CHAPTER 4
(Working Principle of DSCC)

DYE-SENSITIZER
Dye sensitizers are the substances which are coated on the surface of semiconductor in dye sensitized solar cells. They consume the sunlight, get excited and immediately transfer their electrons to the conduction band of semiconductors. The role of dye sensitizer in DSSC is similar to that of chlorophyll in photosynthesis process. The chlorophyll converts sunlight into chemical energy whereas sensitizers convert sunlight into electrical energy. The best photosynthetic performance in terms of both conversion yield and long-term stability has so far been achieved with polypyrrolidyl complexes of ruthenium and titanium as photo sensitizer dyes. The sensitizers used in DSSC were divided into two types: organic dye and inorganic dye according to the structure. Inorganic dye includes metal complex, such as polypyrrolidyl complexes of ruthenium and titanium, metal complex dye and organic dye includes natural and artificial dyes. Dye sensitizer coated at low-cost into electricity. The cell consists of following components:

1. Transparent and conducting SnO2 substrate
2. Titanium dioxide film, photosensitizer dye. (Adsorbed as shown in Figure 4.1)
3. Redox electrolyte (iodide and potassium iodide mixture in Acetonitrile solution) for generating the oxidized dye
4. Conducting SnO2 counter electrode

Absorption of photo sensitized dye which is Ruthenium complex on Titanium Oxide layer through carboxylic groups is shown in Figure 4.1
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**DYE-SENSITIZED SOLAR CELLS**

A dye sensitized solar cell is a cell which is using to convert sunlight on large scale at low cost into electricity. The cell consists of following components:

1) Transparent and conducting SnO$_2$ substrate
2) Titanium dioxide film, photosensitizer dye. (Adsorbed as shown in Figure 4.1)
3) Redox electrolyte (iodide and Potassium iodide mixture in Acetonitrile solution) for generating the oxidized dye
4) Conducting SnO$_2$ counter electrode

Absorption of photo sensitized dye which is Ruthenium complex on Titanium Oxide layer through carboxylic groups is shown in Figure 4.1.
Figure 4.1. Chelation of the dye onto TiO₂ through carboxylic groups.

Before going to discuss about the structure and working principle of Dye-sensitized solar cells first we see about the preparation of TiO₂ film and about the solutions which we can take as electrolyte in these types of solar cells.

**TiO₂ FILM PREPARATION**

The nanocrystalline TiO₂ film is generally prepared as follows: For the preparation of TiO₂ layer the titanium dioxide powder has been grinding thoroughly to the particle size 25-30 nm. The paste of this powder is prepared in nitric or acetic acid (Ph 3-4). The paste is spread over a conducting and transparent SnO₂ substrate and then it is sintered at 450°C for 30 minutes to achieve maximum porosity and maximum surface area in the film. The particle-to-particle contacts establish in the film after sintering. After cooling, the TiO₂ plate is dipped in the dye solution prepared in ethanol (\(-10^{-5}\) M) for 3-4 hours or until the substrate is stained with the dye. A monolayer
of the dye is formed on the surface of the TiO$_2$ and the plate becomes colored. The
counter electrode can be another SnO$_2$ plate with a carbon/graphite coating on the
conductive side. The coating serves as a catalyst in the electrolyte regeneration reaction.
Platinum coated SnO$_2$ substrate is also used as a counter electrode.\textsuperscript{1}

Table 4.1. Surface area, Pore size and Porosity of TiO$_2$ Nanocrystals autoclaved at
different temperatures.\textsuperscript{4}

<table>
<thead>
<tr>
<th>Autoclaving Temperature ($^\circ$C)</th>
<th>Surface Area (m$^2$/g)</th>
<th>Average pore Diameter (nm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Following Peptization</td>
<td>188.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>190</td>
<td>66.1</td>
<td>3.5$^a$</td>
<td>26$^a$</td>
</tr>
<tr>
<td>210</td>
<td>61.2</td>
<td>3.8$^a$</td>
<td>27$^a$</td>
</tr>
<tr>
<td>230</td>
<td>50.3</td>
<td>8.5$^a$</td>
<td>29$^a$</td>
</tr>
<tr>
<td>250</td>
<td>38.9</td>
<td>30$^b$</td>
<td>42$^b$</td>
</tr>
<tr>
<td>270</td>
<td>35.0</td>
<td>35$^b$</td>
<td>44$^b$</td>
</tr>
</tbody>
</table>

$^a$ Prepared at a concentration of 2.9 x 10$^{-3}$ of triton X-100/g of TiO$_2$ from a solution
containing 42 wt % TiO$_2$

$^b$ Prepared at a concentration of 2.9 x 10$^{-3}$ of triton X-100/g of TiO$_2$ from a solution
containing 50 wt % TiO$_2$.\textsuperscript{42}

There is another method of preparing TiO$_2$ thin film on the conducting and transparent
SnO$_2$ substrate. According to this method TiO$_2$ were prepared from Ti (OC$_4$H$_9$) and
C$_2$H$_5$OH and the procedure is termed as the sol-gel sin-coating route which is shown in
Figure 4.2. The flow chart for the preparation of TiO$_2$ thin film is as follow:

Figure 4.2. Sol-gel sin-coating process to prepare nano-TiO$_2$ thin films.\textsuperscript{43}
(C₂H₅OH) 5.85g

Ti(OC₄H₉) 3.6g

(HCl) 1ml

(H₂O) 0.55ml

Stirring for 8 Hours

Spin Coating for 30 seconds

Baked at 100°C for 10 min

Sintered at 600°C for 30 min

Cooling to room temperature

TiO₂ thin film with nano-particle

Figure 4.2: Fixation of sensitizers on the surface and formation of a suprapolar photoelectrochromic layer, reducing the direct contact between the semiconductor surface and electrolyte solution.
Ru(dcbpy)$_2$(NCS)$_2$, that is the photosensitizer dye when anchored to nanocrystalline TiO$_2$ films, achieves very efficient sensitization over the whole visible range, yielding IPCE about 80%. This fixation of sensitizers on TiO$_2$ surface is shown in Figure 4.3.

Figure 4.3. Fixation of sensitizers on TiO$_2$ surface and formation of a supposed hydrophobic layer, reducing the direct contact between semiconductor surface and electrolyte solution.

Nanocrystalline semiconductor films adsorbed a large amount of dye molecules and increased the harvesting efficiency of solar energy. However, the huge surface area also increases the recombination between electrons in the conduction band of semiconductor oxides and the electron acceptor in the electrolyte. One particularly attractive approach involves the coating of the nanocrystalline metal oxide film with a thin overcoat of another metal oxide with a higher conduction band edge, as illustrated in Figure 4.4, with
the aim of increasing the physical separation of injected electrons from the oxidized dye redox couple, thereby retarding the recombination reactions.\textsuperscript{49, 50}

The major redox couple contained I\textsubscript{3}/I\textsubscript{3} as redox couple in organic sensitized solar cells. SCN\textsuperscript{-}/(SCN\textsuperscript{-}) couple, SCN\textsuperscript{-}/(SeCN\textsuperscript{-}) couple were also shown in the literature. Sapp (38) reported the enhanced efficiency of these couples can be achieved by using I\textsuperscript{3}/I\textsubscript{3}\textsuperscript{-} couple in DSC. Alkyl imidazolium cation and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) were used as the counter ions of the redox couple in DSC. Alkyl imidazolium cation is not easily adsorbed on the surface of the semiconductor film in dye-sensitized solar cells. In addition, the contact of triiodide and electrolyte can increase the conduction band of semiconductor and electron in the semiconductor film, and conversion efficiency of the solar cells were improved.

On the other hand, the high solubility of alkyl imidazolium cation in organic solvents and the high activity of iodide increased the light absorption efficiency and photocurrent as well as the stability of the sensitizer.

**Figure 4.4.** Diagrammatic sketch TiO\textsubscript{2} coated with high-conduction band-edge semiconductor or insulating layer.

(a) Injection of electrons into the conduction band of TiO\textsubscript{2} films.

(b) Combination of electrons between electron and triiodide in the electrolyte.

(c) Charge recombination between electrons of TiO\textsubscript{2} films and oxide dye.\textsuperscript{50}

**ELECTROLYTE**

The electrolyte is one of key components for dye-sensitized solar cells. These are the conducting solutions which contain ions. These are used to complete the cell circuit. Its properties have much effect on the efficiencies and on the stabilities of the solar cells.

The electrolyte used in DSC is divided into three types: liquid electrolyte, quasi-solid state electrolyte, and solid electrolyte. Liquid electrolyte could be divided into organic solvent electrolyte and ionic liquid electrolyte according to the solvent used.\textsuperscript{45}

Organic solvent electrolytes were widely used and investigated in dye-sensitized solar cells for their low viscosity, fast ion diffusion, high efficiency, easy to be designed, and
high pervasion into nanocrystalline film electrode.\textsuperscript{35,36} The composition of the electrolytes includes organic solvent, redox couple, and additive. The major redox couple contained I$_3^-$/I$^-$ couple expecting that redox couple, Wang et al. (37) used Br$^-$/Br$_2$ as redox couple in eosin sensitized solar cells. SCN$^-$/ (SCN)$_2$ couple, SeCN$^-$/ (SeCN)$_2$ couple were also shown in the literature. Sapp (38) reported the substituted bipyridyl cobalt (III/II) couple as redox couple in DSC. However, the performance of these couples can hardly match that of I$_3^-$/I$^-$ couple.

Alkyl imidazolium cation and lithium cation were usually used as the counter ions of I$_3^-$/I$^-$ couple in DSC. Alkyl imidazolium cation may be adsorbed on the surface of semiconductor film to form the helmholz layer, which restricted the contact of triiodide and semiconductor films, for the recombination between triiodide and electron in the conduction band of semiconductor. As the result, the fill factor, and conversion efficiency of the solar cells were improved. On the other hand, the high solubility of alkyl imidazolium cation in organic solvent and the high activity of iodide increased the light harvesting efficiency and photocurrent as well as the stability of the sensitizer.

The commonly used additive used in the electrolytes for dye-sensitized solar cells contained 4-tert-butylpyridine (TBP) and N-methylbenzimidazole (NMBI). The addition of these additives could suppress the dark current and improve the photoelectric conversion efficiency.\textsuperscript{46-48}

Ionic liquid electrolytes were developed in recent year in view of the disadvantage of organic solvent electrolyte. Compared with normal organic solvent electrolyte, ionic liquid have a lot of advantage, such as

1) Good chemical and thermal stability,

2) Negligible vapor pressure and non flammability,

3) High ionic conductivity and solubility for organic or inorganic materials,

\textit{Kubo} et al. (39) investigated the physical and physiochemical properties of 1-alkyl-3-methylimidazolium iodides (alkyl chain: C3–C9).\textsuperscript{40,41} Gratzel et al. reported the solar cells based on low-viscosity ionic liquid. Table 4.2 summarizes the photovoltaic performance of DSC based on ionic liquid electrolyte of different composition.
<table>
<thead>
<tr>
<th>Composition of electrolyte</th>
<th>Dye</th>
<th>$\eta$%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_2$, LiI, and NMBI in PMII and EMIDCN (13:7, v/v)</td>
<td>Z907</td>
<td>6.6</td>
</tr>
<tr>
<td></td>
<td>N719</td>
<td>5.0</td>
</tr>
<tr>
<td>HMII, $I_2$ et al.</td>
<td>N719</td>
<td>5.0</td>
</tr>
<tr>
<td>$I_2$ and NMBI in MPII</td>
<td>Z907</td>
<td>6.0</td>
</tr>
<tr>
<td>$I_2$, GuSCN, TBP in PMII and EMINCS (13:7, v/v)</td>
<td>Z907</td>
<td>7.0 and 6.4*</td>
</tr>
<tr>
<td>$I_2$, NMBI, and GuSCN in PMII and EMIB(CN)$_4$ (13:7, v/v)</td>
<td>Z907</td>
<td>7.0 and 6.4*</td>
</tr>
<tr>
<td>$I_2$, GuSCN, and NMBI in PMII and EMINCS (13:7, v/v)</td>
<td>Z955</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>K19, DPA</td>
<td>6.3</td>
</tr>
<tr>
<td>MPII, LiI, $I_2$ TBP in EMIDCA</td>
<td>N3</td>
<td>5.5</td>
</tr>
<tr>
<td>MPII, LiI, $I_2$, TBP in EMITFSI</td>
<td>N3</td>
<td>4.5</td>
</tr>
<tr>
<td>$I_2$ and NMBI in PMII and functional PMII derivative ionic liquids (13:7, v/v)</td>
<td>K19PPA</td>
<td>5.4 ~ 5.9</td>
</tr>
<tr>
<td>EMII, $I_2$, LiI, TBP in EMITFSA</td>
<td>N3</td>
<td>4.5(0.45 cm$^2$), 2.7(69 cm$^2$)</td>
</tr>
<tr>
<td>(Bu$_2$Me)Si and 1% $I_2$, TBP</td>
<td>N719</td>
<td>3.7</td>
</tr>
<tr>
<td>MPII, LiI, $I_2$ TBP in PTFSI</td>
<td>N3</td>
<td>2%</td>
</tr>
<tr>
<td>GuSCN, K(SeCN)$_3$, NMBI in EMISecN</td>
<td>Z907, PPA</td>
<td>7.5</td>
</tr>
</tbody>
</table>

PTFSI: 1-butylpyridinium bis-(trifluoromethane sulfonyl)imide.
NMBI: N-methylbenzimidazole
EMITFSI: 1-Ethyl-3-methylimidazoliumbis(trifluoro-methanesulphonyl)amide
PMII: 1-methyl-3-propylimidazolium iodide
EMIDCN: 1-Ethyl-3-methylimidazolium dicyanamide
TBP: 4-tert-butylypyridine
HMII: 1-hexyl-3-methylimidazolium iodide
MPII: 1-methyl-3-propylimidazolium iodide
GuSCN: amino(imino)methanaminium thiocyanate.
REQUIREMENTS FOR DEVELOPING EFFICIENT DYSES

After discussing about the electrolyte and about the TiO₂ film preparation we must know about the main requirement for developing efficient dyes for photo-sensitization are as follows:

1. The low lying excited state energy level of the dye should be compatible TiO₂ with conduction band.
2. The redox or reduction potential of the dye molecule should match with the mediator redox couple in the electrolyte.
3. The absorbance spectrum of the dye should have large overlap with the solar spectrum or the absorption of visible light of all colors and near IR region (400-900nm)
4. Anchoring groups such as carboxylic acids, sulphonic acids and phosphonic acid for grafting the dye on the semiconductor surface should be present.
5. The dye should be able to inject electrons into the conduction band of TiO₂ with a quantum yield of unity.

THE ENERGY LEVEL SCHEME AND OPERATING PRINCIPLE OF A DSSC

Dye-sensitized solar cells (DSSCs) have been extensively studied in the last decade as a promising renewable energy source, because of their potentially inexpensive manufacturing technology compared to other solar cells specially silicon solar cells. The DSSCs consists of two electrodes (Figure. 4.5). The front electrode is a transparent conductive oxide glass (TCO) coated with nanoporous TiO₂ covered with a monolayer of the Ruthenium-complex dye (-ve electrode) while the counter electrode is a TCO glass coated with a thin layer of platinum (~5 nm). The two electrodes connected with one another through an electrolyte containing an iodide/tri-iodide (I⁻/I₃⁻) redox couple. Besides two different anions an electrolyte also consists of cations being introduced by ionic liquid, usually by propylmethyl-imidazolium iodide. The cations provides electro neutrality of the electrolyte, nevertheless they are not involved in the charge transport process in dye-sensitized solar cell.
Figure 4.5. The cross of the Dye-Sensitized Solar Cell

**Theory of Operation for Dye Sensitized Solar Cells**

DSC's, shown in Figure 4.6; rely on processes likened to photosynthesis. In photosynthesis, light is converted into chemical energy. Chlorophyll and other pigments can eject electrons through photo-induced charge separation when struck by photons. The main component of a DSC is a semi conducting material with a wide band gap. One such material is titanium dioxide (TiO₂). This is deposited as a thin layer onto a transparent conducting oxide (TCO) substrate using a sol-gel technique. The TiO₂ layer is also in contact with a monolayer of polymer dye which has commonly been a ruthenium complex, also known as N₃₄₆. Exposure to sunlight causes electrons in the dye to become excited. This phenomenon is called photo excitation. The electrons are then ejected from the dye and into the conduction band of the semi conducting oxide layer. Regeneration of the lost electrons is handled by a redox process within an electrolyte, commonly an iodide/tri-iodide couple, which is in contact with the dye. The final component is a layer of TCO. The voltage generated is related to the difference between the redox potential of
the electrolyte and the Fermi level of the electron within the solid. The electron that was ejected from the dye diffuses through the TiO₂ layer and into the conductive oxide electrode where it can be used as current.

Figure 4.6. Schematic of Dye-Sensitized Solar Cells
In DSSC the reactions are initiated by the fall of electron on the Ru dye which is denoted by \( S^0 \) (ground state) after the absorption of photon it get excited and become \( S^* \). Then it inject an electron into the conduction band of the TiO\(_2\) means semiconductor and come back to the ground state as \( S^+ \). This electron is transported to the external load via the nanostructured TiO\(_2\) and TCO to the counter electrode and itself come back to the ground state as \( S^- \). While it take an electron from electrolyte and gain original form. Whereas electrolyte iodide (I) is subsequently regenerated by the reduction of tri-iodide (I\(_3^-\)) at the counter electrode (Equation. 1) to complete the circuit. The Pt on the counter electrode

\[
\text{Pt} \quad \Gamma_3 + 2e^{-} \rightarrow 3\Gamma \quad \text{(Eq. 1)}
\]

Acts as a catalyst for the reduction of tri-iodide. So far, the highest reported efficiency for a small area DSSC is 11.3\%, using Acetonitrile electrolytes while many efforts is still devoted to enhance the record efficiency.
Figure 4.7. Energy level scheme and the operating principle of a DSSC.\textsuperscript{43}

Photoexcitation of Ru complex in the cell

\[
\text{hv} \\
\text{Ru(II)} \quad \rightarrow \quad \text{Ru(II)}^* \\
\]

Electron injection

\[
\text{K} \\
\text{TiO}_2 + \text{Ru(II)}^* \quad \rightarrow \quad \text{TiO}_2(e^-) + \text{Ru(III)} \\
\]

Regeneration of Ru(II) by Iodide at TiO\textsubscript{2} Film

\[
\text{Ru(III)} \quad \rightarrow \quad \text{I}_3^- + 2 \text{Ru(II)} \\
\text{3I}^- \quad \rightarrow \quad \text{I}_3^- + 2 \text{Ru(II)} \\
\]

Regeneration of Iodide ions at counter Electrode from trioxide

\[
\text{Pt} \\
\text{I}_3^- + 2e^{-1} \quad \rightarrow \quad 3\text{I}^- \\
\]

The performance of a Dye-Sensitized Solar Cell depends upon some factors. Mainly it depends on three processes:

(i) The electron injection from photo-excited dye to the conduction band in ultra fast time (typically it occurs within $10^{-12}$-10$^{-15}$ s$^{-1}$)

(ii) The slower recombination of the injected electron with the oxidize dye ($\sim 10^{-6}$ s$^{-1}$)

(iii) The regeneration of the dye by electrolyte recombination ($\sim 10^{-8}$ s$^{-1}$).

The performance of DSPV cell can be quantified on a macroscopic level with parameters such as incident photon-to-current efficiency (IPCE), open circuit photo voltage ($V_{oc}$) and short circuit photo current ($I_{sc}$) and the overall efficiency of the cell (h cell).\textsuperscript{1,35,45} The conversion of sunlight into electricity by using Ruthenium photo sensitizer that is the most widely used sensitizer for the DSC has been

[\text{cis-Ru(SCN)}_2\text{L}_2 \quad (L = 2,2'-bipyridyl-4,4'-dicarboxylate), abbreviated as N3 can also shown with the help a diagram shown below (Figure 4.8) \textsuperscript{47,48}](image)
Figure 4.8. Schematic drawing showing the currently used embodiment of the DSC. It employs dye-derivatized TiO₂ nano crystals as light-harvesting units. The sensitizer is cis-Ru(SCN)₂L₂ (L-2,2'-'bipyridyl-4,4'-dicarboxylate). The redox system employed to regenerate the dye and transport the positive charges to the counter electrode is the iodide/tri-iodide couple dissolved in an organic electrolyte or in a room-temperature ionic liquid. The efficiency of an electric power generating electrochemical solar cell is directly related to the fill factor that is calculated from the current-voltage power characteristics. The experimental I-V curve is obtained by measuring the current flowing across a standard resistor. The ratio of the areas under the experiment curve to the ideal curve gives the fill factor. Alternatively, a point in the experimental curve can be chosen to give the V_max and I_max and the fill factor is given by, Fill factor (ff) = (V_max X I_max)/V_oc X I_oc Where V_max and I_max are the maximum photo voltage and photocurrent density generated. V_oc is the
Photo voltage developed under open circuit conditions and $I_{sc}$ is the short circuit current density (1). A typical I-V curve measured for a ruthenium dye is shown in Figure 4.9.

![Graph](image)

**Figure 4.9.** Typical current-voltage (I-V) curve, characteristic of a DSSC.

Over the last 2 decades, ruthenium complexes endowed with appropriate ligands and anchoring groups have been by far the preferred choice of charge-transfer sensitizers for mesoscopic solar cells. Recently, however, there has been a surge of interest in organic dyes, as shown in Figure 4.10, solar to electric power conversion efficiencies have been sharply increasing, reaching 9.5% in 2008 for the indoline dye D205. This rapid development has culminated in the recent report of a 9.8%

**Figure 4.10.** Evolution of standard AM 1.5 solar to electric power conversion efficiencies for Dye-sensitized solar cells based on ruthenium complexes and organic dyes.
CHAPTER-5
(Ruthenium Complexes, Synthesis and Characterization)