CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION TO SOLAR CELLS

Solar energy, the most available renewable energy on earth is more widely used to generate electrical power all around the world due to its environmental, economical and strategic benefits. Solar cells are the devices which convert the energy of sunlight into electricity by photovoltaic effect. They are also considered as a carbon-free energy source which does not contribute to the global warming. Commercially available photovoltaic devices are mainly based on inorganic materials especially silicon (Bernede 2008) with power conversion efficiency (PCE) as high as ~ 25% (Green et al 2011, Rockett 2010). Monocrystalline and polycrystalline silicon are the most widely used materials for these solar cells. By using polycrystalline semiconductor, the production costs have been reduced but at the same time the PCE of the photovoltaic modules fabricated using polycrystalline semiconductor has also got reduced. An alternative way to produce cheaper devices is by thin film technology. In this type of solar cells, thin films of amorphous silicon or cadmium telluride (CdTe), or copper indium gallium selenide (CIGS) are used. Thin film solar cells generally exhibit lower efficiencies than the thick, crystalline, silicon based devices but are more cost-effective. In dye-sensitized solar cells (DSSCs) a dye-sensitized metal-oxide film is used in combination with a liquid electrolyte containing an iodide/tri-iodide redox couple dissolved in an organic liquid. With this architecture, efficiencies beyond 10% have been achieved (Gratzel 2006).
However, considering the application in everyday life, one wants to avoid the use of liquids. To do so, the liquid electrolyte has been replaced by solid-state hole-transport materials (Snaith & Gratzel 2006, Schmidt-Mende & Gratzel 2006) and efficiencies up to 4% have been reported (Schmidt-Mende et al 2005).

The next development in solar cell technology is the organic solar cells which have gained much interest in science as well as in industry due to the low production cost for high volume, high flexibility and cost effective nature (Sun & Sariciftci 2005, Brabec et al 2008). Though, the device efficiency and the stability of these devices have not reached the values as that of inorganic solar cells, several advantages such as the use of cost effective organic materials with high optical absorption coefficient, use of inexpensive solution method for material processing and device fabrication, low weight or mechanical flexibility of devices, render these organic solar cells attractive for large scale application. In organic solar cells a maximum efficiency of 7.4% has been achieved by using the combination of a donor benzodithiophene polymer (PTB) with acceptor as fullerene derivative 6,6-Phenyl-C71-butyric acid methyl ester (PCBM) (Liang et al 2010). However, the use of fullerenes has some disadvantages, like molecular diffusion at elevated temperatures (Yang et al 2004). Therefore, inorganic materials are used to replace the acceptor material resulting in polymer/inorganic hybrid solar cells.

1.2 POLYMER/INORGANIC HYBRID SOLAR CELLS

Hybrid solar cells are fabricated using a p-type polymer semiconductor and n-type inorganic semiconductor, where the p-type polymer semiconductor plays the role of electron donor and the n-type inorganic semiconductor plays the role of electron acceptor. They combine the beneficial properties of both the polymer and the inorganic semiconductor,
and thus, have the conceptual potential to reach efficiencies comparable to inorganic solar cells. Polymer conductors/semiconductors can be easily prepared at relatively low cost and exhibits recyclability and scalability and can be considered as a sustainable material. Inorganic semiconductors, on the other hand, possess better electronic properties like high dielectric constant, high charge mobility and thermal stability, while their nanoparticles exhibit interesting electronic, photo-conducting and luminescent properties. Moreover, it is easy to tune the optical and electrical properties by tailoring the size, shape and composition of the materials. Introduction of nanostructure such as nanowires, nanobelts, nanorods, and even nanosprings in both polymer and inorganic semiconductor materials has received much attention in recent years. The advantages of nanostructures is the large surface area per unit volume which results in efficient light absorption, improved electron mobility as well as device efficiency due to wide absorption of light and changes in electronic structure when the inorganic nanostructures are smaller than the exciton size (typically ~10 nm). This is because the electronic and optical properties of the nanostructures depend not only on the material but also on their size (Fahmi et al 2009).

Today, the highest efficiency reported for hybrid solar cells is around 5.31 % (Yaxiang et al 2015), which is still far away from the efficiencies of commercial solar cell technologies, but the progress in PCE in the last few years and the conceptual advantages, make it more and more realistic and can lead to the fabrication of cost effective, efficient and stable hybrid solar cells. Good combinations of the paired component and well-designed hybrid structure should be among the ways to be explored for achieving good efficiency at low cost.
A variety of combinations of organic conducting polymers and inorganic semiconductors form the candidates for hybrid solar cells. Among the inorganic semiconductors, CdS (Reynolds et al. 2012), CdSe (Greaney et al. 2012), CdTe (Fan et al. 2011), PbS (Wang et al. 2008), PbSe (Tan et al. 2011), ZnO (Li et al. 2012), TiO$_2$ (Ozdal et al. 2012) are some of them which have been attempted so far, while some of the organic semiconducting polymers used so far are poly(3-hexylthiophene) (Greaney et al. 2012), poly(3-methylthiophene) (Sydorov et al. 2012), oligothiophene (Sai et al. 2011), poly(1,4-naphthalenevinylene) (Fan et al. 2011), poly(2-methoxy,5-octoxy)-1,4-phenylenevinylene (Feng et al. 2010), MEH-PPV (Han et al. 2006), PCPDTBT (Jeltsch et al. 2012), PPV (Chen et al. 2013), PDTPBT (Liu et al. 2013). Among these inorganic semiconductors, the metal oxide semiconductors ZnO and TiO$_2$ are highly preferred for hybrid solar cell fabrication because, metal oxides can be synthesized easily, are non-toxic, biocompatible and have suitable charge transport properties.

The structure of a polymer/metal-oxide hybrid solar cell along with three different structures of photoactive layer of the cell is shown in Figure 1.1. The thickness range of each layer of solar cell is given in the figure. In this structure, polymer and metal-oxide coatings are represented as a single photovoltaic layer. The hybrid device generally has a transparent anode through which light enters. Conventional solar cells typically allow light to enter from the anode side while the anode itself consists of a grid of conductive material. The hybrid solar cells consist of at least four distinct layers, excluding the substrate, which may be glass. On the top of the substrate, the anode is laid. Indium tin oxide (ITO) is a popular anodic material because of its good transparency and glass substrate coated with ITO is commercially available. A hole transport layer is present between the anode and the active layer. It not only serves as a hole transport layer and exciton
blocking layer, but it also smoothens the ITO surface, seals the active layer from oxygen, and keeps the anode material from diffusing into the active layer, which can lead to unwanted trap sites. Next, on the top of the hole transport layer, an active layer is deposited which holds the responsibility for light absorption, exciton generation/dissociation and charge carrier diffusion. The active layer is made up of two materials namely donor and acceptor. Polymers with suitable properties are the common donors whereas appropriate inorganic nanoparticles act as common acceptors. Cathode typically made of Al, Ca, Ag and Au is coated on top of the active layer.

There are three different structures which are most commonly used in the hybrid polymer/metal-oxide photoactive layer of solar cells and is shown in the bottom part of Figure 1.1: i) a planar bilayer structure where, either a polymer layer is deposited on top of metal-oxide layer or a metal-oxide layer is deposited on polymer layer (Liu et al 2006a), ii) nanostructured metal-oxide porous structure filled with a conjugated polymer (David et al 2015) and iii) blend of metal-oxide nanoparticles with polymer where metal-oxide nanoparticles and polymer are deposited from the same solution to form a blend film (Ikram et al 2015). Among these structures, the blend of metal-oxide nanoparticles with polymer is mostly preferred for the fabrication of hybrid solar cells because, a large polymer/metal-oxide interfacial area is generated, which enhances the dissociation of excitons generated at the interface leading to improvement in photo conversion efficiency of the solar cells.
Figure 1.1 Structure of polymer/metal-oxide hybrid solar cell along with three different structure of photoactive layer: i) Planar bilayer, ii) Porous structures and iii) Blend

1.3 POLYANILINE

Polyaniline (PANI) has been studied by many researchers among the several available conducting polymers, because of its high electrical conductivity, good charge transport mechanism, easy processability, environmental stability and low synthesis cost. PANI is considered as one of the most potential conducting polymer due to its wide usage in applications like bio sensors such as cholesterol sensor (Shin & Kameoka 2012), glucose sensor (Zhiyuan et al 2016) and gas sensors (Nasirian & Moghaddam 2014),
light emitting devices (Mohsennia et al 2015), photovoltaic applications (Liu et al 2006, Ameen et al 2009, Ibrahim et al 2012), light weight batteries (Lai et al 2010) etc. Basically, PANI can be found in one of the three idealized oxidation states:

- **Leucoemeraldine** – fully reduced state (colorless)
- **Emaraldine** – half- oxidized state (Green for the emeraldine salt, blue for emeraldine base)
- **Pernigraniline** – fully oxidized state (blue/violet)

The chemical structure of all the three idealized oxidation states is shown in Figure 1.2.

![Chemical structure of different oxidation states of Polyaniline](image)

**Figure 1.2 Chemical structure of different oxidation states of Polyaniline**

Leucoemeraldine and pernigraniline are poor conductors even when doped with an acid. Emeraldine form of PANI in undoped condition is an insulator referred as emeraldine base (EB) and if doped with appropriate materials, it becomes highly electrically conductive which is called emeraldine salt (ES). The doping of emeraldine form of PANI with suitable materials introduces high conductivity and this is due to the increase in carrier concentration and this leads to the conjugational defect like solitons, polarons.
and bipolarons in the polymer chain. Doping processes are typically carried out chemically with common acids such as hydrochloric acid, sulfuric acid and phosphoric acid. The conductivity of the PANI is affected by doping and undoping processes which can have dramatic effect on the morphology of the polymer film. Semiconducting PANI finds wide application in the area of electronic device fabrication. PANI can be prepared in semiconducting form by manipulating the oxidation, reduction and doping processes which take place during polymerization and synthesis (Misra et al 1991).

Moreover, nanostructure forms of PANI show a striking diversity. The polymer chains can form one-dimensional structures (nanofibers, nanorods and nanotubes), planar two-dimensional objects (nanoribbons, nanobelts and nanoplates) and three-dimensional particles (microspheres, nanospheres and granules).

1.4 TITANIUM DIOXIDE

In general, metal oxide semiconductors such as titanium-di-oxide (TiO$_2$), zinc oxide (ZnO) are the II-VI compound semiconductors which are used as electron acceptor in solar cells, and have interesting properties like relatively high electron mobility, high electron affinity and good physical and chemical stability. These metal oxides are solution-processable nanocrystalline semiconductors which can be prepared in different morphologies having a large area interface.

Titanium dioxide (TiO$_2$) despite of the large band gap (3–3.3 eV) is also one of the most extensively studied materials. Bulk TiO$_2$ is indirect band gap semiconductor but nanostructured samples exhibit direct band gap. TiO$_2$ absorbs only the violet part of solar spectrum but is used in solar cells. TiO$_2$ has been investigated for many years. TiO$_2$ finds wide application in the field of photocatalysis (Zhou et al 2006), optical materials (Tang et al 1993), solar
cells (Kuang et al 2008) and lithium-ion batteries (Hosono et al 2007). Crystalline TiO$_2$ exists in three forms: rutile, anatase and brookite. Rutile has a body-centered tetragonal crystal structure, anatase is of tetragonal crystal structure and brookite is orthorhombic crystal structure as shown in Figure 1.3.

**Figure 1.3** Crystal structures of Rutile, Anatase and Brookite forms of TiO$_2$

Among these three forms, rutile is the most thermodynamically stable phase (generally at 600–1855 °C), whereas anatase and brookite phases are metastable and readily transform to rutile phase when heated. Rutile TiO$_2$ has some advantages over anatase phase TiO$_2$, such as higher refractive index, higher dielectric constant, higher electric resistance and higher chemical stability. Rutile TiO$_2$ has been traditionally used in pigments, plastics, construction and cosmetic fields because of its good light-scattering and light-reflecting properties, non-toxicity and chemical inertness. In the electronics industry, the rutile TiO$_2$ is used because of the high dielectric
constant. Rutile TiO$_2$ nanoparticles are usually synthesized by calcinating anatase TiO$_2$ nanoparticles or amorphous TiO$_2$ at temperatures above 450 °C. Such high-temperature calcinations unavoidably lead to the agglomeration and growth of nanocrystallites of rutile TiO$_2$.

1.5 LITERATURE SURVEY

A thorough literature survey on solar cells based on PANI polymer and TiO$_2$ nanoparticles has been carried out and is presented in this part of the chapter.

Yongxiang Li et al (1998) have fabricated a photoelectrochromic cell containing a spin-coated polyaniline layer and a dye-sensitized nanocrystalline TiO$_2$ layer having a cell structure ITO/TiO$_2$/dye/electrolyte/PANI/ITO. The cell exhibited an open circuit voltage ($V_{OC}$) of 0.416 V and short-circuits current density ($J_{SC}$) of 0.37 mA/cm$^2$ for white light illumination with an intensity of 80.4 mW/cm$^2$. With further increase in the light intensity to 251.4 mW/cm$^2$, $J_{SC}$ was found to increase to 0.78 mA/cm$^2$.

Senadeera et al (2004) have fabricated volatile solvent free quasi-solid solar cells using acid-doped PANI covalently grafted to surface-modified nanocrystalline TiO$_2$ substrates via self assembled monolayer (SAM) of silane-bearing aniline compound and investigated their photovoltaic performance. They have reported that introduction of ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethyl)sulfonylamid and LiTf$_2$N enhanced the photocurrent of the TiO$_2$/PANI/Au cell by more than two-fold. The cell treated with 1-methyl-3-n-hexylimidazolium iodide delivered a photocurrent of ~450 µAcm$^{-2}$ with photovoltage of ~565 mV, giving an efficiency of ~0.12% (FF = 0.47).
Liu et al (2006) have fabricated p-n heterojunction diodes using spin-coated TiO$_2$ film sandwiched between two ITO glass plates where, polyaniline solution prepared in a mixed solvent of 1:1 m-cresol and chloroform was filled within the inter-electrode space through capillary action to form an assembly of ITO/nano-crystalline TiO$_2$/polyaniline/ITO. They have reported that a p-n junction at nano-crystalline TiO$_2$/polyaniline interface has been created and a novel kind of p-n heterojunction photovoltaic solar cell with nano-crystalline TiO$_2$ and polyaniline can be fabricated.

Zhang et al (2007) have synthesized two kinds of TiO$_2$/sulfonated polyaniline (SPAn) nanocomposite ultrathin films by layer-by-layer (LBL) self-assembly technique where, one was prepared with self-doped sulfonated polyaniline (SD-SPAn) and TiO$_2$ sol and another with externally HCl-doped sulfonated polyaniline (ED-SPAn) and TiCl$_4$. They have reported that the photovoltaic properties of SD-SPAn/TiO$_2$ LBL films show a fast but unstable photocurrent response, whereas the ED-SPAn/TiO$_2$ LBL films show a slow but stable response. They have also suggested that by optimizing the preparation conditions and film properties, the photocurrent can be stabilized and improved.

Chang et al (2008) have fabricated polymer solar cells using P3HT:PCBM by incorporating one-dimensional polyaniline nanotubes as hole transport layer. The high conductivity, controlled tubular nanoscale morphology, and high mobility of charge carriers through the annealed PANI nanotube layer led to efficient extraction of photo generated holes to the buffer layer and suppression of exciton recombination, thereby improving the photovoltaic performance of the polymer solar cell to 4.26%.

Li et al (2008) have prepared an inexpensive microporous polyaniline thin film and used it as a substitute for platinum (Pt) counter electrode in DSSCs and they have obtained an overall PCE of 7.15% which is...
higher than that of the DSSC with Pt counter electrode. They have stated that the excellent photoelectric properties, simple preparation procedure and low cost make PANI electrode a good material for counter electrode in DSSCs.

Ameen et al (2009) have fabricated plasma-enhanced polymerized aniline/TiO$_2$ solar cells, one with dye and of structure FTO/TiO$_2$/Dye/PANI/Pt and another without dye and of structure FTO/TiO$_2$/PANI/Pt. The J-V characteristics show that the fabricated DSSC with dye absorbed TiO$_2$/PANI electrode exhibits a reasonably well over-all PCE of 0.68% with $J_{SC}$ of 2.39 mA/cm$^2$ and $V_{OC}$ of 0.48 V, and the solar cell of TiO$_2$/PANI electrode without dye exhibited a PCE of 0.005% with $J_{SC}$ of 0.036 mA/cm$^2$ and $V_{OC}$ of 0.33 V. The dye and PANI layers on the surface of TiO$_2$ electrode play an important role in the charge transfer at hole conductor (PANI)-dye absorbed TiO$_2$ region, which results in the high $J_{SC}$ and PCE.

Zhang et al (2010) have used the nanostructure PANI thin film as counter electrode in DSSCs and investigated the electrochemical mechanism. It is found that the presence of nanostructured polyaniline (thickness >70 nm) on both the scattered and compact layers simultaneously increased the reactive interface, which supports charge transfer at the interface. By optimizing the preparation conditions, the short-circuit photocurrent density of a dye-sensitized solar cell (DSSC) with PANI counter electrode (CE) was observed to increase by 11.6%.

Bejbouji et al (2010) have used PANI as a hole injection layer (HIL) in on organic solar cells based on P3HT:PCBM and have obtained a PCE of 2.5% with both water and organic solvent-based PANI. They have stated that the conductivity, the thickness, the solvent and the dopant of PANI films when used as HIL seem to greatly affect the performance of photovoltaic devices.
Ameen et al (2010) have doped PANI with sulfamic acid (SFA) via template free interfacial polymerization process and have used as counter electrode in DSSCs. The DSSCs fabricated using PANI nanofibers exhibited a PCE of ~4.0%, while the DSSCs fabricated using SFA-doped PANI nanofibers exhibited an efficiency of 5.5% under 100 mW/cm².

Fan et al (2010) have fabricated PANI-based layered solar cells, consisting of a solution-processed cyanine dye, fullerene C60 and doped PANI anode layers that match the cyanine energy levels and facilitate hole-extraction. The fabricated solar cells exhibited an efficiency of 3%.

Tai et al (2011) prepared highly uniform and transparent PANI counter electrodes by a facile in situ polymerization method and used them in DSSCs which showed a PCE of 6.54% and 4.26% corresponding to front- and rear-side illumination respectively. They have reported that compared to conventional Pt-based DSSCs, the design of the bifacial DSSC fabricated would help to bring down the cost of energy production due to the lower cost of the materials and the higher power-generating efficiency of such devices because of their capability of utilizing the light from both sides.

Chen et al (2011) have reported about the usage of polyaniline nanofiber-carbon film as flexible counter electrode in platinum-free DSSCs. In combination with a dye-sensitized TiO₂ photo electrode and electrolyte, the photovoltaic device with the PANI counter electrode exhibited an energy conversion efficiency of 6.85% under 1 sun illumination. Short-term stability tests indicate that the photovoltaic device with the polyaniline counter electrode almost maintains its initial performance.

Lee et al (2011) have used highly conducting transparent flexible high-performance PANI electrodes, prepared using the thickness-controlled drop-casting method, in the fabrication of the flexible polymer
solar cells which exhibited a power-conversion efficiency of 2%. This efficiency was found to be greater than those of the devices fabricated by the conventional spin-casting method of PANI thin film.

Tessema & Giolando (2012) have fabricated photovoltaic device and did a treatment to fill the pinhole defects in the device structure: glass substrate/SnO$_2$:F/CdS/CdTe/Cu/Au (metal/back contact) using nonconducting PANI using an electrochemical polymerization of the aniline monomer. They have reported that PANI played the role of insulator plug and prevented the shunting of the photovoltaic devices and increased the overall performance of the device.

Jeon et al (2012) have used PANI as a transparent counter electrode in dye-sensitized solar cells (DSSCs). Huang et al (2012) have reported about the synthesis and deposition of hollow spherical PANI particles on ITO/glass substrates and they have used them as counter electrodes in DSSCs which exhibited a PCE of 6.84%.

Park et al (2012) have fabricated a low-cost and bifacial DSSC using a high conductive CSA-doped PANI as counter electrode prepared by spin coating method. They have reported that the DSSC with PANI-CSA counter electrode exhibited better photovoltaic performance compared to DSSC with Pt electrode. Cho et al (2012) have reported a novel method for enhancing the power-conversion efficiency of DSSCs by incorporating PANI porous counter electrodes.

Tan et al (2011) have fabricated organic solar cells based on a blend of poly [2-methoxy-5-(30, 70-dimethyloctyloxy)-1, 4-phenylenevinylene] (MDMO-PPV) and PC$_{61}$BM using electrodeposited PANI films decorated with ZnO nano-islands as anode buffer layers. They have stated that the performance of the solar cells is significantly influenced
by the density of nano-particles on PANI buffer layer surface and also, the performance of solar cell utilizing PANI as anode buffer layer is comparable with that of commonly used PEDOT:PSS.

Ibrahim et al (2012) introduced a new type of solar cell structure using a cotton fabric soaked with the PANI-TiO$_2$ electrolyte sandwiched between two ITO coated polymer substrates to form a single-layer photovoltaic device. They have reported an open circuit voltage of 0.593 V and a short circuit current density of 0.05 mA/cm$^2$ for PANI-TiO$_2$ composites with less than 40% PANI content which is considered as a novel solid electrolyte with photoactive behaviour.

Lim et al (2012) have used CSA-doped PANI in flexible organic solar cells (OSC) as anode and have reported that the efficiency of the device was more than 90% of its initial value even after 500 h, while that of the device made of PEDOT:PSS electrode decreased approximately by 30% of its initial efficiency after 500 h. They have reported that PANI based OSC electrode has the potential to be used as a novel polymer electrode in flexible display.

Zhu et al (2012) have synthesized PANI/ZnO nanograss and used as hole injection layer in DSSCs via a two-step process which involved hydrothermal growth of ZnO nanograss on the fluorine-doped tin oxide (FTO) substrate and subsequently chemisorption of PANI on the surfaces of the ZnO nanorods. PANI is also known as large band gap hole transport material which can be easily deposited as thin film on several substrates. This is ascribed to the more effective charge separation in the hybrid photoanode that enhanced the PCE of DSSC to 0.64% while that of ZnO nanograss HIL based DSSCs reported PCE of 0.40%.
Ameen et al (2012) have used NT10 and Z907 dye sensitized PANI as photoelectrode in DSSCs. DSSCs fabricated using PANI/N719/ZnO and PANI/Z907/ZnO thin film electrodes, showed \( V_{OC} = 0.432 \) V, \( J_{SC} = 2.8 \) mA/cm\(^2\), PCE = 0.6% and \( V_{OC} = 0.521 \) V, \( J_{SC} = 4.56 \) mA/cm\(^2\) and PCE = 1.31% respectively.

Wang et al (2012) have synthesized PANI-graphene hybrid thin films by in situ polymerization of aniline monomer in a graphene dispersion and used as a counter electrode in DSSCs. Highly dispersed PANI nanoparticles compactly covering the graphene surface improved both the electroactive region of PANI and the conductivity of the hybrid material, and thus improved the PCE of DSSC to 6.09% under an illumination of 100 mWcm\(^{-2}\).

Bahramian & Vashaee (2015) have fabricated novel bifacial DSSC using transparent PANI nanofibers based film as the counter electrode and coral-like TiO\(_2\) nanostructured film as the photoanode sensitized using N719 dye molecules and have reported a PCE of 8.22% corresponding to both-side irradiation. In comparison, similar cells employing either a cross-linked PANI- or Pt-based counter electrodes showed efficiencies of 7.81% and 7.75%, respectively.

Based on the literature survey carried out, in the present work an attempt has been made to prepare HCl-doped PANI thin films, CSA-doped PANI thin films and CSA-doped PANI/TiO\(_2\) hybrid thin films and study their properties and fabricate CSA doped PANI/TiO\(_2\) based bulk heterojunction solar cells.
1.6 DETAILS OF THE PRESENT WORK

The objective of the present work is to carry out a systematic study about the preparation and properties of HCl and CSA-doped PANI semiconductor thin films, PANI/TiO$_2$ nanoparticle hybrid thin films and fabrication of hybrid bulk heterojunction solar cells.

The first chapter of the thesis is of introductory nature and has been devoted to explain the importance of the present investigation. The second chapter gives a brief introduction to the different methods used in the present study to prepare PANI polymer, TiO$_2$ nanoparticles and PANI/TiO$_2$ hybrid thin films. The different characterization techniques used in the present work to study the properties of the prepared TiO$_2$ nanoparticles, PANI thin films and PANI/TiO$_2$ hybrid thin films have also been discussed in detail in this chapter.

In chapter 3, the preparation and properties of HCl-doped PANI and CSA-doped PANI thin films are given in detail. In chapter 4, the preparation and properties of CSA-doped PANI/TiO$_2$ hybrid thin films prepared by powder blend and solution blend methods have been discussed in detail. Chapter 5 deals with the fabrication and characterization of the CSA-doped PANI/TiO$_2$ hybrid bulk heterojunction solar cells. The important conclusions drawn from the present study are summarized and given in chapter 6.