage ramp or electric field is applied at one of the electrodes and the corresponding current transient is used to determine the µ and equilibrium carrier concentration n.[97, 137] Furthermore, CELIV also allows studying the relaxation of the charge carriers in the density of states (DOS) [95], thereby enabling simultaneous measurement of time-dependent µ and n.

The CELIV transients observed for the device V and N measured at 3V is shown in Figure 4.8(A). The µ and n were calculated from the CELIV transients and shown in Figure 4.8(B). The µ of the device V (6×10⁻⁴ cm²/V.s) is nearly twice than that of the other (3.2×10⁻⁴ cm²/V.s). The enhanced mobility in the device V attributed to its three-fold lower Δ than the other device. On the other hand, a reversal in the magnitude of n was observed between the devices V and N. The n was ~5×10¹⁵ and ~1×10¹⁶/cm³ for the devices V and N, respectively.
The observed two-fold increase in the $n$ suggests that the carriers in the device N are relaxed in its deeper trap states, whereas they are transported efficiently in the other device V on account of its lower trap depth. Moreover, it is fairly obvious that a metal oxide annealed in vacuum would result in an oxygen deficient structure. Thus, the higher stability of the device V results from its enhanced hole-conducting properties which in turn resulted from the oxygen vacancies produced due to annealing in vacuum.

4.2.4 Origin of enhanced dark stability in device (ITO/Ca/P3HT: PCBM/MoO$_3$/Ag)

Based on the results obtained from all the above studies, an explanation is provided for observed difference in dark stability between vacuum (V) and nitrogen (N) annealed devices. In the case of device N, which is annealed in nitrogen filled glove-box ($< 1$ ppm O$_2$ and H$_2$O) makes the MoO$_3$ interlayer to
react even with minute traces of O\textsubscript{2} and H\textsubscript{2}O. These reactions form defect states/trap states due to oxygen doping into the interstitials of MoO\textsubscript{3} lattice.[138] These trap states are distributed within the band gap of MoO\textsubscript{3} altering the Fermi level and thereby the work function of MoO\textsubscript{3}. [110] Besides, the traps forms a dipole inducing species at MoO\textsubscript{3}-polymer interface which changes over time due to internal diffusion altering the energy levels.

![Interfacial barrier at the P3HT/MoO\textsubscript{3} interface](image)

Figure 4.9 Interfacial barrier at the P3HT/MoO\textsubscript{3} interface (A) for device annealed in Vacuum and (B) device annealed in nitrogen.

Such kind of change in electronic levels in MoO\textsubscript{3} over time, when exposed to ambient conditions, is also reported to have a significant effect on electrical properties of MoO\textsubscript{3}.[110] Under such conditions, valence band of P3HT is not effectively pinned to the Fermi level of MoO\textsubscript{3} due to mismatch in energetic levels thereby reducing the photovoltaic performance of the device. Moreover the carrier build-up or charge accumulation at the interface is expected to chemically degrade the active layer – MoO\textsubscript{3} interface and deteriorate the device stability over time. Figure 4.9(A and B) shows the schematic of interfacial barrier formation at the P3HT/MoO\textsubscript{3} interface as a function of shallow and deep traps in device V and N respectively. In simple, device N with the deep traps correspondingly has high number of reaction sites when
exposed to ambient conditions leading to faster device degradation. On the other hand, in device V with shallow traps, the reaction sites are lesser, therefore the stability is improved.

### 4.3 Photon flux and temperature dependent current-voltage characteristics of the device (ITO/ZnO/P3HT: PCBM/MoO₃/Ag)

As discussed in chapter 3, the Ca interlayer (ETL) is replaced with ZnO NP in order to improve the performance and photo-stability of the device. Two variants of ZnO NPs are used for this purpose i.e. ZnO-A are synthesised by annealing at 240ºC while ZnO-B are annealed at 160ºC. The complete device (ITO/ZnO/P3HT: PCBM/MoO₃/Ag) fabricated with ZnO-A and ZnO-B NPs are termed as device A and B respectively. The underlying mechanism for performance and photo-stability enhancements in the ZnO (ETL) based devices are analyzed in this section, using the similar studies employed in section 4.2 of this chapter.

The variation of $J_{SC}$ as a function of temperature ($T$) for the devices A and B respectively is shown Figure 4.10. The $J_{sc}$ increases with temperature in both devices, but the slope of the $J_{sc}$-$T$ curve varies i.e. device A has lower slope compared to that of the device B. The difference in slopes can be explained based on the fact that the thermal energy provides the activation energy for the charges to hop from one localized state to another thereby improving the charge mobility similar to the mechanism discussed in section 4.2.
Under steady state conditions, the charges undergo trapping and detrapping processes on its path towards the respective electrodes. Here the temperature does not alter the photocurrent generation for the same illumination intensity but it aids in increasing the charge carrier mobility by transcending the charges across the band gap. Therefore if the slope of Jsc-T curve is higher, the trapping and detrapping processes is also higher.

4.3.1 Evaluation of trap depth

Trap depth ($\Delta$) in devices A and B is calculated from $\ln$ Jsc vs $1/T$ curves using the equation (4.3) and it is shown in Figure 4.11. Inset shows the variation of trap depth ($\Delta$) as a function of $\Phi$. Trap depth ($\Delta$) is $\sim$12 and $\sim$22 meV at $\Phi = 100$ mW/cm$^2$ and $T = 323$ K for the devices A and B, respectively. i.e., traps are shallow in the device A and deep in the device B. The reason behind the two-fold difference in magnitude of $\Delta$ is attributed to the effect of surface trap states in ZnO nanostructures (ETL) on the charge transport characteristics.

Figure 4.10 Variation of Jsc as a function of temperature for the devices A and B respectively.
In general, the oxygen molecules act as electron traps on adsorption on the ZnO surface.[139-141] The presence of uncompensated oxygen molecules along the grain boundaries is the reason of low conductivity in ZnO layers.[142, 143] Here, oxygen anions would be formed by combining with the electrons in ZnO.[139-141] The oxygen anions thus produced serves as the prime recombination centers for the photo-produced holes.[122] Greater

Figure 4.11 Trap depth ($\Delta$) in devices A and B calculated from $\ln J$ vs $1/T$ curves. Inset shows the variation of trap depth ($\Delta$) as a function of $\Phi$. 
the number of grain boundaries larger the existence of oxygen anions. UV-Ozone treatment of the ZnO layers have shown to improve the electrical conductivity by UV induced desorption of negatively charge oxygen molecules or oxygen anions which are trapped at the grain boundaries.[142] Oxygen desorption modifies the ZnO electronic properties by the release of neutral oxygen, relieving the once-bound electron free in the conduction band of ZnO thereby improving the conductivity. For the short exposure of UV photons, which causes n-doping of the ZnO layer improves its conductivity and selectivity by shifting the Fermi level upwards thereby decrease the number of minority carriers in the layer.[123] Thereby, electron injection is improved keeping the shunts minimized. This n-type doping further facilitates good electron transport at the PCBM-ZnO interface.[123] In our case both devices are pre-treated with UV ozone, thereby the reason for change in trap depth is due to the difference in crystallinity of the ZnO interlayers. In the case of device A, the crystallinity of the ZnO nanostructures are higher, thereby few defects and trap sites. This denotes that the trap states are superficial, closer to that of the conduction band in which the electron transfer from PCBM to ZnO occurs with fewer impediments and hence lower number of recombination centres was formed at the ZnO/active layer interface. This results in lesser interfacial recombination resulting in higher Jsc. On the other hand when the ZnO is less crystalline as in the case of B, more defect states and trap sites, which are distributed in varying depths are formed within the band gap of ZnO. These states act as recombination centres and need excess thermal phonons or activation to cause the band gap excitation. This depicts
the reason behind the difference in trap depth values for the devices A and B as observed in Figure 4.11.

4.3.2 Effect of trap depth on the open circuit voltage

In order to further understand the role of ZnO interlayer on $\Delta$ and its effect of $V_{OC}$ and subsequent operational stability of the OPVs, we evaluated the dependence of $V_{OC}$ on temperature for varying $\Phi$ employing Eq (4.4). It has been reported that the nanostructure plays a significant role in determining the $V_{oc}$ of the device.[144] Even in freshly prepared cells the crystallinity of the ZnO ETL layer affects the $V_{oc}$ to a considerable extent. The dependence of $V_{OC}$ on temperature as a function of $\Phi$ for devices A and B is shown in Figure 4.12 (A and B) respectively. In Figure 4.12A, the $V_{OC}$ increases linearly with decrease in temperature. This trend can be attributed to decrease in phonon scattering with decreasing temperature in both active layer and ZnO interface. In Figure 4.12B, the $V_{OC}$ increases with decrease in temperature up to 180K, then it saturates. It has been reported that the decrease in resistivity of ZnO as a function of temperature is highly dependent on the ZnO nanostructure.[145] As both the devices have same active layer, the difference in trend as observed in Figure 4.12 can be attributed to the difference in resistivity, which is a function of electron-phonon scattering, which in turn dependent on the crystallinity of the ZnO nanostructure.[145] The change in trend clearly indicates that the trap states affect the $V_{OC}$ when the temperature is decreased. The $V_{OC}$ of the device A obtained by extrapolating the $V_{OC}$ vs T graph at $T = 0$ K, following Eq. (4.4), is $\sim 0.85 - 0.9$ V, which is much greater than the difference in work functions between the electrodes ($0.6 - 0.7$ V).
The $V_{OC}$ in device A is therefore determined by $E_g$ whereas the ohmicity of the contacts gets disrupted at lower temperature in device B owing to the trap states that forms an energetic barrier. The deep traps states affecting the $V_{OC}$ in freshly prepared devices at lower temperature are considered as chemical reaction sites, as noted by Krebs et al.[123] during its long term operation under actual working conditions, will be discussed in detail in later part.

Figure 4.12 Variation of $V_{OC}$ for both devices (A and B) as a function of temperature (T) for different illumination intensities ($\Phi$).
4.3.3 Evaluation of charge mobility from CELIV transients

Effect of the difference in $\Delta$ between the two sets of devices on the charge mobility at the ZnO–P3HT:PCBM was studied by the CELIV technique.

The CELIV transients observed for the devices A and B is shown in Figure 4.13. The characteristic maxima $t_{\text{max}}$ i.e. the peak of the transients is translated towards higher time scale in device B whereas it is at faster time scale in device A. It indicates that the charges are collected faster/efficiently without accumulation in device A. The charge mobility ($\mu$) was extracted from the CELIV transients and shown in Figure 4.10. The $\mu$ of the device A ($\sim 1.3 \times 10^{-3}$ to $8 \times 10^{-4}$ cm$^2$/V.s) was nearly higher by an order than that of the device B ($\sim 2 \times 10^{-4}$ cm$^2$/V.s).
The enhanced mobility in the device A attributed to its lower $\Delta$ than the other device. The observed higher mobility $\mu$ suggests that the carriers in the device A are transported efficiently on account of its lower trap depth. On the other hand an opposite process occurs in device B in which the charge carrier mobility is reduced by an order owing to larger trap depth.

The mechanism behind the enhanced $\mu$ in the device A is shown in Figure 4.15. The ZnO ETL in device A, in which a higher $\mu$ was observed, has a shallow trap with lesser density of localized states. Upon photoexcitation, the mobile carriers reaching the ETL undergo trap filling and excess electrons than that of defects reach ITO. As the trap depth is lower by a factor two in the device A, the amount of electrons undergoing direct hoping through the conduction band with higher mobility is obviously high. The electrons in the

Figure 4.14 Shows the mobility ($\mu$) calculated from the CELIV transients for both A and B devices.
deep trap states eventually contribute to recombination thereby lowering the
$J_{SC}$ as experimentally observed.

4.3.4 Origin of enhanced photo-stability in device (ITO/ZnO/P3HT:PCBM/MoO$_3$/Ag)

The dark and photo-stability studies performed on the device with ZnO interlayers is studied in chapter 3. To summarize, device stability was studied in dark ambient conditions following the ISOS-D-1 (shelf) protocol and constant illuminated conditions following ISOS-L-1 (laboratory simulations) over a period of 700 h (30 days).[146] The devices measured under ISOS-D-1 (shelf) protocol as a function of time shows that the devices A and B are air-stable retaining $\sim$81% and $\sim$78% of their original efficiency even after 30 days of exposure to ambient conditions. The air-stability of both devices is in close agreement with reports on inverted OPVs employing ZnO ETLs prepared by spray coating methods.[121] On the other hand, devices measured under

Figure 4.15 Shows the mechanism of enhanced mobility in devices A and B.
ISOS-L-1 (laboratory simulations) conditions as a function of time shows that the devices A and B retained ~64% and ~48% of their original efficiency after 400 h of constant illumination, respectively. The significant difference in the photo-stability of the devices reveals the consequences of the observed differences in trap depth and carrier relaxation. The device in which the carriers are relaxed decay faster than the other. One another possible source of device instability is an electron doping of ZnO based device upon long term UV irradiation thereby resulting in the formation of several recombination channels. The carrier build up at the ETL – photoactive layer interface would have detrimental effects on the stability of the device for long term operation as it would adversely affect the chemical integrity of the photoactive layer. The device stability is higher in device with shallow trap depth and vice versa. Therefore, this study provides insights into one another source of device instability for long term operation of organic solar cells.

4.4 Conclusions

In conclusion, removal of localized energy states in the band gap of the charge transport layers in inverted organic solar cells greatly enhances the operational stability of the device in addition to enhanced photovoltaic parameters. This conclusion has been drawn from four sets of devices: two sets studied the effect of trap states, charge mobility, and carrier concentration in the HTL (MoO₃) and the other two sets considered similar effects in the ETL (ZnO). The lower trap depth is achieved by (i) improving the conductivity of the HTL through vacuum annealing and (ii) improving the conductivity of the ETL via annealing at an optimized temperature. Such improvements are shown to be
responsible for simultaneous enhancement in PCE and air stability of the devices. Furthermore, the ohmicity of the interfacial contact at the P3HT-MoO₃ and ZnO-PCBM interface is much stable for devices with lower trap depth. CELIV studies showed that the charge mobility in the devices of lower trap depths is an order of magnitudes higher than the other device. High electrical conductivity of the photoactive–charge transport layer interfaces in the devices of lower trap depth resulted in a $V_{OC}$ that approached the ideal limits. On the other hand, a depleted conductivity in the devices of higher trap depth lead to build up of space charges at the electrode resulting in non-ohmic contacts with high energetic barrier for charge collection. In such cases, devices performance decayed over time. Thus, the present study provides innovative ways to improve the stability of the organic photovoltaic devices for long term operation.
5 ZnO nanowire plantations in the electron transport layer for high efficiency and stable IOSCs

5.1 Introduction

In this chapter, extraction of electrons from the bulk of the photoactive layer in IOSCs was enhanced by incorporating ZnO nanowire plantations in the ETL. One of the primary factors reducing the performance parameters of IOSCs is the inferior charge collection efficiency due to increased charge recombination at the photoactive layer as well as at its interface with the buffer layers. Recombination at the photoactive layer occurs because of inferior charge mobility (electron mobility $\mu_e \sim 5-7 \times 10^{-4}$ cm$^2$/V.s, hole mobility $\mu_h \sim 0.5-9 \times 10^{-4}$ cm$^2$/V.s) arise from highly disordered molecular arrangement in polymers and incoherent charge hopping.[147-149] Thereby, inferior electrical conductivity of the nanostructured MOS charge transport layers and consequent carrier build up at the photoactive–buffer layer interface is one another source of recombination.[150] Morphologies of the photoactive and the transport layers are shown to have a major role in charge carrier transport and affect the device performance significantly.[66, 67, 151]

Recent studies show that electron conducting nanowires on the ETL with their length reaching to most of the photoactive layer (P3HT: PCBM) thickness improves charge collection efficiency.[67, 152-154] In the case of IOSCs, these attempts include fabrication of ZnO nanorods using hydrothermal and pulsed current electrolysis methods with a PCE up to ~2.7%.[152, 153] We have now significantly improved the PCE of IOSCs up to ~3.5% by planting
electrospun ZnO nanowires onto ETLs. The devices that employed electrospun ZnO nanowires gave up to ~20% higher PCE than control devices that did not employ them. The enhanced PCE resulted from an increase in the fill factor; and therefore, the electrospun ZnO nanowires reduce the charge recombination rate and improve the collection efficiency. The charge transport through these devices were studied by transient photovoltage decay and charge extraction by linearly increasing photovoltage measurement techniques and observed that the devices employing electrospun nanowires are characterized by high electron lifetime and mobility.

5.2 Synthesis of the ZnO nanostructures

5.2.1 Preparation of ZnO sol-gel thin films on ITO

Zinc acetate dihydrate [Zn (CH$_3$COO)$_2$·2H$_2$O, ZnAc; Alfa Aesar, 99.9%], potassium hydroxide (KOH; Merck, 85%), ethanolamine (NH$_2$CH$_2$CH$_2$OH, EA, Sigma Aldrich, 99.5%, 0.15 g) in 2-methoxyethanol (CH$_3$OCH$_2$CH$_2$OH, ME, Aldrich, 99.8%, 5 mL) were the starting materials. The ZnAc (0.6 g) and EA (0.15 g) were dissolved in ME (5 mL) under vigorous stirring for 24 h in air. Ammonia (1 mL) was then added to the above solution and stirred for 2 h to get a sol and then filtered using 0.25 µm PVDF filter to remove insoluble impurities. The ZnO thin films (~40 nm) were produced by spin coating the above sol onto cleaned ITO substrates at 3500 rpm for 90 s. The films were then annealed at 160 °C in air for 3 h, cooled to room temperature, washed mildly with isopropyl alcohol, and then dried in air.
5.2.2 Preparation of ZnO nanowire plantations

Free standing ZnO nanowires were produced by electrospinning technique.[155] In the typical synthesis procedure, zinc acetate dihydrate [Zn(CH₃COO)₂•2H₂O], polyvinylpyrrolidone (PVP, MW: 130000) and acetic acid (99.7%) were purchased from Aldrich and used without any further purification. In a typical synthesis, homogeneous sol-gel solution was prepared by mixing 1.5 g of PVP in 15 ml ethanol and then stirred for 1h in room temperature. Further, the prepared homogeneous polymer solution is mixed with 2.2g of zinc acetate solution under constant stirring for an hour. Finally, 0.8 ml of acetic acid was added to the solution under vigorous stirring for ~12 h in room temperature. The prepared sol–gel solution was then transferred into a 5 ml syringe (dia. of 11.9 mm) with 18½ G stainless steel needle which has a diameter of 0.084 cm. The humidity level of the synthesis electrospinning chamber was maintained at about 35% for the whole experimental process. The distance between needle and static collector (aluminum foil) was maintained at 10 cm with an applied ac voltage of 20 kV and at a flow rate of 1 ml/h using a syringe pump (KDS 200). Finally, the prepared composite fibers were collected and further sintered at 500 °C for 5 h under air atmosphere, with a heating ramp rate of 5 °C min to yield ZnO nanowires.

The electrospun ZnO nanowire plantations were prepared as follows. First, the sol-gel precursor was spun coated onto ITO substrate and then annealed for 10 min at 70 °C. Subsequently an ethanolic suspension containing electrospun ZnO nanowires were spin coated onto the annealed substrate. Two typical concentrations were prepared (i) a higher concentration containing 5 mg of
nanowires in 5 ml of ethanol and spin coated at 2000 rpm (PNW\textsubscript{H} film) (ii) a lower concentration of 1 mg of nanowires in 5 ml of ethanol and spin coated at 4000 rpm (PNW\textsubscript{L} film).

5.3 Morphology of the ZnO nanostructures

SEM images of ZnO films and wires developed in this study are shown in Figure 5.1. ZnO film (Figure 5.1A) prepared by the sol-gel coating on ITO was smooth, continuous, and uniformly distributed spherical particles of diameter ~10–20 nm. The SEM images of the electrospun ZnO nanowires in Figure 5.1B shows continuous wires of diameter ~50–100 nm and few micrometers in length. Figure 5.1 C&D show high resolution TEM (HRTEM) images and SAED patterns of the ZnO particles and wires. The HRTEM images show that a typical powder particle of ~20 nm is an aggregate of randomly oriented nanocrystals of sizes 2–5 nm whereas nanowires are composed of more oriented particles of size ~10–20 nm. i.e., the nanowires are highly crystalline than the particles. The difference in their crystallinity is more obvious in the SAED patterns, both of which can be indexed for Wurtzite crystal structure (space group: P6\textsubscript{3}mc). The SAED pattern of the particles show polycrystalline ring structures whereas that of nanowires are spotty thereby indicating that they have improved crystallinity than the other. Figure 5.1 E&F show the ZnO–PNW\textsubscript{L} and ZnO–PNW\textsubscript{H} films. The ZnO nanowires are broken down during the ultrasonic dispersion process and are distributed randomly in the composite film.
Figure 5.1 SEM images of A) spin coated sol-gel derived ZnO nanoparticles, B) electrospun ZnO nanofibers, C and D) high resolution TEM (HRTEM) images and SAED patterns of the ZnO particles and wires respectively, E) Composite ZnO nanostructure combining ZnO nanoparticles and ZnO nanofibers (High Conc.) F) Composite ZnO nanostructure combining ZnO nanoparticles and ZnO NFs (Low Conc.).

Figure 5.2 summarizes the results of AFM studies on ZnO modified ITO. The root mean square (rms) roughness values of the ZnO modified ITO electrodes are 6.42 nm, 54.3 nm and 113 nm for the Devices P, PNWL, and PNWH.
respectively. The ZnO interlayer film thickness is in the range of about 20 – 45 nm for the device P. The base thickness of the ZnO interlayer with nanowires in both PNW_L and PNW_H is similar as that of device P (20-45nm). Since the nanowires are deposited randomly on top of this base layer, the surface height varies from 150 – 350 nm and 400 – 800 nm for devices PNW_L and PNW_H, respectively according to the distribution profile of the nanowires; at the spots where it is deposited.

Figure 5.2 AFM images of the ZnO interlayer in devices (A) P, (B) PNW_L and (C) PNW_H respectively. Top three images represent the 3D view depicting the surface height and the bottom three images represent the 2D view of the nanostructure morphology.

5.4 Crystal structure of the ZnO particles and wires

Figure 5.3 shows the XRD patterns of the ZnO particulate and electrospun materials. The films were crystalline and all the XRD peaks can be indexed for
the ZnO hexagonal phase with Wurtzite crystal structure [space group C6V (P63mc)] having lattice parameters \( a = b = 3.25 \, \text{Å} \) and \( c = 5.2 \, \text{Å} \) (JCPDS card no.0-3-0888).

5.5 Device fabrication and characterization

All the above dried films were cleaned by UV-Ozone treatment for 10 min before solar cell fabrication. The device structure was ITO/ZnO/P3HT: PCBM/MoO3/Ag. The devices fabricated using (i) the sol gel film is termed as “Device P”, (ii) the low and high concentration of ZnO nanowire plantations protruding are termed as “Device PNWL” and “Device PNWH”, respectively. A mixture of P3HT and PCBM dissolved in the ratio of 1:0.8 in 1, 2-dichlorobenzene solution was spin coated on the ITO/ZnO layer. The thickness of the photoactive layer was \(~200\, \text{nm}\). The film was then annealed at 240 °C for 10 minutes. The hole transporting MoO3 layer of thickness \(~5\, \text{nm}\)
was then thermally evaporated on to the produced film in a vacuum chamber with a base pressure of $\sim 10^{-7}$ mbar. Finally, silver ($\sim 100$ nm) electrode was deposited onto the MoO$_3$ layer at a pressure $\sim 10^{-5}$ mbar. The devices were annealed at 70 °C for 10 minutes using a hotplate inside the nitrogen filled glove box.

**5.5.1 Effect of ZnO morphology and surface states on photovoltaic parameters**

Figure 5.5 shows the current – voltage characteristics of the three devices at AM1.5G conditions; corresponding photovoltaic parameters are listed in Table 5.1. The device prepared using the ZnO–PNW films showed marginally higher short circuit current density ($J_{SC}$) and considerably higher fill factor (FF), which increased with increase in the nanowire loading. The FF determines the charge collection efficiency and recombination rate constant in solar cells; therefore, increase in nanowire concentration is beneficial for enhanced device performance. The $J_{SC}$ of the devices P, PNW$_L$, and PNW$_H$ were 9.1, 9, and 9.4
mA/cm² respectively. The open circuit voltage (VOC) of the three devices remind at similar values (~0.54 V). The device fabricated using the ZnO–PNW₇ films gave the highest photoelectric conversion efficiency (PCE) of ~3.5% which is 20% higher compared to the device that did not employ nanowire plantations which mainly resulted from 12% enhanced FF.

The difference in electrical property of the three types of devices was determined from the shunt (R_SH) and series (R_S) resistances from the inverse of slopes at J_SC and VOC of the I-V curves, respectively. The R_SH is an estimation of internal currents in the device and is a measure of charge recombination processes whereas R_S denotes the resistance for charge collection.[156, 157] A high R_SH (>1000 Ω) and low R_S (<100 Ω) are therefore preferred for high FF and PCE of IOSCs. Table 5.1 also includes the
$R_S$ and $R_{SH}$ of the devices studied here. The $R_S$ was lowest (~77 $\Omega$) for the device PNW among the various devices, which can be attributed to the improved charge collection efficiency when the nanoparticle/nanowire composite was employed as ETL in the device. Although all devices showed higher $R_{SH}$ the device PNW$_H$ showed ~183% increased value (~13826 $\Omega$) than that of the device P (4883 $\Omega$). The enhanced $R_{SH}$ of the device PNW could be attributed to the enhanced charge transport due to the presence of one-dimensional materials and removal of shunt channels in the grain boundaries which otherwise existed in the devices. Shunt channels refers to current leakage paths. By using nanowires, the disorderliness in the orientation of the grain boundaries is expected to be minimum, thereby shunt resistance is improved significantly.

The observed lower $R_S$ and doubled $R_{SH}$ of the device PNW$_H$ accounts for the considerable enhancement in its FF.

Table 5.1 Photovoltaic parameters of the vacuum and non-vacuum annealed devices

<table>
<thead>
<tr>
<th>Device</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>PCE %</th>
<th>$R_S$ ((\Omega))</th>
<th>$R_{SH}$ ((\Omega))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Device P</td>
<td>9.1</td>
<td>0.54</td>
<td>59.7</td>
<td>2.9</td>
<td>84.1</td>
<td>4883</td>
</tr>
<tr>
<td>Device PNW$_L$</td>
<td>9.0</td>
<td>0.54</td>
<td>64.1</td>
<td>3.1</td>
<td>80.5</td>
<td>10320</td>
</tr>
<tr>
<td>Device PNW$_H$</td>
<td>9.4</td>
<td>0.55</td>
<td>66.1</td>
<td>3.5</td>
<td>77.4</td>
<td>13826</td>
</tr>
</tbody>
</table>

Incident photon-to-current conversion efficiency (IPCE) spectra of the devices ‘P’, ‘PNW$_L$’, and ‘PNW$_H$’ are shown in figure 5.6. The device PNW$_H$ devices showed maximum IPCE of ~ 68% whereas that of the control device P was ~
62%. The measured IPCE integrated values are in good agreement with the short circuit current obtained from the I-V measurements. A drop in IPCE at wavelengths around 400 nm with small increase in UV region is clearly evident in all the three devices due to absorption of the buffer layer film corresponding to the band edge of ZnO. Interestingly, the devices incorporating ZnO plantations showed a peak ~450 nm which was not observed in the other device. This observation indicates that the blend layer morphology including the charge carrier percolation networks are altered beneficially via the incorporation of the ZnO NWs by improved phase separation. The improved vertical segregation of the photoactive layer by ZnO NWs has resulted in increased IPCE of ~58% compared to 45% in device P at 450 nm.

![IPCE spectra of the devices P, PNWL, and PNWH](image)

Figure 5.6 IPCE spectra of the devices P, PNWL, and PNWH
5.5.2 Evaluation of charge carrier lifetime by transient photovoltage technique

To investigate the recombination dynamics, the carrier lifetime ($\tau_n$) was extracted from TPV measurements by back-side illumination. The photovoltage decay was measured by keeping the device at a reference voltage well below the $V_{OC}$ and creating an additional photovoltage using a short laser pulse (~30 mV). The decay time of the additional photovoltage is therefore a measure of recombination time and is monitored in the TPV measurements. Slower decay accounts for longer recombination time. Typical photovoltage transients recorded at a steady-state white light of photovoltage ~240 mV is shown in Figure 5.7A. One may easily observe from Figure 5.7A that the photovoltage of the device employing a higher concentration of electrospun ZnO nanowires, i.e., device PNWL, decays much slower compared to the other two devices. Assuming a first order decay, the decay times of the devices P, PNWL, and PNWH were calculated to be 0.202, 0.294, and 0.771 microseconds, respectively. Thus, clearly, carrier recombination is over three times slower in the device PNWH compared to other devices; therefore, a higher FF could normally be expected from this device. The $\tau_n$ was calculated from the TPV decay (exponential first-order decay) using the equation

$$
\tau_n = \left(\frac{\partial U_n}{\partial n}\right)_n^{-1}
$$

where $U_n$ is the electron recombination rate per unit volume and $n$ is the carrier concentration, respectively. The $\tau_n$ in OSCs depends strongly on its working conditions. At $V_{OC}$, with maximum band bending, the traps in the
photoactive layer are filled up and a bimolecular recombination mechanism operates involving both types of carriers.[44, 158]

Carriers are short lived under such condition.[158] However, below $V_{OC}$, with lesser band bending, the traps above the Fermi level are no longer filled and a monomolecular recombination mechanism operates involving one type of carrier with the other being in the trap.[159] Carriers are comparatively longer lived in this condition and a difference in the extraction efficiency by the ETL is more pronounced.[98] The $\tau_n$ of the devices shown in Figure 5.7B demonstrate this variation with $V_{OC}$ clearly; the $\tau_n$ is of the order of microseconds at the $V_{OC}$ which increases to milliseconds far below from it. At maximum $V_{OC}$, the similarity in the $\tau_n$ of the devices implies that charge transport across the ETL is not influenced by its morphology. Interestingly, the $\tau_n$ showed a large variation among the devices for $V_{OC} \leq 400$ mV. The $\tau_n$ of device PNW$_{H}$ is an order of magnitude higher compared to the other devices for $V_{OC} \leq 200$ mV which imply that the electrospun ZnO nanowires collect electrons from the bulk of the photoactive layer. i.e., the one-dimensional

![Figure 5.7](image)

Figure 5.7 (A) Carrier lifetime obtained from TPV measurements (B) Photovoltage decay transients obtained at 240mV.
nanowires plantations offer more charge collection points at the ZnO-PCBM interface thereby facilitating faster removal electrons through the ETL, increases carrier lifetime, and FF.

![Figure 5.8 Delay dependent Photo-CELIV transients with time delay (A) 5 µs (B) 12 µs (C) 30 µs (D) 50 µs.](image-url)

**5.5.3 Determination of carrier recombination from delay dependent Photo-CELIV**

To corroborate long recombination time in the device PNW₁, delay-dependent photo-CELIV transients of the devices were recorded and analyzed. Rationale of this experiment is that carriers in devices of higher carrier lifetime can still be extracted even after considerable delay time after the light pulse.[137] The delay-dependent photo-CELIV transients obtained with delay times of 5, 12, 30, and 50 µs between the light pulse and an extraction voltage ramp (1V) is
shown in Figure 5.8. The device PNW_H retained a fraction of charges to be extracted even after 50 µs compared to other devices.

The normalized charge carrier concentration \( n \) obtained from the delay dependent Photo-CELIV transients is shown in Figure 5.9. About 40% of the total carriers are extracted even after an extended time delay of 50 µs in the device PNW_H. The other two devices showed extraction of comparatively lower fraction of carriers at such delay times thereby indicating lower recombination time.
The CELIV transients obtained for the three devices P, PNW_L, and PNW_H is shown in Figure 5.10A. In the CELIV technique, a linearly increasing electric field or voltage ramp is applied at one of the contacts under reverse bias condition and the corresponding current transients is used to determine the equilibrium carrier concentration $n$.\cite{97, 137} CELIV technique also enables the analysis of the relaxation process of the charge carriers in the density of states (DOS) thereby facilitating simultaneous measurement of time-dependent $\mu$ and $n$.\cite{147, 160} In general, a device with less dark injection or leakage current at reverse bias condition is suitable for charge extraction measurements as well as to reduce the charge recombination in the operational device. The difference in the heights of the characteristic peak ($J_{\text{max}}$) of the CELIV transients, as observed in Figure 5.10A, depicts that the dark injection is lesser in the device PNW_H whereas it is relatively higher in the device without nanowires P. In addition, the time taken to reach the steady state or capacitance displacement current is shorter in the nanowire based device.

Figure 5.10 (A) CELIV (Dark) transients of the devices P, PNW_L and PNW_H measured at 1.25V with an offset of 0.25V (B) Dark injected charge carrier concentration obtained from CELIV transients at different applied field.
(PNW\textsubscript{H}) compared to the devices without nanowires. The small injection current in PNW\textsubscript{H} based device may indicate that the charge recombination probability in this device is smaller compared to the other two devices. In addition, the width of the CELIV transient indicates the charge dispersion in the system. It was observed that the PNW\textsubscript{H} based device, the width is smaller compared to the other two devices indicating the good charge transport characteristics. The variation of dark injected carrier concentration as a function of applied field (reverse bias) is shown in Figure 5.10B. It can be seen that the dark carrier injection is consistently lesser in PNW\textsubscript{H} compared to its counterparts PNW\textsubscript{L} and P respectively (Figure 5.10B). These results indicate that the device incorporating nanowires enables efficient charge extraction across the ETL whereas they are accumulated in devices without nanowires. Lowering of the charge accumulation at the interface via efficient electron collection pathways in the ‘PNW’ devices is the key for improved shunt resistance as shown in Table 5.1. Carrier mobility obtained from the CELIV transients is shown in Figure 5.11. The $\mu$ gradually increased with increase in the nanowire concentration although the magnitude of this increment was not substantial. It denotes that the improved device performance arise from increased carrier lifetime when the nanowire plantations directly collects electrons from the bulk of the photoactive layer. In the absence of the nanowires, longer transport time through the interfacial layers (ETL), eventually lead to recombination and subsequent lowering of PCE.
In conclusion, we have employed electrospun ZnO nanowire plantations in the electron transporting layer of inverted organic solar cells and found that the resulting device show enhanced photovoltaic performance. The device structure used was ITO/ZnO/ P3HT:PCBM /MoO$_3$/Ag. Three set of devices were fabricated, two with varying nanowire concentration; one without nanowires is used as a control device. The devices that employed a higher loading of ZnO nanowires showed 20% higher photovoltaic conversion efficiency compared to the control device. Transient photovoltage and CELIV measurements showed that the electrons are collected efficiently from the bulk of the photoactive layer by the nanowire plantations in the ETL. The nanowires lowered the electron diffusion pathways (random walk) and hence charges could be collected efficiently. On the other hand, in the control device, the electrons are required to diffuse until it reached the flat photoactive layer –

![Figure 5.11 Charge carrier mobility obtained from the CELIV transients.](image)

5.6 Conclusions

In conclusion, we have employed electrospun ZnO nanowire plantations in the electron transporting layer of inverted organic solar cells and found that the resulting device show enhanced photovoltaic performance. The device structure used was ITO/ZnO/ P3HT:PCBM /MoO$_3$/Ag. Three set of devices were fabricated, two with varying nanowire concentration; one without nanowires is used as a control device. The devices that employed a higher loading of ZnO nanowires showed 20% higher photovoltaic conversion efficiency compared to the control device. Transient photovoltage and CELIV measurements showed that the electrons are collected efficiently from the bulk of the photoactive layer by the nanowire plantations in the ETL. The nanowires lowered the electron diffusion pathways (random walk) and hence charges could be collected efficiently. On the other hand, in the control device, the electrons are required to diffuse until it reached the flat photoactive layer –
ETL interface, which increased the electron diffusion pathway; and therefore the recombination rate is also increased. Thus, the nanowire plantations efficiently reduced recombination and improved the photovoltaic performance parameters.
6 Engineering of Tin Oxide Nanostructures for efficient Dye-Sensitized Solar Cells

6.1 Introduction

In DSCs, till date, mesoporous TiO$_2$ is considered as the most successful material for the charge separation and transport (i.e. photoelectrode) due to a number of reasons such as (i) ease of producing mesoporous particles, (ii) effective band alignment with various organic and inorganic dyes, and (iii) stability. However, low electron mobility ($\mu_n$) through mesoporous TiO$_2$ (~0.1 cm$^2$V$^{-1}$s$^{-1}$) is a crucial issue and impose severe limitations in enhancing the $\eta$ of DSCs closer to the theoretical limits.[161] One of the main hurdles due to inferior $\mu_n$ is the electron recombination with the electrolyte if the photoanode layer thickness is larger than the diffusion length, the transit length above which electrons are lost via recombination. Tin oxide (SnO$_2$) nanostructures, on the other hand, is a well-known transparent conducting oxide for nano-electronics due to high $\mu_n$ (10 – 125 cm$^2$V$^{-1}$ s$^{-1}$) and wider band gap (~ 3.6 eV).[162-165]. However, its conduction band minimum occurs at an energy lower than that of TiO$_2$ [77]; and therefore, DSCs with SnO$_2$ electrode usually give low open circuit voltages ($V_{OC}$ ≤600mV).[166] Recently, $V_{OC}$ up to ~600 mV has been achieved by preparing the SnO$_2$ core/shell electrodes and/or making composite electrode with other wide band gap semiconductors.[167-169] To increase the $\eta$ of SnO$_2$ DSCs, several approaches have been considered: (i) modifying the electrode surface [170] (ii) electrolyte composition [170, 171](iii) combining with other metal oxide nanoparticles
and (iv) by using a core–shell configuration of suitable energy band matched metal oxides.[169, 172, 173]

The efficiency of DSCs depends on various parameters which include morphology and compactness of photoanode, chemical nature and purity of dye, electrolyte composition, counter electrode, and other related parameters.[70, 76, 100, 174-177] The dye-loading and hence the number of photogenerated electrons in DSCs, charge transport, and a number of other efficiency determining factors depend on the photoanode; and therefore, immense research is directed on optimizing suitable material and morphology for this application.[70, 76, 156, 168, 178-181]

### 6.1.1 Synthesis of SnO$_2$ nanostructures by electrospinning

Anhydrous Tin (II) chloride (SnCl$_2$), dimethylformamide (DMF), ethanol, and polyvinyl acetate (PVAc) were the starting materials. Two sets of syntheses were done by simply changing the precursor concentration. In a typical synthesis, 0.4 g of SnCl$_2$ was dissolved in a mixture of 12.5 mL of DMF and 4 g of ethanol and was stirred for ~ 2 h. To the above solution, 1.45 g of PVAc was added and the stirring was continued for ~ 4 h till the solution became clear. The above procedure produced 2.5 mM of SnCl$_2$ solution (Sample S1). Similarly 5.5 mM solution of SnCl$_2$ was produced (Sample S2). The clear solutions thus obtained were electrospun using a 27 G1/2 needle under an applied voltage of 25 kV with a solution injection rate of ~1 mL/h. The solid fibers were collected at distance of 10 cm below the spinneret. The composite fibers were then peeled off from the collector and calcined at 500 °C for ~ 3 h to allow crystallization of the SnO$_2$ phase and removal of the polymer.
6.1.2 Morphological characterization of fibers and flowers

The samples S1 and S2 produced mats composed of fibers of similar diameter (~700 nm) upon electrospinning. The mats were annealed at 500 °C for ~3 h to allow crystallization of the SnO$_2$ phase and removal of the polymer.

Figure 6.1 shows the differences in the morphology of the SnO$_2$ developed from the two mats. Morphologies are clearly different confirming the growth model described in equation 3.1. Sample S1, with a lower precursor concentration, gave conventional electrospun fibrous morphology (diameter ~400 nm) whereas the one with higher precursor concentration, i.e., sample S2, yielded flower-shaped particles (size ~400 nm). Although fibers and flowers
were obtained by annealing the as-spun polymeric fiber at similar temperature, i.e., 500 °C, the degree of crystallinity, judged from the discreteness of the diffraction spots and the extended periodicity in the lattice image, was notably different in both the cases. The flowers showed single crystalline diffraction pattern and lattice images (Figure 6.1). On the other hand, diffraction pattern of the fibers consisted of rings – typical to polycrystalline materials having random orientation of crystallites. A closer examination showed that the flower structure is made up of fibrils of diameter ~80 – 100 nm which in turn made up of particles of size ~ 20 – 30 nm. Owing to the high porosity of the flowers due to polymer permeation during growth, they gave higher BET surface area (40 m²/g) compared with that of the fibers (19 m²/g).

### 6.1.3 Structural characterization of the flowers and fibers

Figure 6.2A shows the x-ray diffraction (XRD) patterns of the fibers and flowers. Positions of all the diffraction peaks were similar for both morphologies; however, it was noted that relative intensity of the (211) plane of the flower was slightly lower than the other. All the peaks in the XRD patterns were indexed for the cassiterite phase (space group \( P4_2/mnm \)) of SnO₂ (JCPDS file 41-1445). The lattice parameters calculated from the XRD patterns were \( a = 4.7380 \) Å and \( c = 3.1865 \) Å. No impurity or secondary phase could be detected in the XRD pattern of both the morphologies. The energy dispersive x-ray (EDX) spectra of the SnO₂ flower also confirmed the absence of impurities. Figure 6.2 (B) and (C) combine the core-level XPS spectra of both morphologies.
The Sn-3d level binding energies (BE) of both morphologies were 487.2 eV and 496 eV, which are assigned to Sn3d5/2 and Sn3d3/2 core levels of Sn⁴⁺, respectively. The O1s level BE of oxygen were 531.0 eV and 532 eV, which are assigned to the oxygen (O²⁻) anion in Sn-O bonds and surface oxygen, respectively. The BEs of Sn⁴⁺-ions are in close agreement with the values reported for the cassiterite phase of SnO₂.[182] All these characteristics lead to the conclusion that the flowers are chemically similar to the fibers.

6.1.4 Evaluation of flat band potential and electron density – Mott-Schottky Analysis

To understand the difference in electrical properties of the two morphologies, MS plots were developed from the EIS measurements in the dark.[183, 184] Samples for MS analysis were prepared by sintering SnO₂ flowers and fibers separately onto fluorine doped tin oxide (FTO) coated glass plates and sealed using a 50 µm spacer. Acetonitrile containing 0.1M lithium iodide, 0.03M
iodine, 0.5M 4-tert-butylpyridine and 0.6M 1-propyl-2,3-dimethyl imidazolium iodide was used as the electrolyte. A platinum coated glass plate was used as the counter electrode. The Mott-Schottky plots were generated from electrochemical impedance spectroscopy (EIS) measurements in the dark for bias voltages from 0.4 to 0.7 V and fitting the observed EIS spectra to a simple RC circuit.[184]

Figure 6.3 shows the MS plots determined from EIS plots for the two morphologies. Sigmoidal plots were observed with an overall shape consistent with the n-type semiconductors with similar flat band potentials,[185] that is potential corresponding to the situation in which there is no charge accumulation in the semiconductor such that there is no band bending, which could be obtained from the x-intercept of the linear portion.

Figure 6.3 Mott-Schottky plot of flowers and fibers.
The electron density \( (n_D) \) obtained from the slope of the \( 1/C^2 \) vs \( V \) curve of the flowers \( (1.054 \times 10^{21}/\text{cm}^3) \) was an order of magnitude higher than that of the fibers \( (0.868 \times 10^{20}/\text{cm}^3) \). The enhanced crystallinity achieved by manipulating the precursor concentration is thought to be the reason for enhanced \( n_D \) of the flower structure.

![Cyclic voltammetry measurements (CV)](image)

Figure 6.4 Cyclic voltammetry measurements of flower and fiber morphology.

### 6.1.5 Cyclic voltammetry studies

High \( n_D \) of the flower structure was also confirmed with the cyclic voltammetry measurements, which is displayed in the area of the cyclic voltammograms (CV).[186] Cyclic voltammetry measurements were carried out on a CHI 760 electrochemical workstation with a three-electrode cell in a solution of \( \text{Bu}_4\text{PF}_6 \) (0.10 M) in acetonitrile at a scanning rate of 100 mV/s. A glassy carbon disk was used as working electrode and a silver wire as reference electrode. Ferrocene was used for potential calibration. Figure 6.4 shows the CV of the two morphologies, which clearly show that flowers have
superior electrochemical properties than the other. The specific capacitance calculated from the area CV curves of the flowers was more than twice that of the fibers, which is expected to arise from the enhanced crystallinity of the flowers.

### 6.1.6 Difference in electronic bands of SnO$_2$ flowers and fibers

Prior to discuss the charge transport kinetics through the SnO$_2$ flowers and fibers, it is essential to discuss their electronic band properties. As depicted in the introduction section, random deviation of equilibrium bond lengths and angles in the lattice of nanocrystalline materials compared to their bulk analogue introduces potential fluctuations that allow energy levels, known as band tail states (synonymously, ‘surface atomic states’, ‘surface traps’) within the forbidden energy gap (Figure 6.5).

Figure 6.5 Schematics showing the difference in charge diffusion mechanism between (A) bulk single crystalline semiconductors and (B) nanocrystalline semiconductors.
The occurrence of band tail states in nanocrystalline, amorphous, and disordered materials is observed in their absorption spectra as a broad exponentially decreasing profile, known as Urbach tail, along the energy scale below the band edge absorbance.[187-189] This distribution has the expression as given in equation (6.1) [79]

\[
g_{\text{LT}}(E) = \frac{N_L}{k_B T_o} \exp\left(\frac{(E - E_o)}{k_B T_o}\right)
\]

(6.1)

where \( k_B \) is the Boltzman constant, \( N_L \) is the total density of states, \( E_o \) is the bottom of the conduction band energy, and \( T_o \) is a parameter with temperature units that determines the depth of the distribution of the localized states.

Figure 6.6 Absorption spectra of flowers and fibers showing band edge and band tail energy states.

The Tauc plot developed from the experimental absorption spectra of the SnO\(_2\) flowers and fibers recorded at identical conditions are shown in Figure 6.6.
The optical band gaps of the two morphologies were deduced from the experimental absorption spectrum using the Tauc equation,[190]

\[
\alpha \nu = C \left[ \frac{h \nu - E_g}{h \nu} \right]^{2/3}
\]

where \( C \) is a constant, \( h \nu \) is the photon energy and \( E_g \) is the band gap energy. \( E_g \) was determined from absorption onset of \( [(\alpha h \nu)^2 \text{ vs. } h \nu] \) curves. Similar absorption onset was observed for both structures; revealing a band gap energy of \( \sim 3.6 \) eV, consistent with other reports.[191] It is noteworthy to mention that the Mott-Schottky analysis also gave similar flat band potentials for both flowers and fibers.[192] The spectra showed exponentially decreasing profile that red shifted to the band edge absorption indicating the existence of band tail states on account of their nanocrystallinity. From the similarity in the absorption spectra, it can be ascertained that the \( E_o \) and \( T_o \) are similar for both nanostructures.

Though these trends revealed the details of the above mentioned parameters; attempt was not made to quantify the trap density from the band tails of the absorption spectra because of the fact that the observed spectra could be a convolution of several scattering parameters that arise from opacity and surface irregularities.

6.1.7 Proposed growth model of nanoflowers

Inorganic fibers from the electrospun polymeric fibers form in three steps; viz. nucleation, growth of the inorganic phase and directional mass transport
within the polymeric template. As the nucleation and growth of the particles takes place in a supercooled liquid, i.e., in polymer, the evolution of ensemble of nanoparticles can be expressed in terms of the Gibbs–Thompson equation:[193]

\[
C(r) = C^0_{\text{flat}} \exp \left( \frac{2\gamma V_m}{rRT} \right) \approx C^0_{\text{flat}} \left( 1 + \frac{2\gamma V_m}{rRT} \right) \tag{6.3}
\]

In the above expression, \(C(r)\) and \(C^0_{\text{flat}}\) are the solubility of the particle with radius \(r\) and of the bulk material, respectively; \(\gamma\) is the surface tension; \(V_m\) is the molar volume of the solid. The supersaturation achieved by heating the fibers result in nucleation of the SnO\(_2\) nanocrystals thereby consuming a large fraction of the precursors. The nanocrystals then grow in the diffusion controlled regime with the leftover precursor concentration. Flux of the precursor \(J^\text{diff}\) reaching to a growing particle is given by the Fick’s law:[193]

\[
J^\text{diff} = 4\pi r^2 D \left( \frac{d[M]}{dx} \right)_{x=r} \tag{6.4}
\]

Here, \(D\) is the diffusion coefficient of the precursors; \(x\) is the distance from the centre of the particles and \([M]\) is the precursor concentration. At high processing temperatures, \(x \to r\); and equation (2) rewrites into:[193]

\[
J^\text{diff} = 4\pi r^2 D \left( \frac{d[M]}{dr} \right) \tag{6.5}
\]

Equation (3) qualitatively predicts that \([M]\) influences (i) activation of the surface of the growing nanoparticle, (ii) the effective growth rate, \(\frac{dr}{dt}\), and (iii) diameter of the final inorganic nanofibers. Li and Xia experimentally
demonstrated that final diameter of the inorganic fibers can be reduced by decreasing the precursor concentration in the electrospun polymeric fibers [194]

In the event of enhancement in activation energy with precursor concentration, an optimal threshold concentration of precursors is required for the formation of continuous fibers. On the other hand, if the concentration of the precursors exceeds beyond the optimal concentration for fibrous morphology, a larger number of nuclei are formed upon annealing. Subsequent growth results in a non-equilibrium state such that all the crystallites are not possible to accommodate within the given fibrous volume. The fibrous structure therefore undergoes disruption in the presence of the polymer and leads to non-equilibrium morphologies upon further annealing as shown schematically in Figure 6.7.

Figure 6.7 Schematics showing the evolution of flower morphology in electrospun inorganic nanostructures when there are difference in precursor concentration. (a1) Polymeric fibers with lower precursor concentration. (b1) growth of SnO$_2$ grains contained within the fiber boundary resulting in fiber morphology. (a2) polymeric fibers with higher precursor concentration. (b2) highly populated growth of SnO$_2$ grains outstrips the fiber boundary and loses one dimensionality giving rise to flower morphology.
6.1.8 Fabrication of solar cells and evaluation of photovoltaic properties

The two polymeric solutions were electrospun separately onto FTO glass substrates (1.5 cm x 1 cm; 25 Ω/□, Asahi Glass Co. Ltd., Japan). Thickness of the electrode was controlled by placing the FTO substrates under the spinneret for different durations of time. The samples were wrapped in aluminium foil and hot-pressed (Stahls’ Hotronix 6×6 press, USA) at ~200 °C with a pressure of 0.4 MPa for 15 min to improve the adhesion of the fibers and the flowers to the FTO substrate. The hot-pressed films were then annealed at 500 °C for 3h to remove PVAc completely and allow nucleation and growth of SnO2. The DSCs were developed by soaking a 0.28 cm² SnO2 electrode in a dye solution containing in a 1:1 volume mixture of acetonitrile and tert-butanol of a ruthenium-based dye [RuL2(NCS)2-2H2O; L = 2, 2’-bipyridyl-4,4’-dicarboxylic acid (0.5 mM), N3 Solaronix]) for 24 h at room temperature. The dye-sensitized photoelectrode samples were then washed in ethanol to remove unanchored dye and dried in air. The dye-anchored electrodes were sealed using a 50 µm spacer. Acetonitrile containing 0.1M lithium iodide, 0.03M iodine, 0.5M 4-tert-butylpyridine and 0.6M 1-propyl-2,3-dimethyl imidazolium iodide was used as the electrolyte. A Platinum sputtered FTO glass was used as the counter electrode. Photocurrent measurements were performed using a XES-151 S solar simulator (San Ei, Japan) under AM1.5G conditions; which is calibrated to standard irradiance (100 mW/cm²) using a calibrated c-Si reference solar cell. Data acquisition was facilitated by an Autolab PGSTAT30 (Eco Chemie B.V., The Netherlands) integrated with a potentiostat. IPCE measurements were performed using the standard equipment from Oriel Instruments (model QE-PV-SI, Silicon detector,
Newport Corporation, US). The AC responses of the cells were studied by electrochemical impedance spectroscopy (EIS) using the Autolab PGSTAT30. The current density ($J_{SC}$) vs. voltage (V) plots as a function of cell thickness fabricated using both fibers and flowers is shown in Figure 6.8. For a cell of 15 $\mu$m thickness, flower-based DSC showed a record $V_{OC}$ ~700 mV, $J_{SC}$ ~7.30 mA/cm$^2$, fill factor (FF) ~59.6% and $\eta$ of ~3.0%. For a cell of similar thickness, the fiber based DSC gave $V_{OC}$ ~600 mV, $J_{SC}$ of ~3.0 mA/cm$^2$, FF ~38.3 and $\eta$ ~0.71%. i.e., the flower based device show ~140% increased $J_{SC}$, ~16% increased $V_{OC}$ and ~55% increased FF than the fiber based device.

The difference in electrical property of the two types of cells was determined from the shunt ($R_{SH}$) and series ($R_S$) resistances from the inverse of slopes at $J_{SC}$ and $V_{OC}$ of the I-V curves. The $R_{SH}$ is an estimation of internal currents in the cell and is a measure of back electron transfer and other charge recombination processes in DSCs whereas $R_S$ denotes the resistance for charge collection.[156, 157] A high $R_{SH}$ (>1000 $\Omega$) and low $R_S$ (<0.01 $\Omega$) are
therefore preferred for high fill factor and efficiency of the solar cells. Best performing flower-based cell gave $R_{SH} \sim 1600$ and $R_S \sim 0.001 \Omega$, which indicate that the flower-based cells were of high quality with lower charge recombination. On the other hand, the cells made using the fibers showed inferior performances. The $R_{SH}$ and $R_S$ of the fiber-based devices were $\sim 600$ and $143 \Omega$, respectively, thereby accounting its inferior performance.

6.2 Estimation of trap density – open circuit voltage decay measurements

The OCVD measurements provides an electrical method of mapping the distribution of band tail states.[195] In this technique, the temporal decay of $V_{OC}$ is analysed by removing the illumination source in a DSC operating at steady state conditions. Under steady state in DSCs, the electron injected into the photoelectrode is equal to that transferred from the contact electrode. The mechanism of OCVD is such that when the electron injection is terminated suddenly by closing the light source, the electrons in the conduction band of $SnO_2$ decays faster through the contact electrode whereas the ones entangled at the trap states will be delayed depending on their lifetime. Consequently, the decay of $V_{OC}$ shows a delay before reaching zero, which is typically measured in the OCVD. As the measurement is carried out in the dark conditions, recombination with the oxidized dye-molecule does not take place but this is acceptable because the electrolyte accounts for majority of the recombination even under illumination.[78] Assuming a first order recombination reaction, the electron lifetime ($\tau_n$) as a function of voltage is expressed by $\tau_n = -(kT/e)(dV_{OC}/dv)^{-1}$,[196, 197] where $kT$ is the thermal energy,
$e$ is the positive elementary charge and $dV_{oc}/dt$ is the first order time derivative of the $V_{OC}$.

The electron lifetime ($\tau_n$) of the flowers and fibers as a function of voltage determined from the OCVD curves is shown in Figure 6.9 compares, which clearly depicts that the decay profile and hence the density of band tail states of both structures (flowers and fibers) vary considerably. The fibers exhibited an enhanced $\tau_n$ for higher Voc, most probably due to more channelled charge transport through them compared with that of the flowers. The $\tau_n$ of both morphologies showed exponential dependences in the range $\sim 0.5 - 0.7$ V depicting the diffusion through bulk traps. Following the exponential dependence, a substantial decrease of $\tau_n$ was observed in the 0.2 – 0.4 V range for both structures, the magnitude of which was small for the flowers but appreciable for the fibers. This lowering occurs due to the electrons captured

Figure 6.9 Calculated lifetime from the OCVD curves. The experimental OCVD curves are in the supporting Information.
in surface deep-traps. i.e., the flower has a lower trap density compared to fibers, the source of which is expected to be the enhanced crystallinity of the flower morphology. Lowering of $\tau_n$ and enhanced trap density are reported in metal oxide materials of lower crystallinity including most frequently used TiO$_2$ in DSCs.[198, 199] A reversal in $\tau_n$ was observed at lower $V_{OCS}$, i.e., after the deep-trap, thereby further confirming that the fibers are characterized by a higher density of surface traps.

Thus, from the absorption spectra and the OCVD studies it could be concluded that (i) band tail states (consisting of localized energy states) arise due to the deviation from ideal atomic packing; exist in SnO$_2$ flowers and fibers, (ii) the depth of the distribution of the conduction band (bottom) energy appears to be similar for both the nanostructures, (iii) however, fibers possess enhanced trap density on account of their lower crystallinity.

### 6.3 Charge transport through the SnO$_2$ nanoflowers and nanofibers

Electrochemical impedance spectroscopy (EIS) is considered as a powerful tool to analyze the charge transport kinetics at the electrodes in DSCs. The EIS data of DSCs is usually evaluated with an electrical equivalent comprising of resistors and capacitors (Figure 6.10), which represents various interfacial and transport processes occurring in DSCs. This model is used to extract the parameters corresponding to the diffusion and recombination processes in DSCs.[200, 201]
A typical EIS spectra of DSCs consists of three semi circles (refer Figure 2.8) on account of three processes, viz., (i) charge transport resistance that occurs at high frequency (> 1 kHz); (ii) charge transfer resistance which occurs at intermediate frequencies (1kHz < f< 1 Hz); and ion diffusion processes that occurs at lower frequencies (< 1 Hz).

The grains composing the flowers and the fibers are of sufficiently larger size (50 – 80 nm) to support a space charge region; and therefore, they could exhibit frequency dependant interfacial capacitance. Hence, the capacitors in the electrical equivalent is replaced by a constant phase element (CPE).[202] The charge transport parameters of the DSCs can be calculated from the transmission line as follows. For a device with an electrode thickness $L$, the

Figure 6.10 Difference in EIS curves in the high frequency region of the flowers and fibers (top); the electrical equivalent of a dye-sensitized solar cell used in this work to elucidate charge transport parameters (bottom).
electron transport resistance in the electrode material is $R_T=r_L$. The interfacial charge recombination resistance, $R_{CT}=r_{ct}/L$ is indicative of recombination with the electrolyte; while the chemical capacitance, $C_c=c_L/L$ is indicative of the electron density of the electrode material.[200] The $\tau_n$ was calculated from $\tau_n = (r_{ct}e)^{1/\beta}$, where $\beta$ is the CPE exponent. The $r_L$, $c_L$, $r_{ct}$, and $\beta$ are components of the transmission line.[200]

### 6.3.1 Effect of trap states on carrier transport – EIS analysis

The characteristic data corresponding to the electron density of states and recombination processes extracted from the EIS spectra using the recombination model described above is shown in Figure 6.11 for both devices. Figure 6.11A is the difference in $C_c$ normalized with respect to the electrode area for the flowers and fibers. Both the trends showed an exponential dependence on applied voltage as expected.[203] Apparently, the flowers are characterized by an order of magnitude higher $C_c$ than that of the fibers.

The chemical capacitance, $C_c$ has contributions from the total density of electronic states in the conduction band ($N_C$) as well as in the band tail ($N_L$) states.[203, 204] Assuming similar $N_C$ for both structures by considering the fact that the particles composing them are much higher than the exciton Bohr radius of SnO$_2$ (~2.7 nm), difference in the magnitude of $C_c$ results from the density of band tail states. For a given Fermi level, the $C_c$ has the expression,[205, 206]

$$C_c = \frac{N_L n_s^2}{k_B T_0} \exp \left[ \frac{-\left(E_0-E_F\right)}{k_B T_0} \right]$$  \hspace{1cm} (6.6)
where $k_B$ is the Boltzman constant, $N_L$ is the total density of states in the band tail, $e$ is the electronic charge, $E_o$ is the bottom of the conduction band energy, and $T_o$ is a parameter with temperature units that determines the depth of the distribution of the localized states. As discussed earlier, $E_o$ and $T_o$ can be considered similar for the flower and fiber morphology. Therefore, it follows that even with a lower $N_L$, if the flowers shows enhanced $C_s$, it certainly indicates that $E_F$ of flowers are at higher energies than that of the fibers. Therefore, considering the expression $V_{OC} \propto (F_{n1} - F_{n2})$, where $F_{n1}$ is the Fermi energy of the photoelectrode and $F_{n2}$ is the electrochemical potential energy of the electrolyte, the flower based DSCs shows an increased $V_{OC}$. Considering the physico-chemical characteristics of these two morphologies,
the enhanced $E_F$ of the flowers can be attributed to its enhanced crystallinity and lowered trap-density. In general, well ordered crystal lattice leads to close lying atomic orbitals thereby resulting in enhanced $E_F$. Therefore, improvement in the $E_F$ is not surprising for materials with higher crystallinity; however, in this case of SnO$_2$ flowers it is accompanied by a twofold increase in the specific surface area which is rather rare.

The interfacial charge recombination resistance, $R_{CT}$ showed an exponential decay with applied voltage for the two types of morphologies (Figure 6.11B). It can be noticed from the trend that the $R_{CT}$ (flowers) $>$ $R_{CT}$ (fibers). Electron recombination with the hole-conductor (electrolyte) in DSCs mainly depends on the (i) energy of the conduction band edge and (ii) electron lifetime ($\tau_n$). As the band edges and band gaps are similar for flowers and fibers, the recombination rate constant as a result of case (i) does not differ. Therefore, the variation in $R_{CT}$ in the two types of morphologies arises from different $\tau_n$. The $\tau_n$ extracted from the EIS spectra, as shown in Figure 6.11C, exhibited an exponential dependence with voltage and also higher values for the flower morphology.

6.3.2 Effect of trap states on carrier lifetime – OCVD analysis

SnO$_2$ flowers exhibited enhanced $\tau_n$ at all voltages unlike that observed in OCVD studies (Figure 6.9). Remember that the OCVD measurements showed that $\tau_n$ was higher at higher voltages and lower at lower voltages for fiber based devices. This variation could arise from the difference in time domain involved in both measurements techniques i.e. the OCVD measures the real time electron decay in the absence of an applied electric field whereas the EIS
measurements employ a bias voltage. The electrons diffuse due to electron concentration gradient with a $D_n$ in the absence of an electric field whereas they are accelerated when a bias voltage is applied. Therefore, the $\tau_n$ and corresponding properties that include a temporal component such as $D_n$ and $\mu_n$ calculated from EIS measurements are expected to be a slight overestimation. Nevertheless, both measurements show that flowers are characterized by a higher $\tau_n$ over an appreciable range of voltage; and therefore, could be a better choice of photoanode to build highly efficient DSCs than the fibers.

The electron transport resistance $R_T$ as a function of applied voltage is shown in Figure 6.11D which is extracted from the EIS spectra using the transmission line model. Ideally, higher $R_{CT}$ and lower $R_T$ are preferred for a high performance device. Interestingly, the flowers are characterized by higher $R_{CT}$ and lower $R_T$ compared with that of the fibres despite the fact that one-dimensional nanostructures, both in the ordered and disordered geometries, such as nanowires, rods, and fibres are shown to have lower transport resistance on account of guided transport. However, crystallinity of the two morphologies is significantly different and, the band gap of fibers has high density of localized energy states (or deep trap states). Therefore, lower $R_T$ of the flowers could be attributed to its high crystallinity as a more ordered lattice contributes to less resistivity. Reports from Dou et al recently showed similar $R_T$ for highly crystalline Zn doped SnO$_2$ flowers.[207] However, in general, it is unlikely that flower morphology is more favourable for enhanced charge transport properties than the one-dimensional nanostructure morphologies; rather it is a function of crystallinity and guided transport. It is also worthy to mention, that removal of band tail states in nanofibers was also been shown to
promote the charge transport properties considerably.[208] Figure 6.11D also shows that the SnO₂ nanostructures exhibit a weak dependence of $R_T$ on applied voltage thereby indicating more metallic conduction through them as similar to charge transport through niobium doped TiO₂.

### 6.3.3 Evaluation of diffusion coefficient and mobility by photocurrent transient measurements

Furthermore, the diffusion co-efficient ($D_n$) and electron mobility ($\mu_n$) through the SnO₂ flowers and fibers in the presence of the iodide/triiodide electrolyte were evaluated from the transient photocurrent measurements. The photocurrent transients observed for the flowers and fibers are shown in Figure 6.12. The photocurrent was observed immediately after the laser excitation in the device and attains the peak at around 90 $\mu$s followed by an exponential decay.
The photocurrent rise time of the flower based device was much faster compared with that of the fiber. The decay time ($\tau_c$) was extracted by fitting the photocurrent transients using a single exponential decay. The decay times normalized with respect to the thickness of the cells as well as $\mu_n$ calculated from $D_n$, using Einstein’s relation are listed in Table 6.1. Table 6.1 also compares the decay times of SnO$_2$ nanowires and nanoparticles,[168] electrospun TiO$_2$ nanowires,[208] and niobium doped TiO$_2$[209]. The SnO$_2$ flowers displayed the lower decay time implying faster charge transport through them; which is in agreement with the results of OCVD and EIS measurements.

Figure 6.12 Charge decay behavior of the flower and fiber based devices. The inset shows the difference in photocurrent rise times.
Table 6.1 Comparison of normalized transition time and electron mobility of the SnO\(_2\) with popular metal oxide semiconductors

<table>
<thead>
<tr>
<th>Morphology</th>
<th>Transit time [ms]</th>
<th>Electron Mobility [cm(^2) V(^{-1}) s(^{-1})] x 10(^{-3})</th>
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</thead>
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<tr>
<td>SnO(_2) Fibers</td>
<td>10</td>
<td>3.75</td>
</tr>
<tr>
<td>SnO(_2) Flowers</td>
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<tr>
<td>Electrospun TiO(_2) Nanowires</td>
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<td>6.74</td>
</tr>
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<td>15</td>
<td>2.47</td>
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</tbody>
</table>

The \(D_n\) of electrons through the flower and fiber structure was evaluated using the relation, \(\tau_e = d^2 / 2.35D_n\), where \(d\) is the thickness of the samples. The factor 2.35 corresponds to the diffusion geometry.[81, 210] The electron collection time or transport time reported in this study is calculated from the long time domain of the transient photocurrent signal, which is independent of the absorption coefficient or the direction of illumination of the probe light.
The $D_n$ through the SnO$_2$ flower and fiber-based devices are shown in Figure 6.13, which was an order of magnitude higher for flowers than the fibers. The flowers exhibited a $D_n$ of $\sim 3.74 \times 10^{-4}$ cm$^2$/s, which for the fibers was $\sim 7.572 \times 10^{-5}$ cm$^2$/s; both were recorded at a photoexcitation density of $\sim 6 \times 10^{18}$/cm$^3$. This value of $D_n$ is nearly four orders of magnitude higher than that reported using TiO$_2$ nanoparticles and 2.5 times higher than electrospun TiO$_2$ nanowires.[208] The $D_n$ of the flowers was observed to be independent of the photoexcitation density (refer Figure 6.13) which indicates that the electron diffusion in this nanostructure occurs predominantly through the band edges with enhanced electron density and Fermi energy.[211, 212] On the contrary, the $D_n$ showed a dependence on photoexcitation density for the SnO$_2$ fibers, thereby indicating a high density of surface traps on account of their inferior crystallinity.[213]
6.3.4 Origin of high $J_{SC}$ in the flower based device

The photoelectric conversion efficiency of DSCs is generally expressed as

$$\eta = \alpha \Phi_{in} \eta_c,$$  \hspace{1cm} (6.4)

Where $\alpha$ is the strength of absorption, $\Phi_{in}$ is the injection efficiency, and $\eta_c$ is the charge collection efficiency.[71, 100] As there is no difference in the flat band potential of flowers and fibers, $\Phi_{in}$ is assumed similar. The two-types of DSCs were fabricated using similar dyes so their absorption cross-section does not differ. However, dye-loading calculated from desorption test for flowers and fibers were 7.8 and 5.6 mmoles, respectively. i.e., i.e., the dye-loading of the device based on the flower structure is only 1.4 times higher than that based on the fibers.

![Figure 6.14 Photoaction spectra (IPCE) of the DSCs using flowers and fibers.](image)

If we assume that one photon absorbed by the dye injects one electron to SnO$_2$, then the dye-loading measurements gives the number of electrons received by flowers and fibers to be $7.8 \times 10^{16}$ and $5.7 \times 10^{16}$ per cycle,
respectively. Despite of this small variation in the received electrons, the $J_{SC}$ of the devices using the flowers were found be higher by a factor of ~2.5 than that of the devices using the fibers, which means that the observed enhanced $J_{SC}$ results from the enhanced charge collection efficiency, $\eta_c$, of the flower based device.

The difference in collection efficiencies of the two-types of DSCs were studied from the photocurrent action spectra of the devices fabricated using the two-types of cells. Figure 6.14 shows the action spectra of the two types of devices. The spectra display significant enhancement in the incident photon to current conversion efficiency (IPCE) of the devices based on flowers. The highest IPCE for the devices based on the fibers and flowers were ~12% and 42%, respectively. The improvement can be attributed to the enhanced electron density and charge transport efficiency as well as a slightly higher amount of the dye-loaded onto the flower based device. However, it is reported that an increase in the dye-loading of 1.4 times result only in an increase in IPCE by ~3.5%.[214, 215] In the present case IPCE of the flower based devices increased by ~30% compared to that of the fibers thereby indicating the enhanced charge transport kinetics in the flower structure. To check the consistency of the results between the photo action spectra and I-V measurements, the $J_{SC}$ of the devices were calculated from their IPCE spectra using the relation

$$IPCE(\%) = \frac{J_{SC}(mA/cm^2)}{P(mW/cm^2)} \times \frac{1240}{\lambda(nm)} \times 100\%. \quad (6.7)$$
The integrated IPCE over the entire wavelength (\( \lambda \)) was used to calculate the \( J_{SC} \). The calculated \( J_{SC} \) of the flower and fiber based devices were 7.57 and 2.97 mA/cm\(^2\), respectively. These values closely match with their measured \( J_{SC} \) from the I-V measurements, i.e., 7.3 and 3 mA/cm\(^2\), respectively.

To determine the electron lifetime, which resulted in enhanced \( \eta_c \), the EIS spectra of the DSCs were recorded in the dark under forward bias of 0.61 V (Figure 6.15). The Nyquist plots (Figure 6.15A) show that radius of the right semicircle of the flower based device is larger compared to that made using the fibers. The larger semicircle observed for SnO\(_2\) flowers indicate that it is characterized by enhanced charge transfer resistance; and therefore, an

![Figure 6.15 Impedance spectra of the flowers and fibers (A) Nyquist and (B) Bode plots.](image-url)
increased electron lifetime. The carrier lifetime $\tau_n$ can be calculated from the Bode plots (Figure 6.15B) using the equation $\tau_n = 1/2\pi f_c \tau_n = 1/2\pi f_c$, where $f_c$ is the peak frequency which for the flowers and fibers were 0.84 and 4.22 Hz at 0.61 V, respectively. These frequencies correspond to a $\tau_n$ of 0.189s and 0.0377s, respectively. i.e., the $\tau_n$ of the flowers is an order of magnitude longer than that of the fibers. The longer $\tau_n$ of the device fabricated using the flower-like morphology indicates more effective suppression of the back reaction between electrons in its conduction band and $I_3^-$ ions in the electrolyte. The increased $\tau_n$ is thought to be the source of high $J_{SC}$ and $\eta$ of the device fabricated using the flower-like morphology.

6.3.5 Origin of high $V_{OC}$ in the flower based device

To the best of our knowledge, the $V_{OC}$ obtained using the flower-morphology (~700 mV) is the highest so far accomplished using SnO$_2$. Origin of high $V_{OC}$ in flower based DSCs could be inferred from the kinetic equation of DSCs under steady state condition, i.e., when the electron injection from the dye to SnO$_2$ is equal to the electron transfer from the counter electrode to the electrolyte, given by [71, 100]

$$V_{OC} = \frac{kT}{e} \ln \left( \frac{J_{in} n_{cb} K_{rec}}{I_3^-} \right).$$ \hspace{1cm} (6.8)

In the above equation $J_{in}$ is the flux of the injected electrons, $K_{rec}[I_3^-]$ is the rate constant of iodide reduction and $n_{cb}$ is the conduction band electron density in the dark. Therefore, the large difference in the $V_{OC}$ would partially result from the difference in the iodide reduction, which occurs in two pathways. First of
which is the reduction by the counter electrode, which is same for similar device geometry. The second is the recombination pathway, i.e., the electron in the SnO$_2$ directly reduces the iodide ions – which account for the majority of the carrier loss. High internal resistance ($R_H \sim 1600 \Omega$) for this back electron transfer from SnO$_2$ to electrolyte measured for the flower based device as well as high $n_D$ accounts the observed high $V_{OC}$ and FF. Remember that $D_n$ and $\mu_n$ through the flowers were much higher than that through the fibers, which accounts for the faster charge collection before recombination and resulted in higher $V_{OC}$.

6.4 Conclusions

In conclusion, tin oxide nanoflowers were developed by a scalable nanofabrication process, electrospinning, by manipulating the precursor concentration for the first time. Several experimental studies was performed to evaluate the difference in band structure and charge transport properties of SnO$_2$ flowers and fibers produced by the electrospinning technique, from polymeric solutions differing in tin precursor concentration. The absorption spectra of the flowers and the fibers reveal that they possess similar band gaps; however, the open circuit voltage decay measurements indicate that the flowers have lower density of surface traps in the band gap on account of their enhanced crystallinity. It is also shown that the SnO$_2$ flowers exhibit a higher Fermi energy than the fibers owing to which a record open circuit voltage was obtained when the flowers were used as photoanode (or photoelectrode) in the DSCs. The flowers are also characterized by higher electron recombination resistance, higher chemical capacitance, and lower charge transport resistance.
which are the prime factors contributing to higher short circuit current density in flower-based DSCs. The superior charge transport properties of the flowers are attributed to their enhanced crystallinity. It is also noteworthy, that enhanced crystallinity in the SnO$_2$ flowers coexisted with a two-fold BET specific surface area than the fibers, the simultaneous occurrence of which is rather rare. The transient photocurrent measurements were employed to evaluate the effective electron diffusivity and mobility of both SnO$_2$ morphologies. The SnO$_2$ flowers exhibited an order of magnitude higher electron diffusivity and mobility compared with the conventional SnO$_2$ and TiO$_2$ nanostructures/morphologies; and therefore, SnO$_2$ flowers could be an acceptable material for various nanotechnology applications requiring high surface area and electron mobility.
7 Future Outlook and Recommendations

In future work, the efficacy of the ETL and HTL can be improved by modifying the processing conditions to alter its electronic properties. For instance, plasma treatment of the interfacial layers is expected to have a significant effect on the work function of these materials. Moreover, the role of interfacial layers in improving the device efficacy in terms of performance and stability can be explored further using TOF SIMS measurement. It would help to map the oxygen and water percolation in the device providing a better understanding of the mechanism of enhancement of charge transport and stability in the devices employing engineered MoO$_3$ (HTL) and ZnO (ETL) interlayers. In-SITU XPS studies on the modified interfacial layers could reveal the precise stochiometric change of its chemical composition which can be correlated to the change in electronic properties in these materials, in turn could be related to the actual device performance. An in-depth analysis of the stability enhancement in the OSC devices can be extended by evaluating the time dependent IPCE measurements. This approach could reveal valuable information on the chemical/structural changes occurring in the active layer of the devices employing the modified interfacial layers. The reason behind the improvement in charge transport properties and photo-stability of the devices can be ascertained clearly using such methods. Furthermore, modelling and fitting of the temperature dependent I-V spectra would reveal valuable information on ideality factor providing a better understanding of the recombination kinetics in the devices. In order to fit the temperature dependent I-V curves, a suitable model has to be developed and simulated before using it.
for fitting, to evaluate the temperature co-efficient to be used, in the final equation to evaluate the ideality factor accurately.

On the other hand, the removal of localized gap states in tin oxide can be facilitated by further engineering of the nanostructure morphology. Apart from that, the doping of tin oxide nanostructures with Antimony is expected to improve its electronic properties favoring enhanced charge collection efficiency and improved Voc. Moreover use of tailored electrolyte with higher redox potential (more electropositive) instead of typical Iodide/tri-iodide for fabricating DSCs with tin oxide nanostructures, could enhance the Voc of the device to a considerable extent. Deposition of a TiO₂ scattering layer onto tin oxide nanostructure could improve the charge injection efficiency from dye to photoanode since most of the efficient dyes available are engineered for TiO₂. Furthermore, the temperature dependent analysis used for OSCs can also be employed for DSCs for understanding the charge transport properties. It would be much suitable for DSCs especially when the liquid electrolyte is replaced with hole conducting polymers (or solid electrolytes) thereby avoiding electrolyte leakage during actual measurement under vacuum conditions. Addressing the above mentioned existing issues could improve the potential prospects of these devices to a significant level, adding to the claim of making excitonic solar cells a promising candidate for cheaper, efficient and stable means of solar electricity.
8 Bibliography


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