CHAPTER 5

CSA-DOPED PANI/TiO$_2$ HYBRID BHJ SOLAR CELLS

5.1 INTRODUCTION

This chapter deals with the application of CSA-doped PANI/TiO$_2$ hybrid thin film as donor/acceptor bulk heterojunction (BHJ) layer in a hybrid solar cell device. Even though PANI:TiO$_2$ hybrid is used for many applications, PANI-TiO$_2$ hybrid, as a photoactive material, has been rarely studied (Liu et al 2006, Ameen et al 2009, Ibrahim et al 2012). Liu et al (2006) in his work on PANI/TiO$_2$ solar cells, fabricated a device structure in the form of ITO/TiO$_2$-PANI/ITO by pouring PANI solution over the TiO$_2$ coated ITO glass plate covered by a second ITO glass plate as in dye-sensitized solar cells (DSSC). They have reported a short circuit current density of 0.12 mA/cm$^2$ and an open circuit voltage of 0.387 V under simulated solar radiation of 45 mW/cm$^2$. They have further suggested that, optimization of the solar cell structure and the increase in absorption of light in the visible region by PANI may enhance the PCE. Following the suggestion, Ibrahim et al (2012) introduced a new 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$^2$. Ameen et al (2009) fabricated a plasma-enhanced polymerized aniline/TiO$_2$ DSSC (FTO/TiO$_2$/Dye/PANI/Pt) which exhibited a reasonable PCE of ~0.68%. They have concluded that dye
absorbed TiO$_2$/PANI electrode is responsible for the high charge carrier transportation between TiO$_2$ and the PANI layer.

The main objective of this study is to fabricate inexpensive hybrid BHJ solar cells using a single active layer of CSA-doped PANI/TiO$_2$ hybrid thin film and to study the influence of TiO$_2$ weight ratio on the photo conversion efficiency of hybrid BHJ solar cell device of structure ITO/PEDOT:PSS/PANI:CSA:TiO$_2$/Al.

### 5.2 STRUCTURE OF HYBRID BHJ SOLAR CELLS

A complete BHJ hybrid solar cell is shown in Figure 5.1. The thickness range of each layer of solar cell is given in the figure. In hybrid solar cells based on bulk heterojunction concept, the donor and acceptor are blended in single photovoltaic layer.

![Figure 5.1 Schematic diagram of hybrid BHJ solar cell](image)

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 due to its transparency and glass substrate coated with ITO is commercially available. A layer of the conductive polymer mixture poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) may be applied between anode and the active layer. The PEDOT:PSS layer does several functions. It not only serves as a hole transport layer and exciton blocking layer, but it also smoothenes 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 PEDOT:PSS, 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 are the common donors whereas inorganic nanoparticles act as common acceptors. Cathode typically made of Al or Ca or Ag or Au is coated on top of the active layer.

5.3 WORKING OF HYBRID BHJ SOLAR CELLS

The overall process occurring in the hybrid donor/acceptor BHJ solar cell may be divided into at least six consecutive steps (Nunzi 2002, Saunders & Turner 2008, Moliton & Nunzi 2006):

- Absorption of photons.
- Generation of electron–hole pairs in photoactive material.
- Diffusion of exciton in the photoactive material to the donor/acceptor interface.
- Dissociation of exciton and separation of the charge carriers at the boundary between donor and acceptor materials.
- Transport of the holes and electrons to the electrodes.
- Collection of the holes and electrons by the electrodes.
Figure 5.2 shows the HOMO-LUMO energy level diagram of hybrid BHJ solar cells. A photon incident on donor material with energy (hν) greater than the band gap (E\textsubscript{g}) of the donor (polymer) produces an exciton. Provided the energy of the donor’s LUMO is at least 0.3 eV greater than the acceptor’s (inorganic nanoparticles) LUMO (or conduction band) then the electron hops to the acceptor. Generally, the HOMO of the donor should be less deep than the acceptor HOMO (or valence band). It should also be deeper than that of the photoanode to insure hole transfer from the polymer to the photoanode. A poly(ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS), layer on top of the photoanode is often used as a hole transporting layer to facilitate this process. The relative positions of the HOMO and LUMO of the donor and acceptor determines whether charge transport will occur and also the values of open circuit voltage (V\textsubscript{oc}) and short circuit current (I\textsubscript{sc}).

![Energy Level Diagram](image)

**Figure 5.2 HOMO-LUMO energy level diagram of hybrid BHJ solar**

### 5.4 SOLAR CELL PARAMETERS

The solar cell characterization is the current-voltage measurements carried out under simulated sunlight. Integration of the spectral response with...
the solar spectrum having the condition of AM 1.5G, normalized 100 mW cm$^{-2}$, provides information on $I_{sc}$, the short circuit current and $V_{oc}$, the open circuit voltage. The I-V curve (Figure 5.3) has been recorded under white light illumination using an Oriel solar simulator (Sol 3A).

![I-V curve of hybrid solar cell](image)

**Figure 5.3 I–V characteristics of hybrid solar cell**

The important parameters associated with the characteristics of a solar cell are given below:

(i) Air mass: It is the ratio of the path length of the sun rays through the atmosphere when the sun is at a given angle $\theta$ to the zenith. An air mass distribution of 1.5, as specimen in the standard condition, corresponds to the spectral power distribution observed when the sun’s radiation is coming from an angle to over head of about 48°.

(ii) Open-circuit voltage ($V_{oc}$): When the cell is operated at open circuit condition, $I = 0$ then the voltage across the output terminals is defined as the open-circuit voltage.
(iii) **Short-circuit current (I\(_{SC}\))**: When the cell is operated at short circuit condition, V = 0 then the current \( I \) through the terminals is defined as the short-circuit current.

(iv) **Maximum power point (MPP)**: \((I_{mpp}, V_{mpp})\) on the I–V curve is the point where maximum power is produced. Power \((P)\) is the product of current and voltage \((P = IV)\) and is illustrated in the Figure 5.3 as the area of the rectangle formed between a point on the I–V curve and the axes. The maximum power point is the point on the I–V curve where the area of the resulting rectangle is largest.

(v) **Fill factor (FF)**: This is the ratio of the maximum power to the product of open circuit voltage \((V_{OC})\) and the short circuit current \((I_{SC})\):

\[
FF = \frac{P_m}{V_{OC} \times I_{SC}}
\]

(vi) **Power conversion efficiency (PCE or \(\eta\))**: The ratio of power output to power input. In other words, PCE measures the amount of power produced \((P_{out} = P_m)\) by a solar cell relative to the power available in the incident solar radiation \((P_{in})\). \(P_{in}\) here is the sum over all wavelengths and is generally fixed at 100 mW/cm\(^2\) when solar simulators are used.

\[
\eta_{AM1.5} = \frac{P_{out}}{P_{in}} = FF \frac{V_{OC} \times I_{SC}}{P_{in}}
\]

5.5 **FABRICATION OF CSA-DOPED PANI/TIO\(_2\) HYBRID BHJ SOLAR CELLS**

The hybrid BHJ solar cells were fabricated on glass substrates coated with indium tin oxide (ITO) anode having a sheet resistance of (8-12)
The substrates were partially etched by concentrated HCl, washed using soap solution, sonicated in deionized water, acetone, isopropanol and methanol for 20 min each, then dried in vacuum oven for around 24 hrs. CSA-doped PANI/TiO$_2$ hybrid solution is used as photoactive material. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) of conductive grade purchased from Sigma Aldrich diluted in equivalent amount of distilled water is used as hole transport material. Both these solutions were filtered through 0.45 µ filters separately after stirring. PEDOT:PSS is spin coated on ITO substrate rotating at 4000 rpm for a time duration of 40 s. The photoactive material CSA-doped PANI/TiO$_2$ is spin coated over the PEDOT:PSS layer at 1000 rpm for a time duration of 1 minute. This photoactive layer is dried in vacuum for 2 days. Al cathode of 100 nm thickness is then coated above the active layer by thermal evaporation using a vacuum of $10^{-5}$ mbar using template. Figures 5.4, 5.5 and 5.6 show the schematic diagram, still image and HOMO-LUMO energy level diagram of the fabricated solar cell with all specifications. The active solar cell area is of $3 \times 3$ mm$^2$ which is represented by dotted lines in the Figure 5.5. Each fabricated hybrid thin film solar cell has four such active solar cell area based upon the solar cell structure.

![Schematic diagram of ITO/PEDOT:PSS/PANI:CSA:TiO$_2$/Al hybrid BHJ solar cell](image)

**Figure 5.4** Schematic diagram of ITO/PEDOT:PSS/PANI:CSA:TiO$_2$/Al hybrid BHJ solar cell
Figure 5.5 Still image of the fabricated hybrid BHJ solar cell

Figure 5.6 Energy-level diagram of fabricated hybrid BHJ solar cell
5.6 J-V CHARACTERISTICS

Figure 5.7 shows the current–voltage (J-V) characteristics of CSA-doped PANI/TiO$_2$ hybrid BHJ solar cell devices of structure ITO/PEDOT:PSS/PANI:CSA:TiO$_2$/Al, fabricated using three different PANI:CSA:TiO$_2$ weight ratio of (1:8:2), (1:8:3) and (1:8:5). The photovoltaic parameters, such as $J_{SC}$, $V_{OC}$, FF and $\eta$ of the devices estimated from these J-V curves, are given in Table 5.1. All the fabricated devices exhibit a better efficiency when compared with the efficiency of the earlier PANI-TiO$_2$ based solar cells (Liu et al 2006, Ameen et al 2009, Ibrahim et al 2012). This must be due to the following reasons i) BHJ approach based on blend of p-type CSA doped-PANI powder and n-type rutile-TiO$_2$ nanoparticles dissolved in a mixed solvent of 1:1 m-cresol and chloroform which improves the donor/acceptor interface creating easy exciton dissociation (Boucle & Ackermann 2012), ii) CSA-doped PANI in m-cresol solvent as donor in solar cells, with higher dopant ratio initiated crystalline root like film morphology, which enhances the charge transportation (Varma et al 2012b, Lee et al 2009), iii) presence of PEDOT:PSS layer which enhances the hole transport at the ITO/PEDOT:PSS interface (Boucle et al 2012). These were not used by earlier workers (Liu et al 2006, Ameen et al 2009, Ibrahim et al 2012) in their PANI/TiO$_2$ based solar cells which may be the reason for their very low $J_{SC}$ value where, efficiency could not be reported (Liu et al 2006, Ibrahim et al 2012).
Figure 5.7  J-V characteristics of CSA-doped PANI/TiO$_2$ hybrid BHJ solar cells having PANI:CSA:TiO$_2$ weight ratio of (1:8:2), (1:8:3) and (1:8:5) under light and dark.

Table 5.1  Solar cell parameters of CSA-doped PANI/TiO$_2$ hybrid solar cell devices with different PANI:CSA:TiO$_2$ weight ratio

<table>
<thead>
<tr>
<th>S. No.</th>
<th>PANI:CSA:TiO$_2$ weight ratio</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>$P_{Max}$ (W)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>(1:8:2)</td>
<td>1.62</td>
<td>0.55</td>
<td>$7.6 \times 10^{-6}$</td>
<td>23.87</td>
<td>0.21</td>
</tr>
<tr>
<td>2.</td>
<td>(1:8:3)</td>
<td>0.78</td>
<td>0.58</td>
<td>$9.2 \times 10^{-6}$</td>
<td>22.61</td>
<td>0.10</td>
</tr>
<tr>
<td>3.</td>
<td>(1:8:5)</td>
<td>0.67</td>
<td>0.51</td>
<td>$7.6 \times 10^{-6}$</td>
<td>24.80</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Among the reported solar cells, the device with the PANI:CSA:TiO$_2$ active layer of 1:8:2 weight ratio shows higher $J_{SC}$ (1.62 mA/cm$^2$) and PCE ($\eta = 0.21\%$). The better value of $J_{SC}$ is due to the enhanced hole transportation as a consequence of film morphology as discussed in TEM analysis. Moreover, the higher exciton dissociation in this hybrid film as discussed in PL analysis, too is a reason for this PCE value. With increase in
TiO$_2$ weight ratio (1:8:3 and 1:8:5) in the active layer, PCE decreases which is due to the reduction of exciton dissociation as reported above. The reason for this may be i) uncontrolled aggregation of nanoparticles, reducing the polymer content along with its light absorption and affect the interpenetrating pathway for hole transport (Li et al 2013) and ii) relatively large polymer domains as appearing in TEM images (Figures.4.22 a-c) which limit the current density and thus PCE of the hybrid solar cells (Oosterhout et al 2009). It is found that, in CSA-doped PANI, the PL quenching in visible spectral region (Figure 4.29) changes by a factor of 3.2 for the decrease in TiO$_2$ ratio of hybrid film from (1:8:5) to (1:8:2) while the PCE increases by ~ 2.6 times. $V_{OC}$ remains constant for all the devices (~ 0.5 V) irrespective of TiO$_2$ ratio, as it is a function of donor/acceptor material combination of the fabricated solar cells (Li et al 2013).

Table 5.2 shows the photovoltaic properties of the fabricated hybrid BHJ solar cell described in present work in comparison with the previously studied PANI-TiO$_2$ solar cells by other researchers. The main positive aspect of the fabricated device over the earlier PANI-TiO$_2$ solar cells are: i) avoiding the usage of two commercially available electrodes (ITO or FTO or platinum counter electrodes) of high cost by a single ITO glass plate with a final Al coating, ii) replacement of a combination of liquid electrolyte (creates sealing problems), dye sensitizer, PANI layer and TiO$_2$ layer by a single layer of PANI-TiO$_2$ BHJ and iii) introduction of hole transport layer PEDOT:PSS which enhances the transportation of hole at the ITO/PEDOT:PSS interface. Among all, by the simple solution method, a solar cell with a simple BHJ device structure has been fabricated which is able to give a reasonable PCE of 0.21%.
Table 5.2 Solar cell parameters of PANI/TiO$_2$ based solar cell devices

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Type of Solar cell</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>$\eta$ (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>ITO/PEDOT:PSS/PANI:CSA:TiO$_2$/Al</td>
<td>1.62</td>
<td>0.55</td>
<td>0.21</td>
<td>(Present work)</td>
</tr>
<tr>
<td>2.</td>
<td>ITO/TiO$_2$-PANI/ITO</td>
<td>0.12</td>
<td>0.39</td>
<td>-</td>
<td>(Liu et al 2006)</td>
</tr>
<tr>
<td>3.</td>
<td>FTO/TiO$_2$/PANI/Pt</td>
<td>0.04</td>
<td>0.33</td>
<td>0.005</td>
<td>(Ameen et al 2009)</td>
</tr>
<tr>
<td>4.</td>
<td>FTO/TiO$_2$/Dye/PANI/Pt</td>
<td>2.39</td>
<td>0.48</td>
<td>0.68</td>
<td>(Ameen et al 2009)</td>
</tr>
<tr>
<td>5.</td>
<td>ITO/cotton soaked TiO$_2$-PANI/ITO</td>
<td>0.05</td>
<td>0.59</td>
<td>-</td>
<td>(Ibrahim et al 2012)</td>
</tr>
</tbody>
</table>

PCE of these hybrid solar cells can further be improved by: i) optimizing the PANI:CSA ratio to increase its absorption in visible region, ii) nano-structured network of both PANI and TiO$_2$ in the hybrid system may be more helpful to increase the mobility of holes and electrons respectively as reported by Ruchuan Liu (2014) and Oosterhout et al (2009), iii) morphology control of hybrid layer - a general issue of BHJ solar cells (Boucle & Ackermann 2012) may be achieved by optimizing the concentration, donor : acceptor ratio and solvents of hybrid solution, iv) optimizing the device structure by introducing PANI and TiO$_2$ as hole and electron acceptor layers respectively like ITO/PANI/PANI:TiO$_2$/TiO$_2$/Al, ITO/TiO$_2$/PANI:TiO$_2$/PANI/Al structures which may drive the PCE of this CSA-doped PANI/TiO$_2$ BHJ hybrid solar cells beyond 0.21%.