Chapter-6

Conclusion and Outlook
In the pursuit of developing new technologies that can provide environmental safe energy with unlimited material availability, the photovoltaic (PV) technology has attracted considerable attention in the past few years, owing to its potential of harvesting energy directly from sunlight without having a harmful effect on the natural balance of our planet. This thesis discusses the processes and limitations that govern the device operation of organic- inorganic bulk heterojunction solar cells, with respect to the charge-carrier transport and photo-generation mechanism. Also the work focus on other class of bulk heterojunction device called Dye Sensitized Solar Cells.

Organic donor materials such as Rosebengal, Cobalt phthalocyanine, Iron phthalocyanine and Dihydroxy Anthra Quinone (DAQ) are optically and electro chemically characterized. Suitable acceptor materials are found out by studying the cyclic voltammograms of the donor materials. It is then mixed with respective inorganic accepter materials like Titanium dioxide (TiO$_2$), Zinc sulphide (ZnS) and Zinc oxide (ZnO) and spin coated over Indium tin oxide coated glass plate (ITO) to get bulk heterojunction device. Silver electrode is made by thermal evaporation process. Solar cells with device structure ITO/RB:TiO$_2$/Ag, ITO/CoPc:ZnS/Ag, ITO/FePc:ZnS/Ag, and ITO/DAQ:ZnO/Ag are fabricated. Current- voltage characteristics of the devices are taken in dark and also under illumination. The photovoltaic parameters obtained are compared. Among the fabricated devices, ITO/DAQ:ZnO/Ag, is giving maximum efficiency. Open circuit voltage ($V_{oc}$) is found to be 1.1 V, short circuit current ($I_{sc}$) 1.87 mA, Fill factor (FF) 0.59 and power conversion efficiency is found to be 1.21%. This is due to the increase in charge carrier mobility. From the dark current characteristics, we calculated the ideality factor ($n$) charge carrier mobility, $\mu$ ($m^2/V.s$) potential barrier, $\phi_b$ (eV) and the carrier concentration ($m^{-3}$). It is evident from this analysis that the DAQ:ZnO device is performing better than the others. For this device, the obtained values are $n = $1.4, $\mu = 7.56 \times 10^{-7} m^2/V.s$, $\phi_b = 1.1$ (eV) and the carrier concentration is $10^{30} m^{-3}$. The increase in charge carrier mobility is the reason for the best convergent efficiency. The impedance spectroscopic analysis verifies this result.

DSSCs were prepared by sandwiching an Iodine based electrolyte between Curcumin sensitized nc-TiO$_2$ nano-particle photo-electrode and graphite coated PEDOT:PSS /FTO counter electrode. At first we extracted Anthocyanine from Hibiscus flower. It was not purified. But we got convergent efficiency about 1.1%. The details of
the study are included in the Appendix. We have shown that the improvement in the power conversion efficiency can be achieved by a simple TiCl$_4$ treatment of TiO$_2$ (pre-annealed at 450$^\circ$C) photo-electrode. The acid treatment is also found to enhance short circuit photocurrent ($J_{sc}$) of DSSC, which is due to the enhancement in dye adsorption by surface protonation. The power conversion efficiency of DSSC based on TiCl$_4$-treated TiO$_2$ photo-electrode was higher than that of HCl-treated one, due to the greater dye adsorption in TiCl$_4$ treated film. We studied the effect TiCl$_4$ treatment of nc-TiO$_2$ photo-electrode and of polar aprotic and polar protic solvents in the sensitization process, respectively over the improvement in conversion efficiency of cell. It is found that treatment of nc-TiO$_2$ with TiCl$_4$ and further its sensitization with curcumin dye in Acetone solvent imparts accelerated diffusion of dye into nc-TiO$_2$ surface having more binding sites and aligned position of its conduction band with LUMO level of dye for faster injection of electrons through relaxation process.

Dye sensitized solar cell with functionalized Multi Walled Carbon Nanotubes (f-MWCNTs) in the working electrode is made and its performance is studied with Rosebengal dye. Incorporation of acid-treated multi-wall carbon nanotubes that is functionalized (f-MWCNTs) in P25 TiO$_2$ films yields considerably increased $J_{sc}$ i.e., about 40% with the same open-circuit voltage and fill factor for the pertinent dye-sensitized solar cells, with respect to the unmodified cell. The enhanced essential $J_{sc}$ is attributed to increased surface area of the films fabricated, in the presence of f-MWCNTs. The $J_{sc}$ enhancement also arises from more favorable cluster formation in P25 TiO$_2$ films in the presence of f-MWCNTs than that in the absence of them. Improved interconnectivity among TiO$_2$ particles in the presence of the f-MWNTs is seen as another reason for the $J_{sc}$ enhancements. The $J_{sc}$ enhancements are consistent with the increase in dye adsorption, light scattering and potential-dependent optical absorbance of the respective cells.

The overall efficiency of all the fabricated devices are compared and tabulated in the Table 6.1
Table 6.1. Comparison of the efficiencies of the fabricated devices

<table>
<thead>
<tr>
<th>Sl No</th>
<th>Device</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>Efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ITO/RB:TiO$_2$/Ag</td>
<td>0.08</td>
<td>0.75</td>
<td>0.35</td>
<td>0.02</td>
</tr>
<tr>
<td>2</td>
<td>ITO/CoPc:ZnS/Ag</td>
<td>0.08</td>
<td>0.80</td>
<td>0.45</td>
<td>0.03</td>
</tr>
<tr>
<td>4</td>
<td>ITO/FePc:ZnS/Ag</td>
<td>0.80</td>
<td>0.85</td>
<td>0.4</td>
<td>0.27</td>
</tr>
<tr>
<td>3</td>
<td>ITO/Aln:ZnO/Ag</td>
<td>1.87</td>
<td>1.10</td>
<td>0.59</td>
<td>1.21</td>
</tr>
<tr>
<td>4</td>
<td>DSSC using Anthocyanine</td>
<td>0.60</td>
<td>0.35</td>
<td>0.4</td>
<td>1.10</td>
</tr>
<tr>
<td>5</td>
<td>DSSC Using Curcumin dye</td>
<td>3.04</td>
<td>0.51</td>
<td>0.44</td>
<td>1.42</td>
</tr>
<tr>
<td>6</td>
<td>DSSC Using RB and f-MWCNTs</td>
<td>9.44</td>
<td>0.68</td>
<td>0.57</td>
<td>3.70</td>
</tr>
</tbody>
</table>

The results of these studies provide a better understanding of the operation principle, and offer a way to design new materials that can further improve the power conversion efficiency of these solar cells. This type of solar cell is very promising because the materials and processing steps are less expensive than those of existing photovoltaic technology; the major issue is performance. In its current state this technology’s performance is so low that, even with the decreased manufacturing cost, the overall cost per unit of energy is still higher. Hybrid solar cell research shall combine the advantages of organic semiconductors and nanoparticles with the properties of the inorganic semiconductors and nanoparticles. The parameter space to choose from is large and only a fraction of possible combinations has been realized. Even such limited efforts have attracted much attention due to the simple processability and low cost processing. Their power conversion efficiencies are still low compared with the conventional inorganic solar cells. Further research and development for optimization is required for different types of hybrid solar cell devices.
In future, researchers working in this area are needed to focus on continued research of various polymers or organic molecules as well as easier fabrication techniques. Further research is needed to improve the mobility and environmental stability of n-type and p-type materials, as well as fundamental understanding of electron injection, metal contact issues, electron transport, surface modification and self assembly. However organic systems offer a great deal of flexibility in their synthesis, and as chemists develop new materials and learn how to better order and process them. It is expected that the mobility will continue to improve, may be reaching the performance of polysilicon and expanding the applications of such materials in all the field of electronics.

To conclude, though the long term research efforts and innovation are needed to provide new organic semi conductors with improved performance, processability and stability should be improved. Continuous multidisciplinary research efforts should impart, an accelerating growth in the field of organic electronics, fueled by the promise of the products and applications that can be derived from electronically and optically active organic and hybrid materials
Major Findings from the Study

- The highest efficiencies reported for hybrid-conjugated polymer devices is 1.6% for the device nc-ZnO:MDMO PPV. We fabricated organic-hybrid bulk heterojunction devices with device structure, ITO/RB:TiO$_2$/Ag, ITO/CoPc:ZnS/Ag, ITO/FePc:ZnS/Ag, and ITO/DAQ:ZnO/Ag. Optical, electrical and electro chemical studies are done to analyze the structure, conducting mechanism and efficiency of the cell. It is found that the ITO/DAQ:ZnO/Ag is performing well under illumination and giving an efficiency of 1.2%.

- The Dye Sensitized Solar Cells (DSSCs) based on natural dyes are now giving an efficiency not more than 1%. DSSC using the natural dye Curcumin, the power conversion efficiency is 0.6%. We found that the surface modification of the photo-electrode by the surface treatment of TiCl$_4$ increases the efficiency to 1.42%. We also showed that the polarity of the solvent affects the sensitization process and there by changing the efficiency.

- Modification of the working electrode, by incorporating MWCNTs in DSSCs and thereby increasing the efficiency of the cell is already reported. We functionalized the MWCNTs using Nitric acid, and then modified the working electrode by incorporating it along with the nc-TiO$_2$. The short circuit current increases by 40% and power conversion efficiency is increased by 60% in comparison with the cell without the incorporation of the f-MWCNTs.
Publications from the thesis

Journal Publications:


3. **C.O.Sreekala**, K.S.Sreelatha, K.B.S.Pavan Kumar, and M. S. Roy, “Functionalized Multi Walled Carbon Nanotubes (MWCNTs) for enhanced Photocurrent in Dye Sensitized Solar Cells”. *Nanomaterials and Nanotechnology* (Communicated)


5. **Conference Publications:**


3. **C.O.Sreekala, K.S. Sreelatha, M.S. Roy** “Electrical and optical studies of Bulk heterojunction device Based on CuPc and ZnS” presented and published in International conference on Materials for the Millennium (MatCon 2010), 11-13 January 2010, Cochin University of Science and technology, Kochi, Kerala, pp 224

4. **C.O. Sreekala, K.B.S. Pavan Kumar, K.S. Sreelatha, M.S.Roy** “Improvement in Conversion Efficiency of Dye-sensitized solar cells using Functionalized Multi-wall carbon Nanotubes in the TiO$_2$ sensitization process” presented and published in International Conference in nanotechnology for Sustainable Energy-2010, organized by European Science Foundation (ESF), 04-09 July 2010, Innsbruck, Austria, pp 100


Appendix

Dye sensitized solar cells using natural dye, Anthocyanine

Dye-sensitized solar cells are emerging as most promising cost effective, easy to fabricate without involving sophisticated lithographic technique being employed towards making conventional solar cells. DSSC works on a principle similar to photosynthesis. We have used some anthocyanine pigment of flowers for sensitization of nanocrystalline TiO$_2$. It has been found that sensitizer substantially enhances the photoconductivity of the material and also broadens the photoaction spectrum towards lower photon energy. The spectral response shows wide band absorption extending from UV to Visible region. Further, the photo response of the cell was evaluated by analyzing its J-V and impedance characteristics.

1. Introduction.

The dye-sensitized solar cell (DSSC) is a device for the conversion of visible light into electricity, based on the sensitization of wide band gap semiconductors [222]. The absorption spectrum of the dye and the anchorage of the dye to the surface of TiO$_2$ are important parameters determining the efficiency of the cell [214]. Natural dyes can be used for sensitization with an acceptable efficiency. The advantages of natural dyes include their availability and low cost [249]. As reported [214, 249], Anthocyanins from various plants gave different sensitizing performances.

In this paper, DSSCs were prepared using natural dyes (Anthocyanins) extracted from Hibiscus flower (Red) as sensitizer, as these flowers are abundant in tropical countries, and rich in anthocyanins [250, 251]. The efficiency of the solar cells related to dye structures is discussed.

2. Experimental

Anthocyanine dye from 30 g of Hibiscus flower is extracted with 150 ml of Methanol and is then concentrated to 10 ml. TiO$_2$ (Degusa P25) porous film was deposited by doctor blade technique on FTO glass substrate (10 Ohm/sq) and the TiO$_2$ layers were dried at 80°C, the film was sintered at 450°C for 1 h in air. Counter electrode was prepared by using modified PEDOT:PSS film as reported elsewhere [252]. The dyes
were attached to the TiO₂ surface by immersing the coated electrodes in the aqueous solution of dye for 24 h. After the sensitization process, quasi-solid-state polymer electrolytes is prepared as reported in [253] and then spin coated on the sensitized TiO₂. Dye-adsorbed TiO₂ electrode and counter-electrode were assembled into a sandwich type cell.

3. Results and Discussion

The current- Voltage characteristics of the prepared device are taken in dark and also under illumination. It is shown in Fig.1

![Current-voltage characteristics for hibiscus flower extract sensitized solar cell.](image)

1. Dark current; 2. Under illumination

The short circuit current, Jsc = 0.06 mA, open circuit voltage, Voc = 0.35 V. The fill factor (FF) is calculated using the formula (1), and is found to be 0.40. The power conversion efficiency of 1.1% was obtained (using formula (2)).

\[
FF = \frac{J_{max} \times V_{max}}{J_{sc} \times V_{oc}}
\]

\[
\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}}
\]
Fig 2 Light absorption spectra of Hibiscus flower extract. It was found that the absorption spectrum was wide and ranges from 350 nm to 750 nm.

Since Anthocyanine extracted is not isolated, the spectrum shows such a continuous variation.

Fig 3. shows the Photoaction spectra of the sensitized DSSC, using Anthocyanine. The spectrum is relatively broad, showing the electron injection in the TiO$_2$ conduction band, which is the characteristic of the dye absorption spectrum. IPCE represents the percentage of incident photons that are converted to electrons at a certain wavelength and is defined by the formula (3)
\[ IPCE(\lambda) = 1240 \left( \frac{J_{sc}}{\lambda \phi} \right) \] (3)

The impedance spectrum is under the frequency range from 100 Hz to 1 MHz. Insect shows Equivalent circuit model of the cell. One part is a parallel connection of resistance (Rp) and capacitance (Cp) for interfacial reaction. The Rs is resistance related to charge-transfer processes occurring at the PEDOT-PSS counter electrode and electrolyte. It should increase with increase in the surface area of the counter electrodes. The poor fill factor of the cell is also due to the high series resistance.

4. Conclusions

DSSC fabricated by adopting Doctor Blade technique using anthocyanines extracted from hibiscus flower provides an alternative over conventional ruthenium complex-based DSSCs. The cell shows reproducible photo response in terms of \( J_{sc} \) 0.06 mA; \( V_{oc} \) 350 mV; FF 0.40 and the conversion efficiency 1.1%.