Chapter -2

Experimental and Characterization Techniques
This chapter deals with the brief description of various materials employed in the fabrication of polymer and dye-sensitized solar cells and details of the fabrication processes. In addition, brief descriptions of the equipment utilized for the fabrication and characterization of the solar cells are presented.

2.1 Materials

The molecular structures of various materials employed in the fabrication of both polymer and dye-sensitized solar cells are presented in Appendix (Fig. A1 & Fig. A2). The key materials employed during this thesis work are presented as follows.

2.1.1 Materials for polymer solar cells

(a) **ITO Substrates**: Indium tin oxide (ITO) coated glass substrates were purchased from Visiontek systems ltd., U.K. The soda lime float glass is coated with a primary layer of silicone oxide (SiO$_2$), which acts as a barrier layer and secondary layer of ITO with a thickness of 150nm. These substrates have a sheet resistance of 6 – 12 ohm/sq as measured by four-probe resistivity, transmittance >80% at 550 nm as measured by UV-Vis spectroscopy, and rms roughness of 0.5 nm measured by atomic force microscopy. These properties make ITO substrates ideal for the fabrication of polymer solar cells.

(b) **PEDOT:PSS**: Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) of make Heraeus Clevios™ (PH1000) was purchased from Ossila, U.K. PEDOT:PSS thin films on glass substrates have conductivities of 100 S/cm measured by four-probe resistivity, transmittance > 80 % at 550 nm as measured by UV-Vis spectroscopy. PEDOT:PSS thin films have a work function of 5.1 eV, which matches
energetically with most p-type conducting polymers and ITO substrate acting as a hole transport material.

(c) **P3HT**: Poly(3-hexylthiophene-2,5-diyl) of make *Plextronics (Plexcore® OS 2100)* was purchased from *Sigma Aldrich, India*. P3HT is an electronic grade material with an average molecular weight $M_n = 54000-75000$, ultra-high purity ($< 25$ ppm trace metals), and regioregularity (98% head-to-tail), was employed as an electron donor material in polymer solar cells.

(d) **PCBM**: [6,6]-Phenyl C$_{71}$ butyric acid methyl ester ([70]PCBM), hereafter termed as PCBM, was purchased from *Sigma Aldrich, India*. PCBM is a functionalized fullerene (suitable for solution processing) with extended visible absorption for more energy harvesting, which is employed as an electron acceptor material in polymer solar cells.

(e) **Porphyrin**: 5,10,15,20-tetrakis(4-hydroxyphenyl)- porphyrin, hereafter termed as THPP, was purchased from *Sigma Aldrich, India*. Porphyrin being naturally occurring chromophore has a strong visible absorption, was employed as an electron donor for bilayer polymer solar cells.

(f) **Fullerene**: Sublimed grade fullerene (C$_{60}$), with 99.9 % purity was purchased from *Sigma Aldrich, India*. Fullerene which has a high electron-affinity, was polymerized via electro-polymerization and later used as an electron acceptor for bilayer polymer solar cells.

(g) **Aluminum**: Aluminum evaporation slug with 99.999% trace metal basis was purchased from *Sigma Aldrich, India* for deposition of top metal contacts for both bilayer and bulk-heterojunction solar cells.
(h) **Sealant:** UV curable encapsulation epoxy has been used for sealing polymer solar cells fabricated in Glove Box, which was purchased from *Ossila Limited, U.K.* The devices fabricated inside the Glove Box are sealed for photovoltaic characterization.

(i) **Kelvin clips:** The contacts for top and bottom electrodes of the sealed devices are made by using a gold coated flat alligator clip (known as Kelvin clips), purchased from *Synkera Technologies Inc.*

(j) **Solvents:** 1,2-dichlorobenzene (anhydrous) was used in the preparation of Active layer mixture, methanol (anhydrous) & dichloromethane (anhydrous) were used for electro-deposition of poly-THPP and poly-fullerene films. Hellmanex-III glass cleaning detergent, ultrapure milli-Q water, semiconductor grade solvents (Acetone, 2-propanol) were used for cleaning ITO substrates.

### 2.1.2 Materials for dye-sensitized solar cells

(a) **FTO Substrates:** Fluorine-doped tin oxide (FTO) coated glass substrates, with trade name “TCO22-7” were purchased from *Solaronix Inc. Switzerland.* As the preparation of nanostructured TiO$_2$ electrodes and platinum counter electrodes involve high annealing temperatures of 450°C, FTO has been the only choice of TCO, stable at these temperatures. These substrates have a sheet resistance of 7 ohm/sq, with transmittance >80% at 550 nm.

(b) **Photoanodes**

(i) **ZnO photoanodes:** For the growth of ZnO nanostructures, Zinc acetate dihydrate of reagent grade with purity >98%, AR grade Sodium hydroxide
(NaOH) pellets (purity >98.5%), reagent grade Zinc nitrate hexahydrate 
(Zn(NO\textsubscript{3})\textsubscript{2} .6H\textsubscript{2}O) with purity 98%, and ACS reagent grade 
hexamethylenetetramine (HMT) with purity >99% were purchased from Sigma Aldrich, India.

(ii) TiO\textsubscript{2} photoanodes: High- transparent nanocrystalline Titanium dioxide (TiO\textsubscript{2}) paste with trade name “Ti-Nanoxide HT” was purchased from Solaronix Inc. Switzerland. The paste containing anatase TiO\textsubscript{2} nanoparticles of 8-10 nm yields highly transparent films after deposition.

(c) Sensitizer Dyes

(i) Organic dyes – High molar extinction coefficient BODIPY based laser dye with trade name “PM567” was synthesized in our research labs. Rhodamine 19 perchlorate (RhCl\textsubscript{3}) with absorption maxima at 517nm was purchased from Sigma Aldrich, India.

(ii) Ruthenium dyes – Widely employed ruthenium polypyridyl complex, N3 dye (cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II)) was purchased from Solaronix Inc. Switzerland.

(d) Electrolyte: Electrolyte containing I\textsubscript{3}/I\textsubscript{3} redox couples were prepared by using Lithium Iodide (LiI) and Iodine (I\textsubscript{2}) purchased from Sigma Aldrich, India. Solvents required for different types of organic, aqueous, and gel polymer electrolyte were purchased from Sigma Aldrich India.

(e) Counter electrodes

(i) Platinum precursor: Hexachloroplatinic(IV) acid with 11-15% Pt in Iso-propanol was purchased from Merck GmbH.
(ii) Pyrrole: Analytical grade pyrrole was purchased from Sigma Aldrich, India to synthesize polypyrrole thin films via electro-deposition and interfacial polymerization.

(f) Sealant: Prior to photovoltaic characterization, the devices were sealed by using either a parafilm or a 60 μm thermoplastic hot-melt sealing foil. (Suryln®, Solaronix Inc.)

2.2 Fabrication of polymer solar cells

2.2.1 Glove box: spin coater and thermal evaporator

Conducting polymers and small molecules commonly employed in the fabrication of solar cells readily degrade (are doped) when exposed to atmospheric conditions. Hence, an inert Glove Box (MB 20G, M. BRAUN INERTGAS-SYSTEME GMBH) with oxygen and moisture levels <0.1 ppm, was used to fabricate the polymer solar cells. The Glove Box system works by the principle of gas circulation, where the working gas circulates between the Glove Box and the gas purifier. The gas purification system removes moisture and oxygen from the inert gas Glove Box atmosphere. It utilizes a proprietary reactive agent to withdraw oxygen from the inert gas and a proprietary adsorbent to remove water, thus maintaining both H₂O and O₂ at <0.1 ppm. The photograph of the Glove Box is shown in the Fig. 2.1. The custom-made Glove Box contains two boxes, Box 1 contains a Spin coater (Delta6 BM/TT, Suss Microtec Lithography GmbH) for deposition of thin films and Box 2 contains a thermal evaporator (custom made by BOC Edwards Inc.) for
metal contacts. The entire fabrication of polymer solar cells starting from solution preparation to final device encapsulation is carried out in Glove Box.

Figure 2.1: The photograph of the MBraun modular glove box system.

2.2.2 Fabrication process

In this section we describe the detail fabrication process of P3HT:PCBM bulk-heterojunction solar cells, porphyrin/polyfullerene diffuse bilayer solar cells, and porphyrin-modified ZnO-NW/P3HT hybrid solar cells

(a) P3HT:PCBM bulk-heterojunction solar cells

Bulk-heterojunction polymer solar cells with a device architecture of ITO/PEDOT:PSS/P3HT:PCBM/Al were fabricated inside Glove Box as depicted in schematically Fig. 2.2. The steps involved in the fabrication are as follows:
(i) ITO substrates were cut into required dimensions of 1” x 1”, and patterned into definite stripes by masking through a tape. These masked substrates are placed in Acid etchant solution for 30 min. The patterned substrates are subsequently cleaned using detergent, de-ionized water, acetone and 2-propanol respectively.

(ii) Hole transport layer PEDOT:PSS (thickness: 50 nm) was deposited onto clean ITO substrates by spin coating, which were then transferred to glove box having moisture and oxygen <0.1 ppm. These samples were then annealed at 130°C for 30 min.

(iii) A mixture of P3HT and PCBM (with 1:1 W/W, 20 mg/ml) were dissolved in 1,2-dichlorobenzene solvent by continuous stirring for 24 hrs and later filtered through 0.45 μm syringe filters. An active layer P3HT:PCBM (thickness:100 nm) layer was deposited by spin coating the filtered solution onto PEDOT:PSS coated ITO substrates. These samples were annealed at various temperatures between 25 and 180°C for 30 min.

(iv) The solar cell configuration was established by thermal deposition of Al under a base vacuum of ~ 10⁻⁶ torr through a shadow mask to obtain an active area of 6 mm².

(v) These solar cells were encapsulated using UV curable epoxy inside the glove box and taken out for the photovoltaic characterization.
Figure 2.2: A schematic depiction of various processes involved in making 3 x 3 array polymer solar cell.

(b) Porphyrin/polyfullerene diffuse bilayer solar cells

Bilayer polymer solar cells were fabricated by sequential deposition of donor and acceptor layers on ITO substrates as mentioned below. A schematic picture representing fabrication of bilayer solar cells is shown in the Fig 2.3. Firstly, porphyrin was electro-deposited on PEDOT:PSS coated ITO substrates which acts as donor, and later poly-fullerene films were electro-deposited on top of porphyrin films, thus forming a bilayer heterojunction. Finally, thermal evaporation of Al defines the active area of the devices. The deposition of porphyrin films and poly-fullerene films are presented individually as follows.
**Figure 2.3:** Schematic depiction of fabrication of bilayer solar cells

*Electro-deposition of porphyrin:* The following procedure was employed for electro-deposition of 5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin (THPP) on ITO substrates.

(i) 1mM THPP in methanol as a monomer solution and 0.1M tetra butyl ammonium perchlorate (TBAP) in methanol as a supporting electrolyte are prepared in volumetric flasks.

(ii) After total dissolution of the above two solutions, they are mixed in 1:1 (V/V) ratio in a separate weighing bottle.
(iii) The solution is now placed in a conventional three electrode cell where ITO substrate acts as working electrode, platinum strip as counter electrode, and Ag/AgCl wire as reference electrode.

(iv) The polymerization is carried out with a potentiostat/galvanostat system by cyclic voltammetry (CV) method. Briefly for electro-deposition, the solution mixture is cycled between 0 to 1V for 5-100 cycles/scans at a scan rate of 50 mVs$^{-1}$.

(v) This yields in uniform growth of polymeric THPP on ITO substrates.

(vi) The porphyrin coated substrates are washed in methanol, dried under N$_2$ stream and stored in desiccator under dark, which are later characterized by spectroscopic techniques and used as a working electrode for deposition of poly-fullerene, to fabricate diffuse bilayer solar cells.

**Electrodeposition of polyfullerene films**: The following procedure was employed to electro-polymerize fullerene on ITO substrates

(i) The ITO coated glass substrates were first cleaned with detergent, ultrasonicated in acetone and isopropyl alcohol, and subsequently dried under Argon flow.

(ii) C$_{60}$ solution (0.72 mM) in Dichloromethane was extensively sonicated prior to use and mixed (1:1, v/v) in a 0.1M TBAP.

(iii) The resulting solution was reduced extensively at -1.5V vs Ag/AgCl reference electrode using platinum strip as working and counter electrode.

(iv) After reduction (a color change from pale pink to pale brown was observed), linear sweep voltammetry was carried using ITO as working electrode and electrochemical measurement was done.

(v) It is observed that the thickness of C$_{60}$ films increased with no. of linear sweeps.
(vi) All characterizations were performed in an ambient environment without a protective atmosphere.

(c) Hybrid solar cells

*Growth of ZnO-NWs on ITO substrates*

A two-step process has been followed to grow ZnO nanowires from ZnO seed particles [70, 71], and the growth of ZnO nanostructures were schematically depicted in Fig 2.4.

**Figure 2.4:** Schematic depiction of ZnO NW growth on ITO substrates via hydrothermal route through ZnO nanoparticles. The schematic shows step by step process from seed layer to nanowire growth.

The major steps involved are:

*Step 1:* ZnO NPs have been synthesized by acetate route, where 50 mM zinc acetate dihydrate and 100 mM NaOH solution in ethanol were reacted for 6 h at temperature, 70–75°C, to produce ZnO nanocrystals of size, 15-30 nm. Our objective was to control the density of the nanorods that were grown on these seeds. The density of the rods grown depends on the density of the seed particles. To grow the nanorod arrays with controlled density, we have optimized the process.
using different amounts of ZnO seed particles. ZnO nanoparticles so formed were of size 30-40 nm, which were used as the seed layer for ZnO NWs array growth. The ZnO nanoparticles were dispersed thoroughly in ethanol and then coated onto ITO substrates by drop casting different amounts of the solution. The seeded substrates were annealed for 1 hr at a temperature of 150°C for good adhesion of seed particles on to the substrate. The seed layer thus prepared, act as nucleating sites for growth of nanowires due to the lowering of the thermodynamic barrier

\[72\].

**Step 2:** The ZnO NWs are grown by solution phase hydrothermal route due to ease of handling, low temperatures, low cost, and scalability for large area applications. A precursor solution containing an equimolar mixture of zinc nitrate hexahydrate (Zn(NO$_3$)$_2$ .6H$_2$O) and alkaline reagent (such as hexamethylenetetramine (HMT)) are used for ZnO NW growth. The various chemical reactions occurring with this precursor solution are presented in Eq. 2.1 - 2.4. The ZnO seeded substrates were dipped in constantly stirred aqueous solution of 30 mM Zn(NO$_3$)$_2$. 6H$_2$O and 30 mM HMT for 6 hrs at a temperature of 95°C. The seed layer promotes the nucleation for the growth of ZnO NW due to lowering of the thermodynamic barrier \[72\]. The resultant substrates were then washed with de-ionized water followed by annealing at 120°C in vacuum for 30 minutes, in order to improve adhesion of ZnO NW onto ITO substrates.

The following chemical reactions occur during the growth of ZnO NW’s

i. Decomposition reaction:

\[
(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \quad (2.1)
\]
ii. Hydroxyl supply reaction:
\[
\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^- \quad (2.2)
\]

iii. Supersaturation reaction:
\[
2\text{OH}^- + \text{Zn}^{2+} \rightarrow \text{Zn(OH)}_2 \quad (2.3)
\]

iv. ZnO nanowire growth reaction:
\[
\text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O} \quad (2.4)
\]

**Fabrication of hybrid solar cells**

Two different solar cells were fabricated by employing device structures (i) ITO/ZnO-NW/P3HT/Au and ITO/porphyrin-modified ZnO-NW/P3HT/Au as depicted schematically in Fig 2.5.

(i) The hybrid solar cells with device configuration as shown in Fig. 2.5 (a) are fabricated by spin-coating P3HT solution onto ZnO-NW electrodes thermally grown on patterned ITO substrates, followed by thermal evaporation of gold.

(ii) The hybrid solar cells with device configuration as shown in Fig. 2.5(b) are fabricated by first electrodepositing porphyrin film onto ZnO-NW electrodes (hereafter called as porphyrin-modified ZnO-NW), followed by spin-coating of P3HT and thermal evaporation of gold.
2.3 Fabrication of dye-sensitized solar cells

2.3.1 Fabrication process

The fabrication of dye-sensitized solar cell involves preparation of three individual components, instead polymer solar cells are fabricated on single substrate. (i) Fabrication of photoanodes on FTO substrates, (ii) Fabrication of counter electrode on either FTO or ITO substrates, and (iii) preparation of redox electrolyte. The fabrication of all these individual components are discussed below briefly.

2.3.2 Synthesis of photoanodes

As mentioned in Chapter 1, typical photoanodes are either prepared by ZnO nanostructures or TiO$_2$ nanostructures. The fabrication of this two photoanodes are discussed briefly.

(a) ZnO photoanodes
ZnO-NWs on ITO substrates as described in above section were used as ZnO photoanodes for dye-sensitized solar cells.

(b) Co-sensitized TiO$_2$ photoanodes

In the present work we used following two dyes for the co-sensitization: (i) Rhodamine 19 perchlorate, which is a very stable and economical laser dye and has not been explored earlier for DSSC, and (ii) N3 dye (widely employed ruthenium polypyrrole complex). RhCl dye was chosen on account of its high molar extinction coefficient ($2 \times 10^5$ M$^{-1}$cm$^{-1}$) as compared to N3 dye ($10^4$ M$^{-1}$cm$^{-1}$) owing to which only a little amount of RhCl dye is required to be absorbed on TiO$_2$ surface for yielding sufficient optical density for effective PCE. Briefly, the co-sensitized electrode is fabricated as follows:

(i) TiO$_2$ photoanodes are prepared by doctor blading TiO$_2$ paste (solaronix make) on FTO substrates, followed by annealing at 450ºC for 30 mins in a tubular furnace.

(ii) Prior to sensitization, the TiO$_2$ electrode was treated with formic acid solution (0.05M in ethanol) for 2 h and later washed with ethanol and dried under N$_2$ stream.

(iii) This formic acid treated TiO$_2$ electrode were refluxed in a round bottomed flask containing RhCl dye solution (0.6 mg/ml in ethanol) equipped with a water-jacketed reflux condenser and a heating source at 70ºC for 2 h. This RhCl dye coated electrodes were later removed and washed with ethanol and dried under N$_2$ stream.

(iv) RhCl sensitized TiO$_2$ photoanodes are later dipped in N3 dye solution (0.3 mg/ml in ethanol) for different time intervals ($t_d$) and later washed with ethanol solvent and dried under N$_2$ stream thus forming co-sensitized TiO$_2$ photoanodes.
2.3.3 Synthesis of electrolyte

Electrolytes typically consist of a redox couple and additives dissolved in a liquid or quasi-gel. The main function of the electrolyte is the dye regeneration and charge transport between the TiO₂ photoanode and platinized counter electrodes. Electrolytes employed in the present thesis work are described below.

a) **Organic electrolyte 1:** Typically this electrolyte is prepared by mixing 0.1 M LiI and 0.05 M I₂ in dry acetonitrile organic solvent.

b) **Organic electrolyte 2:** this electrolyte is prepared by mixing 0.1 M LiI and 0.05 M I₂ in dry 3-methoxypropionitrile solvent.

c) **Aqueous electrolyte 1:** Briefly the electrolyte is prepared with 0.5 M LiI and 0.05 M I₂ in deionized water.

d) **Aqueous electrolyte 2:** Briefly the electrolyte is prepared with 0.01 M FeCl₃ and 0.1M KCl in deionized water.

e) **Gel polymer electrolyte:** The quasi-solid state electrolyte or gel polymer electrolyte (GPE) is the electrolyte being in a state of both liquid and solid coexistence. Generally, this electrolyte is defined as a system which consists of a polymer network (polymer host) swollen with liquid electrolytes. Quasi-solid-state electrolytes are usually prepared by incorporating a large amount of a liquid electrolyte into organic monomer or polymer matrix, forming a stable gel with a network structure via a physical or chemical method. Briefly, it is prepared by first dissolving 1.338 g lithium iodide (LiI) and 0.254 g Iodine (I₂) in 4 ml propylene carbonate and 10 ml acetonitrile solution and then 3 g of polyethylene oxide (PEO,
MW– 1×10^6, Alfa Aesar) was added to this mixture. Later, this mixture was heated at 70–80°C under continuous stirring for 7–8 h. Finally, a homogeneous highly viscous GPE was obtained.

![Schematic depiction of preparation of platinum films on FTO electrodes with hexachloroplatinic acid solution.](image)

**Figure 2.6:** Schematic depiction of preparation of platinum films on FTO electrodes with hexachloroplatinic acid solution.

### 2.3.4 Synthesis of counter electrodes

The fabrication details of counter electrodes used in the present thesis work are briefly discussed in the following:

a) **Pt/FTO counter electrode**: These counter electrodes are prepared by thermal decomposition of platinum either by drop-casting or spin-coating of 5 mM H₂PtCl₆ in 2-propanol solution on FTO substrate, and reducing the Pt precursor in the air furnace at 450°C for 30 min (as schematically depicted in Fig. 2.6). Although the thermal cluster Pt has many advantages, such as, low Pt loading, the superior catalytic activity, and good mechanical stability, it requires heating up to 450°C,
which is energy consumptive and not suitable for commercial applications and flexible solar cells.

b) *Growth of free-standing polypyrrole films:* Pyrrole (Aldrich, 98%) was double distilled under reduced pressure prior to use. PPy free-standing films were synthesized typically by placing 20 ml, 0.1M aqueous FeCl₃ and 20 ml, 0.1M pyrrole in dichloromethane (DCM) in a beaker for varied times (4hrs to 18 hrs). A free-standing PPy film of thickness ~ 1μm is formed at the liquid-liquid interface after 4 hrs. The free-standing PPy film thickness increases with polymerization time, and finally a thick 75 μm film was formed after 18 hrs. These films are later lifted onto glass/plastic substrates, and subsequently, washed with de-ionized water and DCM to remove un-reacted FeCl₃ and pyrrole. The films thus obtained were dried overnight and can be handled using a pair of tweezers (shown in Fig.2.7).

**Figure 2.7:** (a) Schematic showing the formation of free-standing PPy films at the aqueous (0.1 M FeCl₃)/organic (0.1 M pyrrole) interface. (b) & (c) Photograph of the free-standing PPy films mechanically lifted with a pair of tweezers.
2.3.4 Device assembly

All the three components (i.e., photoanode, electrolyte, and counter electrode) are assembled together as described in Fig. 2.8. The dye coated electrode and counter-electrode are either sandwiched together by using a stretched parafilm or surlyn thermoplastic film as spacer. The electrolyte is injected between the electrodes through a perforated counter electrode by using a vacuum syringe filter and later encapsulated with epoxy or surly film. The assembled device is thus characterized by taking connections through alligator clips.
2.4 Characterization techniques

Several characterization techniques were employed during the course of thesis, which are described briefly as follows

**UV-visible spectroscopy**: UV-Vis spectroscopy is an absorption/reflectance spectroscopy technique used to determine the electronic transitions of materials, whose absorption is in the ultraviolet and visible region of an electromagnetic spectrum. The following data were recorded by using (Jasco V-530) UV-Vis spectrophotometer.

a) The transmittance of ITO, FTO, PEDOT:PSS coated ITO, Pt/FTO, electrodeposited platinum on ITO/PEN substrates.

b) Absorption of conducting polymers, PCBM, porphyrin dye in solution and their respective films.

c) Absorbance of dye sensitized photoanodes and the amount of dye loading on TiO$_2$ photoanodes were recorded.

**Fourier transform infrared spectroscopy**: Fourier Transform Infrared spectroscopy (FTIR) provides the information of different vibrational frequencies related to chemical bonds and the nature chemical functional groups present in the organic molecule. FTIR works on the principle of interferometer that gives an interferogram, a plot of light intensity versus optical path difference. This interferogram is finally Fourier transformed to give a spectrum of infrared radiation intensity versus wave number. The following spectra were recorded using Bruker spectrometer (model: Vertex 80 V) in ATR mode from 4000 to 400 cm$^{-1}$ with a resolution of 4 cm$^{-1}$. Prior to measurements, the instrument was calibrated by recording the spectra with a standard sample.
a) The electro-deposited fullerene films were characterized by FTIR for the confirmation of poly-fullerene.

b) Structural changes in TiO$_2$ photoanode after acid treatment, the adsorption of dye molecules onto TiO$_2$ photoanodes are recorded by FTIR spectroscopy.

**Scanning electron microscopy:** The SEM is the focused probe of electrons accelerated to a moderately high energy and positioned on to the sample by electro-magnetic fields. These beam electrons interact with atoms of the specimen by inelastic (energy is transferred to the sample leads to secondary electrons emission) and elastic (energy is not transferred to the sample leads to back scattered electrons emission) collisions. The most widely used signal, produced by the inelastic interaction of the primary electron beam with the sample is the secondary electron signal, which is used for examining surface structure with best resolutions <100 nm. The surface morphologies of thin films deposited by either spin-coating or electro-deposition or interfacial polymerization technique are imaged by TESCAN (VEGA MV2300T/40) scanning electron microscopy at an accelerating voltage 30 kV.

**Atomic force microscopy:** Nanonics (Multiview 4000) atomic force microscopy was used in the present thesis work to image surface morphology of thin films. Briefly, the probe used for imaging is made of the glass fiber tip (diameter 10nm) which is attached to tuning fork with piezocrystal. The images are recorded in the tapping mode by oscillating the tip at resonance frequency (20-50 kHz depending on the tips). The probe was scanned in phase mode. During scan, phase changes due to tip surface interaction. The difference in signal called an error signal; t signal is sent to proportional, integrator and differentiator (PID) controller. PID sends the feedback via high voltage piezo driver to make constant
phase by moving piezo driver in z direction at that x, y point, thus generating an image. The surface morphology with surface roughness of ITO/FTO substrates, thin films deposited by spin-coating or electro-deposition technique were imaged in the present work. Prior to imaging, the system was calibrated by imaging a standard grid (defined Au pads of 10 μm x 10 μm x 120 nm on Si wafer)

**Kelvin probe microscopy:** Kelvin probe microscopy is a versatile technique to measure the surface potentials of the samples. In this technique an AC voltage with frequency of 27kHz is applied to gold coated tip mounted just above the sample surface which is kept at a ground potential. When the tip is at a proximal distance to the sample, it senses an electrical force, which is used as a feedback to estimate the work-function of sample. The work-function measurements were performed at room temperature and ambient conditions using Au electrode having tip diameter of 2mm. 2D work function mapping of ITO/FTO substrates, PEDOT:PSS thin films, electro-deposited porphyrin and polyfullerene films are imaged by KP technology (SKP 5050) kelvin probe system.

**Raman spectroscopy:** Structural characterization of PEDOT:PSS, P3HT:PCBM, Porphyrin thin films are studied by Jobin-Vyon (LabRAM HR800) Raman spectrophotometer. The spectra were collected in the 180° backscattering geometry using the Ar+ laser (514nm) as an excitation source. *In-situ* Raman measurements of P3HT:PCBM films were recorded by placing 1" x 1" substrates in a Linkam (THMS 600) heating stage, which has an accuracy and stability of 0.1°C. Prior to measurements, the system was calibrated by using the spectral position of Si wafer. The obtained spectra were fitted using a Lorentzian function to determine the peak position, bandwidth and intensity ratio with Labspec5 software.
Photovoltaic characterization

a) **Current-Voltage (J-V) characteristics:** current-voltage characteristics of polymer solar cells and dye-sensitized solar cells were recorded with computer controlled Keithley 2400 digital source-meter and PARSTAT32 potentiostat/galvanostat. For photovoltaic characterization, the measurements were measured using a custom made solar simulator (Sciencetech, Canada) under 1sun (AM1.5G), 100 mW/cm² illumination. Prior to measurements, the intensity of the solar simulator was calibrated using a reference silicon solar cell.

b) **Incident-photon to current conversion efficiency (IPCE):** The spectral response of dye-sensitized solar cells were measured using custom made solar simulator (Sciencetech, Canada).

c) **Electrochemical Impedance Spectroscopy:** Electrochemical impedance spectroscopy (EIS) technique is employed to study the various electron transfer processes occurring at the interfaces, during the operation of DSSC. EIS measurements were carried out by using potentiostat/Galvanostat (PGSTAT 30, Autolab, Eco Chemie, Netherlands), the DSSC was kept at open circuit potential and an AC amplitude of 10mV was applied under an illumination of 1 Sun (AM 1.5 G, 100 mW/cm²). The measured data were fitted by using ZSimpwin software.

d) **Solar cell parameter evaluation:** The obtained (measured) current-voltage characteristics of both polymer and dye-sensitized solar cells were fitted by using Shockley one diode equation (Eq. 1.6). The fitted solar cell parameters (ideal diode factor, diode saturation current, series resistance, shunt resistance, and photogenerated current) are presented with respective J-V characteristics.