CHAPTER – VII

STUDIES ON THE FABRICATION OF DYE SENSITIZED SOLAR CELLS (DSSCs)

7.1 INTRODUCTION

The electronics generation has created an ever-increasing demand for energy to fuel the new technologies of the 21st century, therefore, the need for new forms of energy conversion to meet this demand is imperative. Traditional fossil fuel energy sources are finite and their release of waste products into the atmosphere is detrimental to the earth’s global environment. As an alternative, methods for efficient conversion of wind, hydroelectric and solar energy into electrical energy are being explored to solve the world’s energy dilemma [1]. Solar power is attractive due to the abundance and consistency of sunlight, therefore, inorganic semiconductors and more recently, organic-based solar cells have been explored to develop an inexpensive yet efficient method for the conversion of solar light into energy. The genesis of standard silicon solar cells development occurred in the 1950s when Chapin et al reported the first crystalline solar cell with a power conversion efficiency of 6% [2]. To date, modern solar energy conversion is still only between 15 and 20% efficient, yet they remain expensive both in development and commercialization [3, 4]. In this chapter, the basis of solar cell operation is given first and then the literature and details about DSSC are given. The DSSC solar cells fabrication and the results are presented here.

7.2 PHOTOVOLTAICS AND PHOTOVOLTAIC EFFECT

The essence of the photovoltaic effect can be derived from the origin of its name, being made up from photo (from the Greek word photos = light) and voltaic (electrical, derived from the name of Italian physicist Alessandro Volta). Hence, the photovoltaic effect is about electricity from light. In the original experiment by Becquerel, the photovoltaic effect was observed at electrodes immersed in a liquid electrolyte, but today most solar cells are solid state semiconductor p-n junction devices, which use p-type and n-type semiconductor materials to make the junction and solar cells.
Fig. 7.1 A schematic showing the basic operation of solar cells
Fig. 7.2 Schematic representation of the structure and components of the dye-sensitized solar cell.
Fig. 7.3 (a) Working principle of the dye-sensitized nanostructured solar cell

Fig. 7.3 (b) The respective components of the DSSC
Fig. 7.4a The equivalent circuit of a solar cell with single diode

Fig. 7.4b The typical I-V behaviour of a solar cell and the associated basic cell parameters
Fig. 7.5 Qualitative electron energy-level diagrams for transition metal oxides
Fig. 7.6 Molecular structure of photosensitizer for DSSC - EOSIN B
Conducting Glass (ITO)

TiO₂ and Dye

Electrolyte (I⁻/3I⁻)

Counter Electrode (Pt)

Spacer (Teflon)

Conducting Glass (SnO₂:F)

Fig. 7.7 Arrangement of each part of the fabricated DSSC
Fig. 7.8 (a) Front side (TiO$_2$/dye electrode) and (b) Back side (counter electrode side)
Fig. 7.9 I-V curves of TiO₂ films deposited under (a) EBE, (b) DCRS and (c) CSP technique
When a solar cell is illuminated, typically with solar irradiation, photons enter the structure and excite electrons from the valence band to the conduction band, creating electron-hole pairs. In the p-type part of the device electrons diffuse and are driven by the electric field towards the n-type part of the device. The opposite is true for generation in the n-type part of the device, with holes diffusing and being driven towards the p-type side. This creates a charge separation, which leads to a voltage difference between the two sides, which can drive current through an external load and the charge carriers are circulated through the system.

Fig. 7.1 illustrates this operating principle. With a low impedance load, the current will be close to that delivered into a short circuit connection ($J_{sc}$) while the voltage is low. For a high impedance load the converse is true, with a voltage close to the open circuit voltage ($V_{oc}$) and a low current. During normal operation the current is defined as negative. This is merely a convention that stems from the current being defined as positive in the forward direction of the p-n junction, which means that power is delivered to the external load circuit in the fourth quadrant of a current-voltage plot measured under illumination. The device is illuminated with solar irradiation. The radiation excites carriers across the band gap of the absorber material, and charge is separated by the p-n junction.

7.3 CURRENT STATUS OF PHOTOVOLTAICS

The driving force for the development of new photovoltaic materials is the reduction of the manufacturing costs of the photovoltaic cells and modules.

There is essentially two ways of reducing PV module prices: improvement of performance (or in other words efficiency) and reduction of direct manufacturing costs. With this respect, two different strategies may be separated: the high efficiency strategy and the low manufacturing cost strategy. Efficiency defined as conversion efficiency from solar light to electrical power. The various types of solar cells, their efficiencies and the R&D needed in their respective field are given in Table 7.1.
Table 7.1 Performance of photovoltaic and photo electrochemical solar cells

<table>
<thead>
<tr>
<th>Type of Cell</th>
<th>Efficiency (%)</th>
<th>Research and Technology needs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline Silicon</td>
<td>24</td>
<td>Higher reduction yields, Lowering of cost and energy content</td>
</tr>
<tr>
<td></td>
<td>10-15</td>
<td></td>
</tr>
<tr>
<td>Multicrystalline Silicon</td>
<td>18</td>
<td>Lower manufacturing cost and complexity</td>
</tr>
<tr>
<td></td>
<td>9-12</td>
<td></td>
</tr>
<tr>
<td>CuInSe₂</td>
<td>19</td>
<td>Replace indium (too expensive and limited supply, replace CdS Window layer, scale up production</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Dye-sensitized nanostructured</td>
<td>10-11</td>
<td>Improve efficiency and high temperature stability, scale up production</td>
</tr>
<tr>
<td>materials</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Organic Solar Cells</td>
<td>2-3</td>
<td>Improve stability and efficiency</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

7.4 DEVELOPMENTS IN DSSCs

Organic materials are being investigated to determine the effectiveness of charge carrier mobilities and charge injection mechanisms in polymer-based solar cells [5], light emitting diodes (LEDs) [6], and field effect transistors (FETs) [7, 8]. One approach to low cost organic PV devices is based on the sensitization of a high band gap material, such as TiO₂ with organic dyes such as cis-(SCN)₂bis(2,2’-bipyridyl-4,4’-dicarboxylate)ruthenium (II) [9]. This dye coordinates to the TiO₂ surface at the interface between the two materials and forms a new light absorbing composite with unique photophysical properties. This dye sensitized solar cell (DSSC) approach was pioneered by Michael Gratzel and co-workers at the Swiss Federal Institute of Technology in Lausanne. It has yielded PV devices with efficiencies that are comparable to commercially viable inorganic thin film solar cells (AM1.5, Jₛₑ = 16 mA/cm² and in sunlight to electrical energy conversion efficiency of 7-10%, as well as quantum efficiencies of 80-90% from 400 to 700 nm) [9]. Only a monolayer of the dye is utilized as the light absorber on the high surface area semiconductor support. The high surface area multiplies light absorption while allowing for efficient charge collection at the dye-TiO₂ interface. Photon-induced charge carrier production and transport are carried out by two different types of materials, the dye, and electron and hole conductors respectively.
The inorganic layer plays two important roles in an inorganic-organic hybrid DSSC. The main purpose of the inorganic semiconductor is to accept the electron from the excited state of the dye, formed upon absorption of light, while at the same time, preventing recombination of the newly formed electron-hole pair. The better optimized the band gap of the inorganic material is, vis-à-vis organic sensitizer, the more efficient the charge separation and PV device performance. An astute approach to controlling the interfacial charge recombination dynamics has been recently reported by Palomares et al [10]. The inorganic layer also acts as a blocking layer by preventing direct, physical contact and thus avoiding an electrical short between the SnO$_2$:F electrode and a hole conductor. Inorganic oxides with appropriate band gaps are typically chosen as inorganic layers in DSSC applications. We have chosen TiO$_2$ because of its optical and physical properties and our familiarity with its synthesis.

The originally developed DSSC PV device utilizes an iodine-iodine redox mediator dissolved in acetonitrile of transparent holes [11].

7.5 DYE-SENSITIZED NANOSTRUCTURED SOLAR CELLS

Historically the dye-sensitization dates back to the 19th century, when photography was invented. The work of Vogel in Berlin after 1873 can be considered the first significant study of dye-sensitization of semiconductors, where silver halide emulsions were sensitized by dyes to produce black and white photographic films.

The use of dye-sensitization in photovoltaics remained however rather unsuccessful until a breakthrough at the early 1990's in the Laboratory of Photonics and Interfaces in the EPFL Switzerland. By the successful combination of nanostructured electrodes and efficient charge injection dyes professor Gratzel and his co-workers [11] developed a solar cell with energy conversion efficiency exceeding 7% in 1991 and 10% in 1993. This solar cell is called the dye sensitized nanostructured solar cell or the Gratzel cell after its inventor.

7.5.1 Basic Operating principle of the dye-sensitized solar cell

At its simplest configuration (Fig. 7.2), the dye-sensitized solar cell is comprised of a transparent conducting glass electrode coated with meso porous nanocrystalline TiO$_2$
(nc-TiO$_2$), dye molecules attached to the surface of the nc-TiO$_2$, an electrolyte containing a reduction-oxidation couple such as $I^-/I_3^-$ and a catalyst coated counter-electrode. At the illumination, the cell produces voltage and current through an external load connected to the electrodes.

The absorption of light in the DSSC occurs by dye molecules and the charge separation by electron injection from the dye to the TiO$_2$ at the semiconductor electrolyte interface. A single layer of dye molecules however, can absorb only less than one percent of the incoming light. While stacking dye molecules simply on top of each other to obtain a thick dye layer increases the optical thickness of the layer, only the dye molecules in direct contact to the semiconductor electrode surface can separate charges and contribute to the current generation. A solution to this problem, developed by the Gratzel group, was to use a porous nanocrystalline TiO$_2$ electrode structure in order to increase the internal surface area of the electrode to allow large enough amount of dye to be contacted at the same time by the TiO$_2$ electrode and the electrolyte. Essential to the optical operation of this porous electrode structure is the fact that TiO$_2$, as a large band gap semiconductor, absorbs only below about 400 nm, letting the major part of the solar spectrum available for the dye molecules.

7.5.2 Regenerative Working Cycle of DSSC

The regenerative working cycle of the DSSC is depicted in Fig. 7.3a, showing schematically the relative energy levels of a working DSSC. The incoming photon is absorbed by the dye molecule adsorbed on the surface on the nanocrystalline TiO$_2$ particle and an electron from a molecular ground state $S^0(0)$ is exited to a higher lying excited state $S^*(1)$. The exited electron is injected to the conduction band of the TiO$_2$ particle leaving the dye molecule to an oxidized state $S^+(2)$. The injected electron percolates through the porous nanocrystalline structure to the transparent conducting oxide layer of the glass substrate (negative electrode, anode) and finally through an external load to the counter-electrode (positive electrode, cathode) (3). At the counter-electrode the electron is transferred to triiodide in the electrolyte to yield iodine (4), and the cycle is closed by reduction of the oxidized dye by the iodine in the electrolyte (5).
Fig. 7.3b shows the inner components corresponding to the working cycle shown in Fig. 7.3a.

The operating cycle can be summarized in chemical reaction terminology as,

Anode:

\[ S + hv \rightarrow S^* \]  \hspace{1cm} \text{Absorption}

\[ S^* \rightarrow S^+ + e^- (TiO_2) \]  \hspace{1cm} \text{Electron injection}

\[ 2S^+ + 3I^- \rightarrow 2S + I_3^- \]  \hspace{1cm} \text{Regeneration}

Cathode:

\[ I_3^- + 2e^- (Pt) \rightarrow 3I^- \]

Cell:

\[ e^- (Pt) + hv \rightarrow e^- (TiO_2) \]

Due to the energy level positioning in the system, the cell is capable of producing voltage between its electrodes and across the external load. The maximum theoretical value for the photovoltage at open circuit condition is determined by the potential difference between the conduction band edge of the TiO\(_2\) and the redox potential of the I\(^-/I_3^-\) pair in the electrolyte. The operation of the cell is regenerative in nature, since no chemical substances are neither consumed nor produced during the working cycle, as visualized in the cell reaction.

7.6 SOLAR CELL OUT-PUT PARAMETERS

Figure 7.4 (a) shows the equivalent circuit of the p-n junction solar cell under illumination. Fig. 7.4 (b) shows the I-V curves that can be represented by an ideal junction in order to introduce some additional device parameters commonly used in describing the exact behaviour of a solar cell output under dark and illumination. These include the open circuit voltage \(V_{oc}\), the short circuit current \(I_{sc}\), the voltage at maximum power \(V_m\), the current at maximum power \(I_m\) and the Fill Factor (FF). Solar cell behaviour can conveniently be examined through these parameters and they may
be derived by plotting its current (I) and voltage (V) output under dark and illumination.

7.6.1 Short-Circuit Current (Isc) under illumination

The short circuit current Isc is the current that flows through the p-n junction under illumination at zero applied bias. It can be explained that Isc is the current output when the load impedance is much smaller than that of the solar cell impedance. In the ideal case (when Rs and Rsh resistance effects are not present), it is equal to the light generated current IL and proportional to the number of incident photons, i.e., the illumination intensity. In the short-circuit condition the total photo current density (short-circuit current density) is given by the relation.

\[ I_{sc} = I_L = I_p + I_n + I_{dr} \]  

(7.1)

where \( I_p \) is the hole photocurrent density, \( I_n \) is the electron photocurrent density and \( I_{dr} \) is the photo current collected from the depletion region.

The short circuit current Isc is determined by the spectral content of the light source. The spectral response in turn depends on the optical absorption co-efficient \( \alpha \), the junction depth, the width of the depletion region \( W \), the lifetime \( \tau \) and mobilities of carriers on both sides of the junction, the presence or absence of electric fields on both sides of the junction, and the surface recombination velocity \( S \). The energy contained in sunlight is distributed over a wide range of wavelengths, and efficient conversion requires a wide spectral response. The band gap dependence enters through the absorption coefficient; generally speaking, wider band gap materials absorb less sunlight and have smaller short circuit currents than narrow band gap materials.

7.6.2 Open Circuit Voltage (Voc) under illumination

The open circuit voltage Voc is the voltage output when current through the device is zero, or it can be explained that, Voc is the voltage output when the load impedance is much greater than the solar cell impedance and it can be derived as
For an ideal junction, \( n \) is equal to \( l \) and \( V_{oc} \) attains its highest value, while for larger values of \( n \), \( I_o \) is larger so that \( V_{oc} \) is reduced much. The logarithmic nature of the equation 7.2 causes \( V_{oc} \) to effectively saturate as a function of light intensity. The reverse saturation current \( I_o \) is mainly determined by the band gap of the material and the temperature. \( I_o \) decreases because \( V_{oc} \) increases with increasing band gap of the semiconductor or decreasing temperature.

The increase in band gap \( E_g \), decreases the photogenerated current, at the same time increases the photo voltage. Hence the compromise between these two effects produces a maximum in the solar conversion efficiency at band gap values between 1.4 and 1.5 eV.

### 7.6.3 Power Output (\( P_m \)) of a Solar Cell

The output power is given by

\[
P = IV = I_o V \left( \exp \frac{qV}{nkT} - 1 \right) - I_{sc} V
\]

(7.3)

The condition for maximum power can be obtained by setting \( \partial P / \partial V = 0 \) hence

\[
I_m = \left[ (I_{sc} + I_O) \frac{qV_m / nkT}{1 + qV_m / nkT} \right]
\]

as the current output is at maximum power and

\[
\exp \left( \frac{qV_m}{nkT} \right) \left[ 1 + \left( \frac{qV_m}{nkT} \right) \right] = \frac{I_{sc}}{I_o} + 1
\]

\[
= \exp \frac{qV_{oc}}{nkT}
\]

(7.5)

allows the voltage at the maximum power point, \( V_m \) is to be calculated. The maximum output power is given by \( P_m = I_m V_m \).
7.6.4 Fill Factor (FF) of a Solar Cell

The fill factor (FF), which is defined as $\frac{V_m I_m}{V_{oc} I_{sc}}$, measures the squareness of I-V curve, and is expressed by the relation.

$$FF = V_m \left[ 1 - \frac{I - (I/I_{sc})[\exp(qV_m/nkT) - 1]}{nkT/q \ln[(I_{sc}/I_s) + 1]} \right]$$ (7.6)

$$= \frac{V_m}{V_{oc}} \left[ 1 - \frac{\exp(qV_m/nkT) - 1}{\exp(qV_{oc}/nkT) - 1} \right]$$ (7.7)

The relationships expressed by the eqns (7.6) and (7.7) apply only when there are no series and shunt resistance effects involved and where the current can be expressed by a single exponential. The two ratios $V_m/V_{oc}$ and $I_m/I_{oc}$ and also FF improve with increasing values of $V_{oc}$ and with decreasing values of $nkT/q$ and $T$. Higher band gap materials yield higher ratios and FF because of the associated higher open circuit voltages.

7.6.5 Conversion Efficiency ($\eta$) of a Solar Cell

The efficiency of a solar cell in converting solar light into useful electric power is given by

$$\eta = \frac{V_m I_m}{P_{in}}$$ (7.8)

The input power $P_{in}$ is

$$P_{in} = A_t \int \alpha F(\lambda) \left( \frac{hc}{\lambda} \right) d\lambda$$ (7.9)

where, $A_t$ is defined as the total active area of the solar cell, $F(\lambda)$ is the number of photons per square centimeter per second per unit bandwidth of light incident on the device at wavelength $\lambda$, and $hc/\lambda$ is the energy associated with each photon.

The maximum power output $P_m$ is given by the equation

$$P_m = I_m V_m = V_{oc} I_{sc} FF$$ (7.10)
Therefore, the conversion efficiency of a solar cell is expressed by

$$\eta = \left( \frac{V_{oc}}{I_{sc}} \frac{FF}{P_{in}} \right) \times 100\% \quad (7.11)$$

7.7 R&D IN MATERIALS FOR DSSCs

Gratzel type dye-sensitized (DS) photoelectrochemical cells [11] (PECs) made from nanocrystalline TiO$_2$ films sensitized with ruthenium bipyridyl dyes are reported to have efficiencies ~10% [12]. Despite many attempts, an increase of efficiency above this optimum seems to be exceedingly difficult. Broadening of the spectral response and reduction of recombination losses are avenues available for improving the efficiency of the cell. Broadening of the spectral response requires synthesis of new dyes or devising ways of adopting dye mixtures for sensitization and this challenging issue has not been resolved. Although the incident photon to photocurrent conversion efficiency (IPCE) corresponding to the peak absorption position of the dye reaches values nearly unity, the short-circuit photocurrent ($I_{sc}$) at high intensities (one sun) in general does not commensurate with IPCEs measured at low intensities owing to trap filling and its effect on recombination. A more clearer sign of recombination is the deficiency of nearly 300 mV of the open circuit voltage ($V_{oc}$) from the theoretical value.

### Table 7.2
**Photovoltaic Parameters**

<table>
<thead>
<tr>
<th>Cell</th>
<th>$I_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (mV)</th>
<th>$\eta$ (%)</th>
<th>FF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$_2$</td>
<td>12.0</td>
<td>330</td>
<td>1.3</td>
<td>32</td>
</tr>
<tr>
<td>ZnO</td>
<td>9.5</td>
<td>550</td>
<td>2.4</td>
<td>46</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>17.6</td>
<td>693</td>
<td>8.2</td>
<td>67</td>
</tr>
<tr>
<td>[SnO$_2$]MgO</td>
<td>15.1</td>
<td>725</td>
<td>7.1</td>
<td>65</td>
</tr>
<tr>
<td>[SnO$_2$]ZnO</td>
<td>16.9</td>
<td>665</td>
<td>6.5</td>
<td>58</td>
</tr>
<tr>
<td>[SnO$_2$]Al$_2$O$_3$</td>
<td>7.0</td>
<td>637</td>
<td>2.6</td>
<td>58</td>
</tr>
</tbody>
</table>

Recombination could occur via following paths: (1) geminate recombination of the injected electron with the dye cation D$^+$; (2) non-geminate D$^+$, e$^-$ recombination; (3) leakage of the electron to an acceptor in the electrolyte during transit through the nanocrystalline matrix (i.e., I$_3^-$).
The familiar high band-gap oxide semiconductors TiO\textsubscript{2}, SnO\textsubscript{2} and ZnO have similar band gaps and band positions and adsorbs N3 dye more or less to the same extent. Nevertheless when DS PECs are constructed from these materials (similar film thickness and morphology, same level of dye loading, same electrolyte) distinct differences are noted. TiO\textsubscript{2} cells yield the highest values of \textit{I}_{sc}, \textit{V}_{oc}, \eta and also the IPCE. SnO\textsubscript{2} happens to be the most inferior and ZnO gives slightly higher values for \textit{V}_{oc} and \eta \[13-15\] (Table 7.2). Again we found that variation of crystallite size, film thickness and morphology, etc. did not enable the construction of DS PECs with ZnO or SnO\textsubscript{2} having efficiencies comparable to TiO\textsubscript{2}-based cells. As there is no evidence for large differences in the electron injection rates (\varphi_{in}) from excited dye molecules to these materials, we conclude that the inferior photovoltaic performance of DS SnO\textsubscript{2} and ZnO results from higher rates of recombination. If SnO\textsubscript{2} crystallites in a nanocrystalline film of SnO\textsubscript{2} are coated with an ultra-thin outer shell of MgO, ZnO or Al\textsubscript{2}O\textsubscript{3} (we denote such films by the symbol [X]Y, where X and Y are core and shell materials, respectively) and a DS PEC is constructed in the usual manner, the cell was found to have an efficiency comparable to the TiO\textsubscript{2} cell \[14-16\]. Undoubtedly, MgO acts as barrier greatly preventing recombination. In our earlier experiments \[14, 15\], we did not observe an enhancement of the efficiency in depositing outer shell materials up to \(~0.5 – 1\) nm on crystallites of TiO\textsubscript{2} films (i.e., [TiO\textsubscript{2}] MgO, [TiO\textsubscript{2}] Al\textsubscript{2}O\textsubscript{3}, [TiO\textsubscript{2}] ZnO).

7.8 IMPORTANT MATERIALS FOR THE FABRICATION OF DYE-SENSITIZED SOLAR CELLS

In this section an engineering point of view is taken to the preparation of the standard DSSCs. Materials used in the literature in the different cell components are reviewed and the key material properties required for the materials as well as some of the preparation methods are discussed.

7.8.1 Substrates Used

The electrodes of the standard DSSC are prepared onto transparent conducting oxide (TCO) coated glass substrates, between which the cell is assembled. The conducting coating of the substrate works as a current collector and the substrate material itself both as a support structure to the cell and as a sealing layer between the cell and the
ambient air. Fluorine-doped tin oxide (SnO$_2$:F) and indium tin oxide (In$_2$O$_3$:Sn or ITO) are the most frequently used TCOs in thin film photovoltaic solar cells. As the only TCO coating stable at these temperatures, the SnO$_2$:F has been the material of choice for DSSCs.

### 7.8.2 Selection of Oxide semiconductor electrodes

Oxide semiconductors are preferential in photo electrochemistry because of their exceptional stability against photo-corrosion on optical excitation in the band gap. Furthermore, the large band gap (>3 eV) of the oxide semiconductors is needed in DSSCs for the transparency of the semiconductor electrode for the large part of the solar spectrum. In this regard the selected oxide semiconductors materials are: SnO$_2$, ZnO, MgO, TiO$_2$ and their composites as given in section 7.6. Out of these, TiO$_2$ is the best choice and selected for use in DSSC design in the present study.

The elements in Groups IIIB through IIB are termed the transition metals, which have partially filled d electron states. However, there is overlap in the energy of a 3d state in the M shell with an adjacent 4s state in the N shell as shown in Table 7.3.

<table>
<thead>
<tr>
<th>Z</th>
<th>Element</th>
<th>K</th>
<th>L</th>
<th>M</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>O</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>22</td>
<td>Ti</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>2</td>
</tr>
</tbody>
</table>

As shown in Table 7.3, electrons fill up 4s state first and proceed to the 3d state. Therefore, the element Ti has an electron configuration of $3d^2$ and $4s^2$. Oxygen is seen in Table 7.3 to have four 2p-electrons in its outermost shell. Two more electrons will bring O$^2-$ into the closed-shell configuration. Four electrons are needed to accomplish the same for two oxygen ions, such as in TiO$_2$. These four electrons are provided by the titanium (from its 3d- and 4s-shells).
Thus, in the case of TiO\textsubscript{2}, all involved elements are in the noble gas configuration. Since ionic bonds are involved, any attempted removal of electrons would require a considerable amount of thermal energy. Therefore, TiO\textsubscript{2} is an insulator having a wide band gap.

TiO, however, is not an insulator. Since only two titanium valence electrons are needed to fill the 2p-shell of one oxygen ion, two more titanium electrons are free to serve as conduction electrons. Thus, TiO has metallic properties. One of the transition metal oxides, TiO\textsubscript{2}, is also termed a d\textsuperscript{0} insulators. The D\textsuperscript{0} insulators are stoichiometric oxides with a d\textsuperscript{0} electron configuration. They are good insulators with quite large band gaps (e.g. 3 eV in TiO\textsubscript{2}), and they show other properties expected of insulators: they show optical transparency at photon energies less than the band gap, and are diamagnetic with paired electrons. The band gap is between a filled band of bonding orbitals, with a predominantly oxygen 2p atomic character, and an empty metal d band of antibonding orbitals as shown in Fig. 7.5. Many d\textsuperscript{0} insulators are susceptible to loss of oxygen, which gives rise to semiconducting properties. In Fig. 7.5, (a) The bands of a d\textsuperscript{0} compound, with a gap between the oxygen 2p valence band and the empty metal d conduction band. (b) Localized d levels appropriate to a transition metal impurity. (c) Donor level associated with semiconduction in a non-stoichiometric oxide. (d) Partially filled conduction band of a metallic oxide.

7.8.3 Preparation of nanostructured TiO\textsubscript{2} electrodes

The TiO\textsubscript{2} is deposited on conducting glass by Vacuum Coating Techniques, tape casting technique, screen printing, and spray painting, and sintered in 450 °C for 30 minutes. The sintering is needed to burn out organic binders and surfactants and to establish a good electrical contact between adjacent TiO\textsubscript{2} particles in the porous layer as well as between the TiO\textsubscript{2} electrode and the conducting SnO\textsubscript{2}:F layer.

Other reported methods include the sol-gel technique, sputter deposition, spray pyrolysis, and a pressing technique Cell efficiency of about 1.4% was reported for the sol-gel method, 3.2% for the spray pyrolysis, and about 7% (at 10 mW/cm\textsuperscript{2}) for the sputter deposition.
7.8.4 Dyes for sensitizing the oxide electrodes

As discussed above, the absorption of incident light in the DSSCs is realized by specifically engineered dye molecules placed on the semiconductor electrode surface. To achieve a high light-to-energy conversion efficiency in the DSSC, the properties of the dye molecule as attached to the semiconductor particle surface are essential. Such desirable properties can be summarized as:

1. **Absorption:** The dye should absorb light at wavelengths up to about 920 nanometers, i.e. the energy of the exited state of the molecule should be about 1.35 eV above the electronic ground state corresponding to the ideal band gap of a single band gap solar cell.

2. **Energetics:** To minimize energy losses and to maximize the photo voltage, the exited state of the adsorbed dye molecule should be only slightly above the conduction band edge of the TiO₂, but yet above enough to present an energetic driving force for the electron injection process. For the same reason, the ground state of the molecule should be only slightly below the redox potential of the electrolyte.

3. **Kinetics:** The process of electron injection from the exited state to the conduction band of the semiconductor should be fast enough to outrun competing unwanted relaxation and reaction pathways. The excitation of the molecule should be preferentially of the MLCT-type.

4. **Stability:** The adsorbed dye molecule should be stable enough in the working environment (at the semiconductor-electrolyte interface) to sustain about 20 years of operation at exposure to natural daylight, i.e. at least 10⁸ redox turnovers

5. **Interfacial properties:** good adsorption to the semiconductor surface

6. **Practical properties:** e.g. high solubility to the solvent used in the dye impregnation.

The breakthrough in the dye-sensitization of semiconductor electrodes for solar cells was made at EPFL laboratories at the Grätzel group by the use metallo-organic ruthenium complexes along with nanostructured TiO₂ electrodes. For example dyes having the general structure ML₂(X)₂, where L stands for 2,2’-bipyridyl-4,4’-dicarboxylic acid, M for ruthenium or osmium and X for halide, cyanide, thiocyanate, or water have been found promising.
Among these the \textit{cis}-RuL2(NCS)$_2$, also called the N3 dye has shown superior performance and has been the top choice for dye-sensitized solar cells for long. Recently, the \textit{tri}(cyanato)-2,2',2''-terpyridyl-4,4',4'´-tricarboxylate)ruthenium(II) named black dye, has exceeded the performance of the N3 dye extending the spectral response further to the infrared wavelengths and yielding the record cell efficiency of 10.4\%. As these dyes are very costly, the low cost dye, EOSIN B (Fig. 7.6) has been selected for the present study and used as the sensitizer in the fabricated DSSC here.

\subsection*{7.8.5 Dye impregnation of the electrodes}

The dye molecules are adhered onto the nanostructured TiO$_2$ electrode by immersing the sintered electrode into a dye solution. During the impregnation process the electrode is sensitive to water. To minimize water vapor content inside the pores of the electrode, the electrode should be warm upon immersion to the dye solution. The impregnation process lasts from one to several hours depending on the TiO$_2$ layer thickness and whether the dye solution is heated or kept in room temperature.

\subsection*{7.8.6 Electrolytes used in DSSC}

The electrolyte used in the DSSCs consists of iodine (I$^-$) and triiodide (I$_3^-$) as a $\Gamma$/I$_3^-$ redox couple in a solvent with possibly other substances added to improve the properties of the electrolyte and the performance of the operating DSSC. The $\Gamma$/I$_3^-$ redox electrolyte is prepared by adding I$_2$ to the solvent together with some iodine salt such as KI, LiI, alkyl methylimidazolium iodide and methyl-hexylimidazolium iodide (MHImI). The photocurrent output was found to increase linearly with decreasing cation radius, the smallest cations Li$^+$ and K$^+$ showing the best performance. The results also showed that the relative concentration of I$_3^-$ to $\Gamma$ in the electrolyte is an important factor to the cell performance.

\subsection*{7.8.7 Selection of Solvents}

Examples of the solvents used in the electrolytes in DSSCs are: acetonitrile, methoxyacetonitrile, methoxypropionitrile, glutaronitrile, butyronitrile, ethylene carbonate and propylene carbonate. Among all other solvents, methoxypropionitrile

162
seems arise as a potential candidate for the commercial DSSCs. In contrast to acetonitrile and propionitrile, it is nontoxic and has a boiling point of 160 °C.

7.8.8 Catalytic Counter-electrode

For stimulating sufficiently fast reaction kinetics for the triiodide reduction reaction at the TCO coated cathode, a catalyst coating is needed.

As a traditional and usually most efficient catalyst, platinum has been used almost exclusively in the literature. However, the performance of the catalyst layer depends on the method by which the Pt is deposited onto the TCO surface. Platinum catalyst coating has been performed by electrochemically, by sputtering, pyrolytically or by spin coating.

While showing excellent catalytic action, platinum has the disadvantage of being very expensive. The latest DSSC design utilizes a porous carbon counter-electrode as a catalyst layer. This carbon electrode is made from a mixture of carbon black, graphite powder and nanocrystalline TiO₂ particles. It is claimed that the very high surface area of these electrodes is caused by the carbon black and these electrodes are as active for triiodide reduction as the conventional Pt electrodes and low cost.

7.8.9 Electrical contacts

Similarly to the amorphous silicon and the other thin film solar cells deposited on TCO coated glass, the design of dye cells and modules is affected by the limited conductivity of the TCO layer. To keep the resistive losses in the TCO layer reasonably low, the longest distance from a photoactive point to a current collector should not exceed about 1 cm. For example silver paint and adhesive copper tape can be used to extend the contact area of the current collector to fulfill this geometric requirement. A iodine based electrolyte is highly corrosive attacking most metals, such as silver, aluminum, copper, nickel and even gold, and can thus be particularly problematic when it comes to designing an electrical contacting of single cells in an integrated DSSC module.

7.8.10 Sealing

Sealing the DSSCs has long been a difficult question because of the corrosive and volatile liquid iodide electrolyte used in the cells. Being directly related to the long term
stability of the cells it seems to be one of the main technological challenges of the DSSC technology. Several sealing materials have been used, such as epoxy glue, water glass (sodium silicate), an ionomer resin Surlyn® (grade 1702) from Du Pont, aluminum foil laminated with polymer foil, a vacuum sealant Torr Seal®, or a combination of these. Especially for research purposes sealing techniques based on O-rings and glass soldering have been developed.

7.9 FABRICATION STEPS OF DYE-SENSITIZED SOLAR CELL

The consolidated steps involved in the fabrication of a DSSC are given below:

1. Scotch tape taken on the conducting side of ITO glass.
2. TiO$_2$ coated ITO substrates.
3. Prepare a dye solution. (20 ml of 1 mM Eosin B in Methanol) Eosin B - MW=624.06.
4. Dip the TiO$_2$ electrode into the dye solution for 10 min. (The dipping time can be varied depending upon the selected dye. The solution can be heated up mildly (60-80 °C).
5. Take out the TiO$_2$/dye electrode from the dye solution and wash it with fresh Methanol.
6. Place the spacer on the TiO$_2$/dye electrode and put some drops of the electrolyte solution into the hole. This and next step should be done quickly to prevent the solvent (acetonitrile) from drying out.
7. Combine them with counter electrode to face them each other. Important is to let all bubbles out of the hole.
8. Fix them with binder clips.

7.9.1 Materials

TiO$_2$ film, Dye (Eosin B, etc.), Methanol, Spacer (Cut a plastic film (like as Teflon or Scotch tape) having dimensions of 1.5 cm by 2 cm and make a hole(s) on the film.), Liquid electrolyte (0.5M Potassium iodide and 0.05 M iodine in acetonitrile), Binder clips (small, 2 pieces for 1 cell). Conducting glass plates (ITO glass, fluorine doped SnO$_2$ overlayer, sheet resistance 8 $\Omega$/cm$^2$, made by Kinetic Company, Hong Kong) were used as a substrate for deposit TiO$_2$ films on and were cut into 2x1.5 cm$^2$ sheets.
Sensitizing dye EOSIN B was purchased from SOLARONIX SA. All other reagents, material, KI, I (from Merck, India) were used without further purification.

7.9.2 Preparation of nanocrystalline TiO$_2$ electrode

A conducting ITO glass sheet was immersed in an iso-propanol solution for 24 hrs to remove any impurities. A Teflon adhesive tape was fixed on the four sides of conducting glass sheet to restrict the area of TiO$_2$ film. About 1x1 cm$^2$ of TiO$_2$ film was prepared on described in Chapter IV, V and VI under the optimized conditions. The TiO$_2$ coated glass sheet was immersed in a 5x10$^{-4}$ M Methanol solution of EOSIN B for 24 hrs to absorb the dye adequately, the other impurities were washed up with anhydrous Methanol and dried in moisture-free air. After that, a TiO$_2$ film electrode absorbed with dye was prepared.

7.9.3 Pt deposited SnO$_2$:F electrode

Prepared 5mM H$_2$PtCl$_6$ solution in 2-propanol and put some drops of the solution on SnO$_2$:F glass, over an area of 1.5 cm x 1.5 cm. Heated it upto 350-400 °C for 1 hr. When cooled down, it looked almost transparent and became metallic conducting.

7.9.4 Assembling of the DSSC

A DSSC was assembled by filling an electrolyte solution (0.5 M KI + 0.05 M I$_2$ dissolving in the solution of acetonitrile) between a TiO$_2$ film electrode (anode) and a Pt plated conducting (SnO$_2$:F) glass sheets. The arrangement of each part of the fabricated DSSC is shown in Fig. 7.7 which is self explanatory. The two electrodes were clipped together and a cyanoacrylate adhesive was used as sealant to prevent the electrolyte solution from leaking. Two binder clips are used to keep these two plates and the system in contact as shown in Fig. 7.8 a & b.

The photovoltaic test of DSSC was carried out by measuring the I-V character curves under irradiation of white light from a 100 W xenon arc lamp in ambient atmosphere. The FF (fill factor) of DSSC was obtained according to FF = (I x V)$_{max}$/($I_{sc}$ x $V_{oc}$) by I-V curves.
7.10 PHOTOVOLTAIC I-V PERFORMANCE OF DSSCs

DS solar cells fabricated using TiO₂ films prepared by EBE, DCRS and CSP techniques were characterized for their Current-Voltage (I-V) output and solar energy conversion efficiency. Fig. 7.9 a, b, c show the I-V curves of TiO₂ films deposited under the optimized conditions given in Chapter IV, V and VI using EBE, DCRS and CSP techniques respectively. The respective $V_{oc}$ (V), $I_{sc}$ (mA/cm²), FF (%) and $\eta$ (%) are given in Table 7.4.

The overall output of the DSSCs are very low since these are the preliminary results obtained by using the TiO₂ films prepared without further post treatment.

Table 7.4
Photovoltaic performance data of DSSCs fabricated with various thin films and EOSIN B sensitizer

<table>
<thead>
<tr>
<th>Thin Film</th>
<th>$V_{oc}$ (V)</th>
<th>$I_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EBE – TiO₂</td>
<td>0.46</td>
<td>0.17</td>
<td>46</td>
<td>0.06</td>
</tr>
<tr>
<td>DCRS – TiO₂</td>
<td>0.58</td>
<td>0.37</td>
<td>54</td>
<td>0.14</td>
</tr>
<tr>
<td>CSP – TiO₂</td>
<td>0.60</td>
<td>0.55</td>
<td>54</td>
<td>0.22</td>
</tr>
</tbody>
</table>

The short-circuit current density ($I_{sc}$) is directly connected with the electrical properties as well as the surface morphology of the TiO₂ films. Further the open circuit voltage ($V_{oc}$) is determined by the difference between the potential of the redox electrolyte $I/3I^-$ and the quasi-Fermi level of electrons in the TiO₂/dye network system. The $V_{oc}$ value is higher for TiO₂ films prepared by the chemical spray pyrolysis technique which shows the porous nature of these films. Due to their porous nature EOSIN B dye is absorbed into the network in larger volume. Since the sprayed TiO₂ films are formed at 450 °C, nanoparticles in TiO₂-based network are subjected to partial sintering, which renders them chemically bonded and physically connected for more conduction. Such a process not only increases the charge transport but also improves the scattering of photo-excited electrons in the TiO₂ network. These physico-chemical phenomena leads to increased $V_{oc}$ and $I_{sc}$ for the CSP prepared TiO₂ films than the other films.
7.11 CONCLUSION

Dye Sensitized Solar Cells have been fabricated using the TiO$_2$ films deposited by EBE, DCRS and CSP techniques. EOSIN B was used as the dye due to its low cost. The fabricated DSSC cells have the system arrangement as: ITO/TiO$_2$-EOSIN B-I$^-$/3I$^-$/Pt/SnO$_2$:F. Conversion efficiencies of 0.06, 0.14 and 0.22\% are observed for these DSSC cells respectively. The higher $V_{oc}$, $I_{sc}$, FF and $\eta$ are observed for the DSSC cell fabricated using TiO$_2$ film deposited by chemical spray pyrolysis technique. This due to its porous nature.
REFERENCES


