CHAPTER 2B

Fabrication and Characterizations of DSSC

Fabrication of TiO₂ base DSSC
Photovoltaic characterizations of DSSC
Electron transfer kinetic of DSSC

Source: www.nature.com, www.news.rice.edu and www.sony.net
2B.1 Introduction

This chapter covers the fabrication and characterizations of dye sensitized solar cells using the dyes introduced in Chapter 2A. Various parts such as photoelectrode, sensitizer, counter electrode and electrolytes for DSSC have been deeply discussed in Chapter 1 (Section 1.4). Generally, DSSC fabrication has been achieved by sealing the working and counter electrode together in a sandwich type configuration [1,2]. Dye sensitized solar cell is very versatile electrochemical device having too many different component working in coherent manner. Working electrode in this study was made up of thin film (10-12 µm) of nanocrystalline anatase TiO₂ nanoparticles while counter electrode contains a layer of Pt nanoparticles. A liquid electrolyte based on I⁻/I₃⁻ was used as a redox mediator. Choice of sealing material is important in DSSC since electrolyte component may corrode it leading to leakage of the device. Following Scheme 2B.1 shows the schematics of the fabricated DSSC.

Scheme 2B.1 Schematic diagram of DSSC along with component assembly

Like other solar cells, DSSC also characterizes using current voltage characteristics (I-V) and incident photon to current conversion efficiencies (IPCE). DSSC is a well
synchronized electrochemical system hence there are some electrochemical techniques which are routinely used to study the detailed electron transfer kinetic of the device. Electrochemical impedance measurements and Tafel polarization techniques are the prominent to study the basic charge transfer process of dye sensitized solar cell. Recombination kinetic of DSSC is also explained in details using intensity modulated photovoltage/photocurrent spectroscopy. Following are the details of all the techniques used to characterize the solar cell and interpretations of the measurements.

2B.2 DSSC Characterizations Techniques

2B.2.1 I-V Characteristics

The basic of the solar cell performance parameter determination lies in the physics. This set up consists of the power source (DSSC) connected to a variable resistor along with a parallel voltmeter and series ammeter as shown in Scheme 2B.2.

![Diagram](image)

**Scheme 2B.2** Schematic diagram of solar cell IV measurement set up

Voltmeter determines the voltage of the device and ammeter measure the current as a function of variation in series resistance of the devices [3]. *I-V* measurement in DSSC utilizes the simulated white light from the solar simulator as a light source with standard irradiance spectrum with Air Mass (A.M.) 1.5 G. If the light is not upto standard level (AM 1.5) then spectrum mismatch needs to be carefully corrected [4]. Current obtained under zero load condition is known as the short circuit current (*I_{sc}*).
Increase in series resistance leads to increase in voltage and decrease in current as shown in the Figure 2B.1. At infinite resistance, when current becomes zero and corresponding maximum voltage is known as open circuit voltage ($V_{oc}$) of the device. Data are collected at various resistor values, and current voltage response is plotted as $I-V$.

Figure 2B.1. Typical $I-V$ characteristics of dye solar cell

While an alternative method for the $I-V$ characterization is measuring the generated photocurrent from the device by applying different potential. This process is same as we have discussed previously using variable resistor. This process is widely used now a days and it is available in auto mode. To apply voltage bias to a device leads to increase in series resistance hence this technique is user friendly and can be automated easily. Because dye-sensitized solar cells have a relatively slow electrical response due to their high interfacial capacitance, the voltage scan should be sufficiently slow to avoid errors in the current measurement due to capacitive charging/discharging. From this measurements various parameters are extracted like short circuit current density
(Jsc), open circuit voltage (Voc), Fill factor (FF) and solar to electricity conversion efficiency (η). First two parameters are directly determined from the I-V plot while remaining two parameters are calculated as shown below in equation 2B.1 and 2B.2.

\[
FF (\%) = \frac{J_{sc} \times V_{oc}}{P_{max}} \times 100 \quad (2B.1)
\]

\[
\eta(\%) = \frac{P_{max}}{P_{in}} \times 100 \quad (2B.2)
\]

Where, \( P_{max} \) is maximum power point

\( P_{in} \) is intensity of incident white light

### 2B.2.2 Incident Photon to current conversion efficiency (IPCE)

This is very important parameter, particularly for the dye solar cell whose response is basically centered on the discrete wavelength of the solar spectrum. Basic idea lies behind this technique is the measurement of generated photocurrent at different light wavelength. A typical IPCE spectrum is shown in **Figure 2B.2** which has been plotted as *IPCE Vs Wavelength* of light.

![typical IPCE spectrum of DSSC](chart.png)

**Figure 2B.2.** Typical IPCE spectrum of DSSC (for the dye having \( \lambda_{max} = 430 \text{nm} \))
Following equation 2B.3 is used to calculate the IPCE from the generated photocurrent as a function of wavelength. The response of the light by DSSC is solely dependent upon the absorption maxima of the sensitizing molecule.

\[
IPCE\ (\%) = \frac{1240 \times I_{sc} (\mu A/cm^2)}{Wavelength\ (nm) \times P_{in} (watt/m^2)}
\]  

(2B.3)

IPCE maxima represent that the photons of particular wavelength are extensively absorbed by device. This measurement gives exact idea about the % light absorption by sensitizing molecule at specific wavelength giving better insight into the light harvesting properties of molecule.

2B.2.3 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (broadly speaking dielectric spectroscopy) deals with the dipolar polarization of electronic systems [5]. In this technique, a sinusoidal waveform of current or voltage with definite frequency is used to study the response of electrochemical system. Impedance is defined as the opposition to flow of alternating current (AC current). In this technique, an AC signal of fixed amplitude (generally small voltage) is applied to the electrochemical system and generated current is measured as a function of frequency. Electrochemical impedance is normally measured using a small excitation signal in order to maintain the pseudo-linear response from cell. In a linear (or pseudo-linear) system, the current response to a sinusoidal potential will be a sinusoid at the same frequency but shifted in phase as shown in Figure 2B.3. By analyzing the data, one can have two components i.e. real and imaginary. Real part of the impedance (solution resistance in electrochemical cell) response is related with the resistive components while imaginary part deals with
capacitive components (electrode/electrolyte interface where charge storage occurs due to electric double layer) of the system.

Figure 2B.3 Sinusoidal Current Response in a Linear System (a) Input signal and (b) Output signal

Mathematically, this can be expressed as follow. If small amplitude AC voltage is applied to an electrochemical system, (equation 2B.4) the system would generate corresponding AC current in response to voltage (equation 2B.5). \( E \) is defined as the voltage, \( I \) is current while \( \omega \) stands for frequency in following equations,

\[
E_t = E_0 \sin(\omega t) \quad (2B.4)
\]

\[
I_t = I_0 \sin(\omega t + \phi) \quad (2B.5)
\]

In a linear system, the response signal, \( I_0 \), is shifted in phase (\( \phi \)) and has a different amplitude than \( I_0 \) as can be seen from equation 2B.5. An expression analogous to Ohm's law allows us to calculate the impedance (Z) of the system as equation 2B.6.

\[
Z = \frac{E_t}{I_t} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)} \quad (2B.6)
\]
The total impedance ($Z$) is therefore expressed in terms of a magnitude, $Z_0$, and a phase shift, $\phi$. It should be noted that the impedance response of a particular system is highly dependent upon the frequency of AC signal. The typical impedance data are represented in form of Nyquist plot as shown in following Figure 2B.4 (behavior is attributed to parallel RC circuit as shown right to Figure 2B.4).

**Figure 2B.4**  
(a) Typical impedance response of an electrochemical system with electrode electrolyte interface (Figure taken from [www.gamryinstruments.com](http://www.gamryinstruments.com))  
(b) Typical Bode phase plot for the DSSC
A semicircle in the complex plane of Nyquist plot indicates parallel combination of resistor and capacitor while straight line shows series combination of them. There is another plot in the impedance measurement which is known as Bode phase plot. It is plotted as Frequency Vs Phase angle ($\phi$) in which $\phi$ is derived from the phase analysis of output signal. This plot dictates the phase behavior of the sample as a function of frequency and gives detailed insight into capacitance of the system.

Following Figure 2B.4 shows the typical bode phase plot for the DSSC. In terms of DSSC, there are mainly two interfaces i.e. TiO₂/Dye/Electrolyte and Pt/Electrolyte along with diffusive components in electrolyte [6]. Diffusion of the electro active species in electrolyte is generally represented as Warburg impedance (W). Electron transfer kinetic of DSSC is generally studied by using small amplitude voltage signal (10 mV to 30 mV) using frequency ranging from 120 kHz to 0.01 Hz. A typical nyquist plot for the DSSC consists of three distinguishable semicircles in complex plane (Figure 2B.5).

Figure 2B.5 Typical Nyquist plot of a dye sensitized solar cell in impedance spectroscopy ($Z'$ is real part and $Z''$ is imaginary part)
Higher frequency (120 kHz to 10 kHz) response can be attributed to electron transfer reaction at Pt/electrolyte interface. Lowest frequency (1 Hz to 0.01 Hz) response is due to diffusion of the triiodide through electrolyte. Middle frequency response (10 kHz to 1 Hz) is attributed to the TiO$_2$/dye/electrolyte interface. This response is fitted using appropriate circuit models in order to determine the electron transfer parameters of DSSC [7]. Transmission line model is widely used to simulate the impedance response of complex electrochemical systems. Adachi et al have thoroughly studied the electron transport properties of DSSC and derived all ubiquitous equation [8]. They have shown the experiments using variable parameters thereby supporting the equations. Following circuit diagram (Figure 2B.6) is used to fit the impedance response of DSSC which is composed of discrete electronic components like resistor (R), capacitor (C) and constant phase element (CPE) [8].

![Figure 2B.6](image)

**Figure 2B.6** Equivalent circuit to fit impedance data of DSSC

R$_1$ is the real part of Nyquist plot at 120 kHz which give resistivity of FTO glass. Charge transfer resistance ($R_{ct}$) and capacitance ($C_{pt}$) at Pt/electrolyte interface is extracted by fitting first arc in Nyquist plot. While fitting of second arc (TiO$_2$/dye/electrolyte) is approximated using a capacitor like component known as constant phase element due to the porous nature of TiO$_2$ film. CPE element is made up of two components CPE-P and CPE-T. CPE-P depends upon the surface roughness and porosity of electrode while CPE-T gives the value of capacitance. $R_k$ is known as the recombination resistance of electron in TiO$_2$ film. Lower frequency response is fitted using Warburg element. Warburg element composed of $W_s-P$, $W_s-T$ and $W_s-R$ in
which \( Ws-T \) is used to determine the triiodide diffusion coefficient. Using this fitting technique, one can estimate the \( R_{ct}, C_{sp}, R_k, \omega_{max} \) (peak frequency of middle arc), \( CPE-P, CPE-T, Ws-T \). Following equations 2B.6 and 2B.7 are used to determine electron lifetime (\( \tau \)) in TiO\(_2\) film as well as diffusion coefficient (\( D \)) of triiodide ion in electrolyte.

\[
\tau = \frac{1}{\omega_{max}} \quad (in \ second) \quad (2B.6)
\]

\[
Ws - T = \frac{L^2}{D} \quad (2B.7)
\]

### 2B.2.4 Tafel Polarization Experiment

In order to study the electron recombination in DSSC, Tafel polarization technique is used [9-10] (Figure 2B.7). Tafel analysis takes insight into the interfacial charge transfer properties for I\(^-\)/I\(_3^-\) redox couple on the TiO\(_2\) surface. Following equation 2B.8 is well known Butler-Volmer equation which gives the rates of cathodic and anodic reactions in the semiconductor/Electrolyte interface.

\[
j = -j_o [\exp(\frac{\alpha_a nF}{RT} (E - E_{eq})) - \exp(\frac{\alpha_c nF}{RT} (E - E_{eq}))] \quad (2B.8)
\]

\( j_o \) is the exchange current density, \( E \) is the applied voltage, \( E_{eq} \) is the equilibrium potential of I\(^-\)/I\(_3^-\) redox system, \( \alpha_a \) and \( \alpha_c \) are the anodic and cathodic transfer coefficients respectively. It is clear from this equation that \( j = j_o \) as \( E = E_{eq} \) in dark. Experimentally, this measurement for DSSC is carried in dark condition where \( E = E_{eq} \) giving as exact value of exchange current density (\( J_0 \)). A potential (\( E \)) from -0.7 to 0.7
is swept onto DSSC under dark and generated current is measured. Typical tafel curve is plotted as \( \log j Vs E \) as shown in Figure 2B.7.

![Figure 2B.7 Typical Tafel polarization curve for DSSC](image.png)

Figure 2B.7 Typical Tafel polarization curve for DSSC

Exchange current density, obtained from this experiment is a direct measure of the recombination reactions occurring in DSSC [9]. Recombination reaction takes place between the electrons in TiO\(_2\) film with electrolyte components. As the magnitude of \( J_o \) increases, recombination becomes more pronounced in DSSC leading to diminished open circuit voltage (\( V_{oc} \)). Hence, this measurement is useful for the justification of \( V_{oc} \) trend in different DSSC.

2B.2.5 Intensity Modulation Techniques

This technique is widely used for the detailed study of recombination dynamic in dye solar cell. In this technique, DSSC is biased with light having AC modulation and generated photovoltage (Intensity Modulated Photovoltage Spectroscopy, IMPS) or photocurrent (Intensity Modulated Photocurrent Spectroscopy, IMVS) is measured.
Following Figure 2B.8 shows the experimental set up for the IMVS and IMPS measurements.

Figure 2B.8 Experimental set up for intensity modulated spectroscopy of DSSC

A. J. Frank and coworkers were the first to study the DSSC using IMPS. They have developed theoretical model for the frequency dependence of the photovoltage in DSSC [11]. In this study, IMVS is shown to be valuable in elucidating the contributions of band edge shift and recombination kinetics to changes of the open-circuit photovoltage ($V_{oc}$) resulting from surface modifications of the semiconductor. This group has extended the application of IMVS and IMPS to evaluate the charge collection efficiency of the DSSC. The charge-collection efficiency of the photoinjected electrons from dye sensitization was estimated from the respective time constants for charge recombination at open circuit $\tau_{oc}$ and the combined processes of charge collection and charge recombination at short circuit $\tau_{sc}$ obtained by IMVS and IMPS measurements [12]. This technique was further extended to study the role of electrical potential, charge transport, and recombination in determining the photopotential and photocurrent conversion efficiency (IPCE) of dye-sensitized solar cells [13].
2B.2.6 Transient Absorption spectroscopy

This technique is also known as time resolved spectroscopy, flash spectroscopy or pulsed-probe technique. Transient-absorption spectroscopy is an extension of absorption spectroscopy. Here, the absorbance at a particular wavelength or range of wavelengths of a sample is measured as a function of time after excitation by a flash of light. In a typical experiment, both the light for excitation (‘pump’) and the light for measuring the absorbance (‘probe’) are generated by a pulsed laser. If the process under study is slow, then the time resolution can be obtained with a continuous (i.e., not pulsed) probe beam and repeated conventional spectrophotometric techniques. These measurements are used to get insight into the subtle electron injection kinetic of the DSSC. Typical transient absorbance spectra is shown in the following Figure 2B.9 which represents spectra of N3 dye sensitized TiO₂ in methoxy propionitrile and iodide/triiodide electrolyte.

![Graph showing transient absorption spectra of N3 on TiO₂](image)

**Figure 2B.9** Typical transient absorbance spectra of N3 dye sensitized TiO₂ photoelectrode film (Reprinted with permission from *J. Phys. Chem. C* 2014, 118, 7772-7780. Copyright 2014 AMERICAN CHEMICAL SOCIETY)
These measurements also yield lifetime for the excited state of dye molecule and reaction rate constant for the electron injection process. This study was carried out by Antila et al in order to study the complete profile of dye injection and regeneration in solvent and electrolyte [14]. They have found that typical dye injects electron to TiO$_2$ in femto to pico second scale but in presence of electrolyte this process slows down to nanosecond scale. O’Regan and coworkers have also carried out the transient absorption study of N719 and C109 dye molecules using Vis-NIR and IR pump probe spectroscopy. They have used low volatility electrolyte with and without addition of Li ion into it [15].

2B.3 Experimental Section

2B.3.1 Materials

All the chemicals like ethyl cellulose, $\alpha$-terpineol, acetonitrile, tert.-butanol, lithium iodide, iodine, 3-methoxy propionitroile, 4-tert.-butyl pyridine (4-TBP) and guanidinium thiocyanate were purchased from sigma Aldrich, India with maximum purity and used as received. TiO$_2$ nanoparticles (TiO$_2$-P25) with average particle size 20-25 nm were purchased from Degussa, Germany. FTO (Flourine doped Tin Oxide) coated glass (surface resistivity 8 ohm/cm), hot melt sealing tape and N719 reference dye were purchased from Solaronix Inc., Switzerland.

2B.3.2 Methods

2B.3.2.1 Fabrication of DSSC

2B.3.2.1.1 Washing of TCO glass

FTO coated TCO substrates were washed thoroughly in ultrasonic bath before use. First wash was given with 0.1 N surfactant solution in ultrasonic bath followed by water and ethanol. This substrate was dried in oven at 110°C for 2 hour.
2B.3.2.1.2 Preparation of Photoelectrode

A thin TiO₂ buffer layer was prepared onto pre-cleaned FTO substrate to avoid direct contact of electrolyte from FTO surface. This was achieved by spin coating of ethanolic solution of titanium tetraisopropoxide using a spin coating system from Apex instruments, India. TiO₂ paste was prepared by using ethyl cellulose and α-terpineol [2]. 0.2 gm of TiO₂ nanopowder was thoroughly grounded in mortar (Agat) followed by heating at 110°-130°C in air. This powder was transfer to a bottle containing 5 ml of ethanol. This bottle was subjected to ultrasound in an ultrasonic bath for 15 min. 0.1 ml of conc. HNO₃ solution was added into this bottled and further sonicated for 15 min. then 1.65 gm of 5 wt% ethanolic ethyl cellulose (0.1 gm ethyl cellulose in 2 ml ethanol) and 1.6 gm of α-terpineol was added into it followed by vigorous stirring. This viscous mass was further subjected to ultrasound for 25 min followed by vigorous stirring overnight. This was further sonicated for 10 min and transferred to mortar and grounded thoroughly until a sticky paste is obtained (removal of ethanol leads to paste formation). This paste is applied onto the buffer layer coated TCO glass using doctor blading method. Two layers of scotch tape was used as spacer and glass rod as paste applicator. Film was allowed to settle for 2 min and spacers were removed followed by heating on hot plate until it gets visibly dry. This film was finally calcined at 450°C for 15 min and 500°C for 5 min in an open air tubular furnace. This film was allowed to cool to 80°C and then soaked into the dye solution for 12 hour in dark (same time for dye adsorption was set for each dye). The concentration of dye in dye bath was set to 30 mmole for each dye. After dye sensitization was over, electrode was washed thoroughly using ethanol and dried under the flow of air. This electrode is known as working electrode or photoelectrode or photoanode.
Following Figure 2B.10 shows the SEM micrographs of the photoelectrode showing the nanopores into the TiO₂ matrix.

**Figure 2B.10** SEM micrographs of TiO₂ film onto FTO substrate

### 2B.3.2.1.3 Preparation of counter electrode

Counter electrode for this study was made up of Pt based coating on TCO coated glass. Platinum coating onto the TCO glass was achieved by using thermal decomposition of H₂PtCl₆ solution. 50 mM of H₂PtCl₆ solution (diluted 3 times with ethanol) was spin coated onto TCO glass at 3000 rpm for 120 sec using a spin coating system from Apex Instruments, India. This electrode was rapidly fired into a tubular furnace at 450°C for 20 min. Sintered electrode is semitransparent with a thin layer of platinum nanoparticles. This sintered electrode was studied using the Atomic force microscopy (AFM) at different resolution (**Figure 2B.11**). We have found that the roughness factor of the Pt nanolayer 3 to 5 nm with average dimension of the crystal was found to be 311x115 nm. Surface roughness of this counter electrode improves its catalytic activity due to increased surface area. This process is known as the Pt nanoparticle synthesis by thermal decomposition of the Pt precursor solutions. This process makes a uniform layer of Pt onto the TCO coated glass substrate.
2B.3.2.1.4 Preparation of electrolyte solution

0.5 M LiI, 0.05 M Iodine, 0.5 M 4-TBP and 0.1 M guanidinium thiocyanate were dissolved in 3-methoxy propionitrile. This solution was allowed to stand at room temperature in dark for 12 hour in order to make homogenize. The electrolyte was stored in dark throughout the study.

2B.3.2.1.5 Assembly of DSSC

DSSC were assembled in sandwich type configuration of working electrode and counter electrode. Small stripes of hot melt tape were set to the side of photoelectrode, and counter electrode was put onto it. Both these electrodes were carefully transferred to a hot plate by applying pressure onto it. As the heating progresses, tape got melt and looks transparent. At this stage assembly was removed from hot plate and cooled to room temperature. Electrolyte was inserted to the predrilled holes onto counter electrode. These holes were sealed by using cover glass and epoxy adhesive. Cells were stored in dark for 12 hour prior to measurement in order to equilibrate whole system. Figure 2B.12 shows that photographic image of the transparent DSSC devices fabricated in our laboratory.
2B.3.2.2 Characterizations of DSSC

$I$-$V$ characteristics of DSSC were recorded using Solartron 1287 electrochemical analyzer (Figure 2B.13) by sweeping potential from 0 to 0.8 V (scan rate 15 mV/sec) under simulation of white light from xenon lamp (100 mW/cm²). Xenon lamp was calibrated using standard Si photodiode.

Figure 2B.12 Photograph of DSSC fabricated in our laboratory

Figure 2B.13 Photograph of Solartron electrochemical analyzer with impedance and Gain phase analyzer (both interfaces are connected with each other)

IPCE measurements were carried out by using spectrophotometer (source of monochromatic light) and generated current photocurrent was measured using
multimeter Rish *mit30* (Rishabh Instruments, India) at different wavelength. Light intensity from the spectrophotometer was monitored by using calibrated Si photodiode. Impedance measurements were carried out by using Solartron 1260+1287 (*Figure 2B.13*) by sweeping 10 mV AC amplitude having frequency from 120 kHz to 0.1 Hz. Cells were biased at -0.6 V under dark condition during impedance measurements. Data were analyzed using ZView software (Scribners Associates Inc.). Tafel polarization experiment was carried out by using Solartron 1287 electrochemical interface. Cells were swept with DC potential from -0.7 to 0.7 with scan rate of 15 mV/sec in dark. tafel data were fitted by using Corrview software (Scribners Associates Inc.). Above *Figure 2B.13* shows the photograph of Solartron instrument having different interfaces.

### 2B.4 Characterizations of DSSC based on Anthracene bridged dye (AN 1)

This section deals with the characterization of DSSC sensitized with anthracene based dye molecule. This molecule carries primitive design of the sensitizer in which donor (phenyl group), bridge (anthracene) and acceptor (cyano acetic acid) configuration is designed. DSSC was characterized by using various techniques like *IV*, Impedance and Tafel polarization curves. Impedance and Tafel polarization techniques take better insight into the electron transfer kinetic in dye solar cell.

#### 2B.4.1 Photovoltaic Characterizations of AN 1 dye based DSSC

*I-V* characteristic of the DSSC was determined by potentiodynamic technique using Solartron electrochemical analyzer (*Figure 2B.14*). Photocurrent was measured by applying different bias potential onto the DSSC under white light simulation with intensity 100 mW/cm². *I-V* curve of the anthracene dye sensitized DSSC has been depicted in above *Figure 2B.14* and extracted parameters are given in *Table 2B.1*. It
can be seen from the Table 2B.1 that the fill factor and photovoltage of the device are quite lower than N719 based dye. This dye generates 3.5 mA/cm² of the current density along with 0.2V photovoltage while fill factor of the device is 34%. In order to take better insight into the electron transfer reactions in DSSC impedance and Tafel polarization methods were used. From these measurements we can justify the performance of the DSSC.

![Figure 2B.14](image_url)  
**Figure 2B.14** $I-V$ characteristics of DSSC sensitized with anthracene dye

**2B.4.2 Electrochemical Characterizations of AN 1 dye based DSSC**

**Figure 2B.15** shows the Nyquist plot of the dye solar cell derived by sweeping AC signal (10 mV) with frequency ranging from 120 kHz to 1 Hz in dark under DC bias.

**Table 2B.1** Photovoltaic and electron transfer parameters of AN 1 dye based DSSC

<table>
<thead>
<tr>
<th></th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF (%)</th>
<th>η (%)</th>
<th>$R_{ct}$ (Ohm)</th>
<th>$\tau_{ele}$ (ms)</th>
<th>$j_o$ (µA/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN 1</td>
<td>3.5</td>
<td>201</td>
<td>34</td>
<td>0.25</td>
<td>3.8</td>
<td>17.6</td>
<td>148</td>
</tr>
</tbody>
</table>
Inset of the Figure 2B.15 represent the equivalent circuit model used to fit the impedance data. As we have seen earlier that the charge transfer parameters from the Nyquist plot are extracted by fitting the semicircles in equivalent circuit models. First arc yields charge transfer at Pt/electrolyte interface while second arc give charge transfer processes at TiO₂/dye/electrolyte interface. Third arc mostly invisible in EIS shows the ionic diffusion of the redox species in the electrolyte solution. We have extracted charge transfer resistance \( R_{ct} \) and electron lifetime \( \tau_{ele} \) from this measurement and are depicted in Table 2B.1 [8].

![Figure 2B.15 Nyquist plot of AN 1 dye sensitized solar cell recorded in dark](image)

Charge transfer resistance is estimated from the first semicircle of the Nyquist plot which is embedded at higher frequency range (i.e. \( Z' = 30 \) to 60 Ohm). \( R_{ct} \) is related to the charge transfer at Pt/electrolyte interface. Magnitude of \( R_{ct} \) suggests that there is smooth interfacial reaction takes place at Pt/electrolyte interface leading to reduction of triiodide. But total impedance of the device is quite higher suggesting that there is inefficient charging of TiO₂ film. This may be due to the low adsorption of dye.
molecules thereby decreasing the surface coverage of TiO$_2$ matrix. Decreased surface coverage results in the electron transfer reaction of TiO$_2$ with electrolyte components which has been further supported by Tafel polarization experiment. This experiment was carried out in dark by applying potential in forward bias and reverse bias manner and measuring generated current from the device. A plot of $\log i$ Vs potential is known as the Tafel polarization curve which is fitted into Buttler-Volmer equation (Figure 2B.16).

![Figure 2B.16 Tafel polarization curves for the AN1 dye sensitized solar cell](image)

Tafel polarization (Figure 2B.16) experiment takes insight into the dark reactions occurring in the DSSC [9]. This technique gives the measure of spontaneous reaction of electron form TiO$_2$ with electrolyte components in dark. Intersection point of the Tafel curves gives exchange current density ($j_o$) which is directly related to the recombination reactions occurring in the DSSC. Table 2B.1 shows that the exchange current density of the DSSC in dark is quite higher suggesting higher magnitude of recombination of electrons by electrolyte components.
2B.5 Characterizations of DSSC from Hemicyanine dyes with –COOH anchoring group

This section covers the characterizations of carboxy anchored hemicyanine dye (HC1, HC2, HC3) based DSSC. We have used different alkyl chains in this dye and studied the effect of the chain length on the performance of the DSSC in terms of photovoltage and photocurrent. We have also discussed the origin of $V_{oc}$ in DSSC as well as its dependence on the recombination kinetic. The observations were experimentally supported by using various techniques.

2B.5.1 Photovoltaic characterizations of hemicyanine dye DSSC

Current-Voltage characteristics of the DSSC were determined by potentiodynamic technique using Solartron electrochemical analyzer. Cells were biased at different potentials and generated photocurrent was recorded under radiation of light having intensity 100 mW/cm$^2$. Combined I-V curves of the DSSC sensitized with hemicyanine dyes is depicted in Figure 2B.17.

![Figure 2B.17](image_url)  
**Figure 2B.17** Photovoltaic Characteristics of hemicyanine dye molecules recorded using potentiostat at 20 mV/sec scan rate under simulation of 100 mW/cm$^2$ white light
This figure shows the photovoltaic performance of the various DSSC assembled using different sensitizers. Various performance parameters extracted from this are depicted in Table 2B.2. Reference cell was also fabricated by following the same procedure but using N719 standard dye. It is clear from the above figure that overall performance of the DSSC is increased as the alkyl chain length is increased. This increase in efficiency is due to enhanced $J_{sc}$ as well as $V_{oc}$. Koumara et. al. have reported that presence of longer alkyl substituent in carbazole based dye molecule would enhance the efficiency using MK-1 and MK-2 dyes and also they have concluded that the reduction in electron recombination is responsible for the same [16]. Moreover, it has been reported that the surface potential of the sensitizer is also a function of the alkyl chain length [17] and later on Pandey et al. have revealed that the surface potential of sensitizer increases with increasing alkyl chain length and could therefore, be attributed to the increase in $V_{oc}$[18].

<table>
<thead>
<tr>
<th></th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (mV)</th>
<th>$FF$ (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC 1</td>
<td>4.00</td>
<td>516</td>
<td>49</td>
<td>1.0</td>
</tr>
<tr>
<td>HC 2</td>
<td>5.61</td>
<td>524</td>
<td>50</td>
<td>1.5</td>
</tr>
<tr>
<td>HC 3</td>
<td>8.72</td>
<td>583</td>
<td>57</td>
<td>2.9</td>
</tr>
<tr>
<td>N719</td>
<td>16.00</td>
<td>720</td>
<td>63</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Enhancement in $J_{sc}$ can be attributed to the enhanced dye adsorption on the titania surface. This fact was supported by recording UV-Vis spectrum of dye loaded TiO$_2$ electrodes as shown in Figure 2B.18. This figure reveals that there is marked increase in the dye adsorption as the alkyl chain length increases. It is fact that increase in adsorbed dye on TiO$_2$ leads to enhanced surface trap passivation leading to the increased in current density [19].
Figure 2B.18 UV-Vis light absorbance of hemicyanine dyes on adsorbed on TiO\textsubscript{2} surface

Incident Photon to Current conversion Efficiency (IPCE) was recorded using the spectrophotometer which was served as a light source for the monochromatic radiation while a multimeter was used to measure the photocurrent. Equation 2B.3 (Section 2B.2) was used to measure the incident photon to current conversion efficiencies from the measurements. Figure 2B.19 shows the IPCE of the hemicyanine based DSSC suggesting that the quantum efficiencies of the dyes increases as the substitution of longer alkyl chain is carried out. It can be seen from the figure that the IPCE of the solar cells are 9.5%, 13.0% and 21.6 % for HC1, HC2 and HC3 dyes respectively. It has been found that all the dyes have maximum quantum efficiency around 450 nm but broader photo harvesting properties makes them better sensitizer. Hence, we can conclude that the varying chain length of alkyl group also affects the light harvesting properties of the dye molecule apart from the electron transfer kinetic of the dye solar cell.
2B.5.2 Voc Vs Electron Recombination study

2B.5.2.1 Theory of electron recombination and Photovoltage

There exist a correlation between the recombination of electron with the electrolyte species and the observed photovoltage in regenerative Photoelectrochemical cell. Following equation 2B.9 relates the photovoltage with the concentration of triiodide species and rate constant of the recombination reaction.

\[
V_{oc} = \frac{kT}{e} \ln \frac{I_{inj}}{n_{cb}k_c[ox]}
\]

(2B.9)

Where, \(I_{inj}\) is the incident photon flux, \(n_{cb}\) is the electron density in the titania film, \(k_c\) is the rate constant for the back electron transfer, \([ox]\) is the concentration of triiodide species in electrolyte. A decrease in the \(k_c\) would ensure the higher photovoltage.
generation in the DSSC. There are three pathways by which the recombination of the injected electron takes place viz. electron transfer from the conduction band of TiO₂, electron transfer through the surface states of semiconductor and electron transfer via conducting substrate.

We have covered the conducting substrate using a thin layer of TiO₂ in order to retard the direct exposure of electrolyte with the TCO (Transparent Conducting Oxide). Hence the possibility of recombination by TCO is neglected. So, the most important mechanism of loss of electron in our case is due to the reduction of triiodide ion by conduction band electron of the semiconductor known as the dark reaction. One possible route for the suppression of this dark current is passivation of the bare TiO₂ surface where dye is not adsorbed. This has been achieved by the addition of nitrogen containing heterocycles to the electrolyte which adsorbed onto the bare TiO₂ surface thereby retarding the recombination [20]. Conformations of the dye onto the TiO₂ surface are equally important for the suppression of recombination since adsorption of the foreign molecules onto the semiconductor would also cover the surface. So the proper design of the light harvesting molecules will help to cover the bare TiO₂ surface thereby lowering the recombination rate.

2B.5.2.2 Tafel Polarization study

In order to study the back electron transfer reaction in dye solar cell, Tafel polarization technique was used and the same has been represented in Figure 2B.20 [9]. Tafel analysis takes insight into the interfacial charge transfer properties of I/ I₃⁻ redox couple on the photoelectrode surface as discussed in Section 2B.4. Kinetic of the cathodic and anodic reactions occurring at the semiconductor electrolyte interface can be explained using the Buttler-Volmer equation 2B.8. It should be noted that the tafel data were fitted using CorrView software and the exchange current densities were estimated
therefrom. Generally, $j_0$ is estimated from the intersection of the cathodic and anodic branch of the Tafel polarization curve.

![Figure 2B.20 Tafel polarization curves for hemicyanine dye based DSSC recorded in dark](image)

Dark current densities found for HC1, HC2, HC3 and N719 are 3.68, 5.06, 0.58 and 0.46 respectively. It can be seen from these values that the intensity of the dark current ($j_0$) increases as the chain length decreases which indicates that longer chain retards the recombination of electron from the conduction band of titania with the species of electrolytes. It is fact that there are chances of recombination of electron from the conduction band of titania to the components of electrolyte. This phenomenon will render the DSSC unstable and would lead to the impotent device as the time passes. This recombination would also reduce the magnitude of photovoltage thereby lowering overall performance of device. So it is desirable to reduce the contact of electrolytes with the titania film. This can be achieved by designing dye molecules with long
pendant groups which would be aggregated on TiO₂ film in compact manner which will reduce the contact of electrolyte with titania film.

2B.5.2.3 Electrochemical Impedance study

Impedance of the electrochemical cell has been studied using small amplitude AC stimuli of either current or voltage in order to maintain the linearity of the system [8]. EIS of the cells were recorded under the reverse bias condition in dark using 10 mV AC stimuli and the output has been plotted in terms of Nyquist plot (Figure 2B.21). The detailed account of EIS measurement is given in Section 2B.2.3. Nyquist plot of all the DSSC have been combined in following Figure 2B.21. Various parameters can be extracted from the measurement of impedance of dye solar cell [8].

![Figure 2B.21](image_url)

**Figure 2B.21** EIS spectrum of hemicyanine dye based DSSC recorded in dark under reverse bias condition (Inset shows the Frequency Vs Phase Angle graph)

Impedance data are fitted into the equivalent electronic circuit model with various combinations of electronic components like resistor (R), capacitor (C) and inductor (L).
In electrochemical cell, charge transfer resistance and electrochemical capacitance are important to study the nature of the system. We have used equivalent circuit to model our system by considering the each interface as parallel \( RC \) circuit (Figure 2B.6). It should be noted that in our circuit capacitor is replaced by CPE (Constant Phase Element), which is a modified capacitive component for the electrochemical system. In electrochemical cells, electrode used is not having flat geometry so the electrode/electrolyte interface can not be treated as an ideal capacitor. The impedance data were fitted using ZView software by selecting appropriate equivalent circuit.

**Scheme 2B.3** shows the various electron transfer processes along with the recombination reactions in DSSC. \( R_{eq} \), known as the charge transfer resistance, is due to the charge transfer at Pt/Electrolyte interface whose values were obtained by fitting the first semicircle in parallel RC circuit and \( R_k \), electron recombination resistance, was estimated by fitting central arc in parallel RC circuit. While electron lifetime (\( \tau_{ele} \)) was calculated from peak frequency (\( \omega_{max} \)) using the equation 2B.6.

![Scheme 2B.3](image)

**Scheme 2B.3** Electron transfer processes in DSSC (*Energy Environ. Sci.*, 2010, 3, 1170-1181)

While \( D_{off} \) provides the effective diffusion length of the electron through the porous titania matrix which was calculated by the following Equation 2B.10.
\[ D_{\text{eff}} = \left( \frac{R_k}{R_w} \right) L \cdot k_{\text{eff}} \quad (2B.10) \]

In this equation, \( R_k, R_w, L \) and \( k_{\text{eff}} \) are known as the recombination resistance, electron diffusion resistance, thickness of TiO_2 layer and rate constant for electron transfer reaction (\( k_{\text{eff}} = \omega_{\text{max}} \)) respectively. \( R_k \) was estimated from the diameter of the central arc while \( R_w \) was calculated using following Equation 2B.11, where \( R_{dc} \) denotes the DC resistance which was estimated at \( \omega \rightarrow 0 \).

\[ R_{dc} = \sqrt{R_k R_w} \quad (2B.11) \]

Table 2B.3 shows the parameters extracted from the impedance measurements. Electron lifetime (\( \tau \)) charge transfer resistance (\( R_{ct} \)) and Electron diffusion coefficient (\( D_{\text{eff}} \)) are important parameters for the efficient working of dye solar cell.

Table 2B.3 Electron transfer parameters extracted from the EIS measurements

<table>
<thead>
<tr>
<th>( \omega_{\text{max}} ) (Hz)</th>
<th>( \tau ) (ms)</th>
<th>( R_{ct} ) (( \Omega ))</th>
<th>( D_{\text{eff}} ) (cm(^2)/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC 1</td>
<td>53.6</td>
<td>18</td>
<td>5.4</td>
</tr>
<tr>
<td>HC 2</td>
<td>30.1</td>
<td>33</td>
<td>6.3</td>
</tr>
<tr>
<td>HC 3</td>
<td>19.0</td>
<td>52</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Electron life time tells us that how much time electron spent in the titania film before recombination while charge transfer resistance is due to the resistance of electron transfer at counter electrode surface. From this table it is clear that \( R_{ct} \) is in the range of 4-12 \( \Omega \) which is an optimum range for the working of dye solar cell. While electron lifetime is increasing as the alkyl chain length increases which further supports the fact that there marked suppression in recombination as we move from ethyl to hexyl. This suppression is recombination would lead to the decrease in dark current thereby
leading to high $V_{oc}$. Moreover, we have found that electron diffusion coefficient is almost double in the HC3 dye than HC1 and HC2 which suggest that the electron can travel more through the TiO$_2$ matrix in case of HC3. As the electron diffusion length increase, chances of charge separation at TCO surface increase leading to higher photon to electron collection efficiency.

### 2B.6 Characterizations of DSSC from $-\text{SO}_3\text{H}$ anchored hemicyanine dyes

This section elaborates the characterizations of two sulphonate ($-\text{SO}_3\text{H}$) anchored hemicyanine dye i.e. INS 1 and INS 2. We have designed these molecules so as to study the effect of $p$-OH and $p$-OMe group on donor moiety.

#### 2B.5.1 Photovoltaic characterizations of DSSC

Figure 2B.22 indicates the photovoltaic performance of DSSC sensitized with various dyes like INS1, INS2 and N719. Photons to electricity conversion efficiency and fill factor (Equations 2B.1 and 2B.2) of the devices were calculated using the parameters obtained from $I-V$ curves and are summarized in Table 2B.4.

![Figure 2B.22 Photovoltaic performance of DSSC fabricated using hemicyanine dyes along with standard dye](image.png)
Table 2B.4 reveals that the solar to energy conversion efficiency is increased as the methoxyl group is replaced by hydroxyl group. INS 1 dye containing the $p$-OH group in the donor unit outperforms by attaining 3% photon to electricity conversion efficiency as compared to INS 2 dye containing the $p$-OMe group in the donor unit. We have also measured the photovoltaic performance of DSSC using N719 dye as a reference device and achieved 7.3% solar to electricity conversion efficiency.

Table 2B.4 Photovoltaic characteristics of the DSSC sensitized with hemicyanine dyes

<table>
<thead>
<tr>
<th></th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (mV)</th>
<th>$FF$ (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>INS 1</td>
<td>10.3</td>
<td>497</td>
<td>58</td>
<td>3.0</td>
</tr>
<tr>
<td>INS 2</td>
<td>2.3</td>
<td>484</td>
<td>53</td>
<td>0.6</td>
</tr>
<tr>
<td>N719</td>
<td>16.00</td>
<td>720</td>
<td>63</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Dye loading onto the photoelectrode was measured by desorbing the dye in ethanol overnight followed by recording the UV Vis spectra of solution. The data reveals that the amount of INS 1 dye onto electrode is $3.27 \times 10^{16}$ molecules/cm² and that of INS 2 is $3.06 \times 10^{16}$ molecules/cm². The dye loading amount for the both dyes are comparable even INS 2 shows slight less adsorption. Current density in case of INS 1 is 10.3 mA/cm², which is quite higher than 2.3 mA/cm² for INS 2 while trend in photovoltage is observed same for both the dye molecules. This observation suggests that the molecular orientations and surface coverage of dye molecules is somehow comparable in both cases but the remarkable difference may be there in the electron injection efficiency or regeneration of excited dyes. It is a fact that the open circuit voltage of the device is the difference between the Quasi Fermi level of TiO₂ and the redox potential of the electrolyte but molecular orientation of dye as well as surface coverage also determine the magnitude of $V_{oc}$ to certain extent.
2B.6.2 Electrochemical study of DSSC

In order to ensure the smooth functioning of the DSSC electron transfer kinetic of the device should be optimized [8]. The response of the AC signal to the electrochemical system is represented in the form of Nyquist plot, ideally consisting of three semicircles depending upon the time constant of the electron transfer reactions as shown in Figure 2B.23.

![Figure 2B.23](image)

**Figure 2B.23** Nyquist plots of various DSSC fabricated using hemicyanine dyes and N719 dye recorder under forward bias in dark

Response of the electrochemical system to the AC signal was plotted in form of Nyquist plot as shown in Figure 2B.23. In order to extract the required parameters to study the electron transfer kinetic in DSSC, the impedance data are fitted using equivalent circuit models consisted of discrete electronic components like resistor, capacitors, constant phase element etc. as shown in Figure 2B.6.

We have extracted some important parameters for the impedance technique by fitting the data into the above equivalent circuit. We have calculated electron lifetime ($\tau_{ele}$),
Charge transfer resistance ($R_{ct}$) and recombination resistance ($R_k$) which are tabulated in Table 2B.5. Electron lifetime (equation 2B.6) in case of INS 1 is quite comparable to that of reference DSSC (with N719) while in case of INS 2 it is quite high. Charge transfer resistance of all the DSSC is quite comparable which indicates the electron transfer at Pt/electrolyte is almost same. The high values in recombination resistance for INS 2 dye is due to the inefficient charging of TiO$_2$ by dye molecules and low values in recombination resistance may be due to the faster back electron transfer.

**Table 2B.5** Electron transfer parameters of hemicyanine dye based DSSC

<table>
<thead>
<tr>
<th></th>
<th>$\tau_{ele}$ (Sec.)</th>
<th>$R_{ct}$ (Ohm)</th>
<th>$R_k$ (Ohm)</th>
<th>$j_o$ (μA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>INS 1</td>
<td>0.026</td>
<td>3.9</td>
<td>96.6</td>
<td>3.1</td>
</tr>
<tr>
<td>INS 2</td>
<td>0.052</td>
<td>4.5</td>
<td>174</td>
<td>2.9</td>
</tr>
<tr>
<td>N719</td>
<td>0.026</td>
<td>4.0</td>
<td>41.9</td>
<td>0.3</td>
</tr>
</tbody>
</table>

In order to study the recombination kinetic in the DSSC, Tafel polarization technique has been employed [9]. Exchange current densities for all the DSSC extracted from Tafel polarization curves (Figure 2B.24) are summarized in Table 2B.5.

**Figure 2B.24** Tafel polarization curves for DSSC sensitized with hemicyanine dyes and N719
This table reveals that the dark current is quite lower in reference cell as compared to the DSSC based on hemicyanine dyes. The intensity of dark current is directly related to the back electron transfer from the TiO₂ matrix to the electrolyte component. Moreover, the higher dark current would lead to the lower open circuit voltage due to the recombination of electrons but in the hemicyanine dyes dark current densities are almost comparable leading to the almost equal photovoltage. These data also support the fact that the surface coverage of both the molecules is same as can be inferred from the strength of dark currents.

2B.6.3 –OH Vs -OMe

Above experimental evidences clearly set forth that there are major differences in the dyes INS 1 and INS 2 even though they are only differ in the substituent at para position. In order to justify this anomalous behavior, molecules were studied using theoretical approach by Density Functional Theory (DFT) with GAUSSIAN 03 package on BRAF supercomputing environment and Materials Studio 4.0 with DMol3 programme package. We may hypothesize that the substitution of –OH group by –OMe group at para position in sensitizer changes the molecular properties in terms of dipole moment and light absorption. Geometry optimizations with vibrational frequency, without symmetry constraints, for both the molecules were carried out at the Becke’s three-parameter hybrid exchange functional [21] coupled with the Lee - Yang - Parr nonlocal correlation functional (B3LYP) [22] density functional level of theory using 6-31++g(d,p). The optimized structures of the compounds are presented below (Figure 2B.25) and their corresponding minimum energies are tabulated in Table 2B.6. We have attempted to study the dipole moments of the molecules using DMol3 Programme package in Materials Studio 4.0 using GGA-BLYP. While dipole moments were estimated using Hirshfeld population analysis.
Figure 2B.25 The geometry optimized structures of INS1 and INS2

The position para to the aromatic ring seems to involve in the key operations of the dye systems. The presence of two –OMe groups at meta position exerts electron withdrawing effect (electronegativities predominates over electrodonating activities of methoxy moieties at meta position). On the other hand –OH group at para position retaliates over this through active influx of electron to aromatic ring (perhaps through deprotonation). Contrast to that in INS 2, the \( p-OMe \) group being non-ionisable unlike \( p-OH \) can not match the electron withdrawing effect of two \( m-OMe \) moieties. This view has got a strong support from the dipole moment of the molecule (Table 2B.6). The \( \mu_x \) of INS 2 is not only significantly different from the INS 1 but it is of opposite sign whereas \( \mu_y \) and \( \mu_z \) are almost equivalent (Figure 2B.26). This might be responsible for disturbing the directional flow of electron over the molecular skeleton of INS 2 thereby rendering the remarkable decrease in efficiency.
Figure 2B.26 Molecular orientation of dyes on TiO$_2$ surface showing the dipole vectors in the $x$ directions

It has been cleared from the Table 2B.6 that the changes in dipole moments of the dyes are amplified by changing the substituent at para position. But there is only remarkable difference in the $x$ direction while there is no change in the dipole moments along the $y$ and $z$ direction. We can summarize that the increase in the dipole moment along the $x$ direction enhances the resonance and that in $z$ direction enhances the charge injection to the semiconductor film since the binding with TiO$_2$ film would occur in the $z$ direction (Figure 2B.26). It has been reported that the increase in the dipole moment along $z$ direction will lead to the enhancement in $V_{oc}$ due to the shifting of TiO$_2$ quasi-fermi level [23]. But in our case both the dyes are having comparable open circuit potential showing that the dipole moment in $z$- direction is almost comparable for both molecules. The same fact has been observed in the dipole moment calculated by using theoretical calculations. Moreover, estimation of electrostatic dipole also suggest that there is only changes of charge density along the $xy$ plane suggesting that the conjugation is highly influenced by para substitution. Scheme 2B.4 shows the excited state structures of the molecules from donor side revealing that in
INS 1 presence of hydroxyl group leads to the stable quinonoid form while in INS 2 stability of the quinonoid form is decreased due to the presence of methyl substituent.

Scheme 2B.4 Excited electron transfer in hemicyanine dyes INS1 and INS2

It has been reported that the presence of o-hydroxyl group on the dye molecule enhances the current density drastically but it was due to the binding of the hydroxyl functionality to the TiO2 film [24]. A remarkable difference in the current was reported by putting o-OH group but in our case –OH moiety is at para position and hindered by two –OMe groups so chances for the direct bonding are curbed.

The electronic transitions of the compounds were studied computationally under Time-Dependent Density Functional Theory (TD-DFT) using B3LYP (solvent free and ethanol solvent) and PBE0 (ethanol solvent) functional. Both of these functionals have been reported to provide reasonable estimate of transition energies of different types of compounds [25]. The lowest 40 vertical excitation energies were estimated in all calculations. The basis set used 6-31++g(d,p) included the polarization effects of the unoccupied orbitals d and p on the occupied p and s orbital present in the INS 1 and
2. The calculated optical absorptions along with oscillator strengths are tabulated in Table 2B.6.

Table 2B.6 Minimum energies, dipole moment, electronic transitions values of optical absorption of hemicyanine dyes obtained from theoretical calculations

<table>
<thead>
<tr>
<th>Minimum Energy (Ha)</th>
<th>Dipole Moment (D)</th>
<th>Electronic transitions in nm ($\lambda_{max}$)</th>
<th>Dielectric constant $\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\mu_x$</td>
<td>$\mu_y$</td>
<td>$\mu_z$</td>
</tr>
<tr>
<td>INS 1</td>
<td>-1796.96629</td>
<td>0.098</td>
<td>0.319</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.126)*</td>
<td></td>
</tr>
<tr>
<td>INS 2</td>
<td>-1836.25723</td>
<td>-0.204</td>
<td>0.346</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.045)*</td>
<td></td>
</tr>
</tbody>
</table>

*Oscillator strength of the corresponding transition $^*$ Dye adsorption TiO$_2$ surface and measured 10kHz-1Hz

The theoretical studies indicated only one antibonding orbital (LUMO) and six bonding orbitals (HOMO, HOMO-1, HOMO-2, HOMO-3, HOMO-4 and HOMO-5) to be associated in all the transitions probable under UV and Visible range. Out of those the HOMO – LUMO transition was with the highest oscillator strength under solvent system. Interestingly, when calculated for neat compound, the HOMO-LUMO energy difference was found to be much smaller and the corresponding transition went to very long wavelength region than in solvent, which might be attributed to the solvochromic properties of the dyes.

Further investigation of the polarity of the dyes was made using relative permittivity measurements since the polarity of the dye is indirectly related with the dipole moment [26,27]. We have recorded the relative permittivity of the dyes adsorbed onto TiO$_2$ nanoparticles in order to justify the polarity of the dyes. These data were collected by sweeping the AC frequency from 10kHz to 1Hz onto the sample in pallet form (Dye
adsorbed onto TiO\textsubscript{2} surface). The graph of Relative permittivity Vs Frequency is given in the Figure 2B.27 and the final results are tabulated in Table 2B.6.

![Graph of Relative permittivity Vs Frequency](image)

Figure 2B.27 Relative permittivity of the dyes on TiO\textsubscript{2} at different frequencies

It can be seen from this graph that the relative permittivity of the TiO\textsubscript{2} decreases upon adsorption of the foreign molecules. This might be due to the insulating behavior of the organic molecules leading to reduction in the permittivity. The magnitude of the decrement in the both the dyes are quite different showing that the insulating properties of the dyes are different. We have found that the INS 1 is showing less insulating property on TiO\textsubscript{2} film as compared to INS 2. It can be seen from the Figure 2B.27 that the relative permittivity of the INS 1 is lower than the pure TiO\textsubscript{2} but higher than that of INS 2 in given frequency range. These data reveals that the polarity of the INS 1 dye is higher than that of INS 2 since the later is showing better insulating properties of TiO\textsubscript{2}. Moreover an attempt was made to determine the absolute energies of frontier orbital of dye molecules from the onset of oxidation potential and optical band gap and is
tabulated in Table 2A.4 (Chapter 2A). From this table it is clear that the HOMO energy level of INS 2 dye is partially aligned with the redox potential of electrolyte (Scheme 2A.5 in Chapter 2A) This leads to the poor regeneration of sensitizing molecule while there is no issue of dye regeneration by electrolyte in INS 1. Hence conclusion can be drawn from these experimental and theoretical facts that dipole moment and dye regeneration is responsible for the inefficient photovoltaic properties of INS 2 dye.

2B.7 Characterizations of alkyl substituted carbazole dyes based DSSC

This section deals with the characterizations of DSSC sensitized with carbazole based D-π-A dye having different acceptor unit i.e. SK2 dye with rhodanine-3-acetic acid and SK3 dye with cyanoacetic acid unit. Photovoltaic performance and electron transfer kinetic of the DSSC fabricated by using carbazole based dyes are discussed in this section. These dyes are found to be most effective sensitizer for DSSC in our study. These molecules were synthesized using noble metal free synthetic approach using facile synthetic strategies in order to increase the commercial importance of this molecule. Details of synthesis are given in Chapter 2A (Section 2A.5). DSSC were characterized by using I-V, IPCE, EIS and Tafel measurements. SK3 dye is having more than 7% solar to electricity conversion efficiency which beats N719 (PCE ~4.5%) dye in our set up.

2B.7.1 Photovoltaic performance of DSSC

Solar to electricity conversion efficiencies of the DSSC were estimated using $J-V$ curves. DSSC fabricated using carbazole dyes were biased at different voltage and generated photocurrent was measured using Solartron electrochemical analyzer in
potentiodynamic mode. This response was plotted as photocurrent $Vs$ voltage applied as shown in Figure 2B.28 (a). While incident photon to current conversion efficiencies were determined by applying white light having different wavelength and generated photocurrent was measured. IPCE spectrum has been demonstrated in Figure 2B.28 (b).

**Figure 2B.28** (a) $J-V$ curves for the fabricated device with SK2 and SK3 dyes (along with N719 reference dye) at 100 mW/cm$^2$ under AM 1.5G solar irradiation. (b) Incident photon-to-current conversion efficiency (IPCE) plot for the same device showing a maximum of $\sim$81%.
The photocurrent-voltage ($J-V$) characteristics of DSSCs sensitized with SK2 and SK3 on 8 μM TiO₂ films (without scattering layer) are shown in Figure 2B.28 (a) and photovoltaic parameters are depicted in Table 2B.7. The photovoltaic parameters, including short-circuit photocurrent density ($J_{sc}$) and PCE for SK3 is much higher than that of SK2. We have achieved a highest PCE value of 7.1% for DSSCs based on SK3 (cyanoacrylic acid) dye while relatively low PCE value (2.0%) was observed for the device with SK2 (rhodanine-3-acetic acid) dye. Koumara and coworkers have synthesized carbazole dye with N-alkyl fictionalization and thiophene bridge with cyanoacetic acid acceptor unit (MK dye series) [28].

Table 2B.7 Photovoltaic parameters for DSSC sensitized with SK2 and SK3 dyes

<table>
<thead>
<tr>
<th></th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SK2</td>
<td>7.08</td>
<td>534</td>
<td>53.0</td>
<td>2.0</td>
</tr>
<tr>
<td>SK3</td>
<td>17.23</td>
<td>645</td>
<td>65.0</td>
<td>7.1</td>
</tr>
<tr>
<td>N719</td>
<td>16.00</td>
<td>720</td>
<td>63.0</td>
<td>7.3</td>
</tr>
</tbody>
</table>

These dyes were synthesized through noble metal catalyzed coupling reaction in many steps. They have achieved more than 8% solar to energy conversion efficiency. Srinivas et al have synthesized dyes having carbazole donor, ethynyl bridge and cyanoacetic acid acceptor. Bridge is directly attached to the N atom of the carbazole moiety while in our case bridge is attached to the 3-position of carbazole donor [29]. They have achieved maximum 0.8% solar to photoconversion efficiency. Lai et al have synthesized dyes with multiple carbazole moieties as donor with ethylenedioxythiophene as bridge and cyanoacetic acid as acceptor [30]. They have achieved more than 6% solar to electricity conversion efficiency. Hence, It can be conclude that the attachment of bridge at 3$^{rd}$ position of carbazole make better sensitizer for the DSSC application. Under similar conditions, the N719 dye gives a
PCE value of 7.3%. The lower $J_{sc}$ of SK2 may be due to poor charge injection capacity originating from close value of LUMO of this dye (-0.75V) and CB of TiO$_2$ (-0.50V). The incident photon-to-current conversion efficiencies (IPCE) of SK2 and SK3 dyes in DSSCs are shown in the Figure 2B.28 (b). SK3 gives higher IPCE value than the SK2 dye, with the highest value of 81% obtained at ~500 nm. The lower IPCE value of SK2 dyes indicate that rhodanine-3-acetic acid is a poor acceptor or anchoring group in comparison to cyanoacrylic acid (SK3). It is also important to note that the SK3 dye with simple vinylene-phenylene bridge and cyanoacrylic acid as an acceptor gives a better or comparable solar cell performance than the other carbazole dyes where thiophene derivatives were used [28,31] as a bridge although its (SK3) molecular structure is simpler.

2B.7.2 Electron transfer kinetic in DSSC

Devices were further studied using electrochemical impedance and Tafel polarization technique in order to take better insight into the electron transfer kinetic [8,11]. Figure 2B.29 shows the Nyquist plot for the DSSC recorded in dark and electron transfer parameters i.e. charge transfer resistance ($R_{ct}$), Electron life time ($\tau_{ele}$) and recombination resistance ($R_k$) are tabulated in Table 2B.8. Impedance data were fitted using widely accepted transmission line model in order to extract the electron transfer parameters of DSSC. In the Nyquist plot, high frequency response is attributed to the Pt/Electrolyte interface; middle frequency response is associated with Dye/TiO$_2$ interface while lower frequency senses the diffusion of electroactive species in electrolyte. Charge transfer resistances of all the devices are comparable owing to the same electrocatalyst and electrolyte in all devices. But recombination resistances are different since the later is associated with dye/TiO$_2$ interface.
Figure 2B.29 (a) Nyquist plot for the DSSC recorded in dark (b) and Tafel polarization curves for dye solar cells

Electron life times are comparable for SK3 and N719 dyes but SK2 is having shorter electron lifetime. This fact suggests that the recombination is quite pronounced in case of this dye which was further supported by Tafel polarization experiment (Figure 2B.29 (b)). Tafel polarization technique yields better insight into electron transfer reactions at TiO2/dye/electrolyte interface. Magnitude of the dark currents is direct measure of recombination reaction at the semiconductor/electrolyte interface. Tafel polarization data were fitted in Butler Volmer equation in order to determine the magnitude of dark current densities ($J_0$) in solar cells [3]. Tafel polarization shows the enhanced dark current in the SK2 dye as shown in last column of Table 2B.8.

Table 2B.8 Electron transfer parameters of the DSSC sensitized with carbazole dyes

<table>
<thead>
<tr>
<th></th>
<th>$R_{ct}$ (ohm)</th>
<th>$\tau_{ele}$ (sec)</th>
<th>$R_k$ (ohm)</th>
<th>$J_0$ ($\mu A/cm^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SK2</td>
<td>1.6</td>
<td>0.01</td>
<td>26.3</td>
<td>1.82</td>
</tr>
<tr>
<td>SK3</td>
<td>1.8</td>
<td>0.24</td>
<td>20.4</td>
<td>0.36</td>
</tr>
<tr>
<td>N719</td>
<td>1.9</td>
<td>0.11</td>
<td>13.7</td>
<td>0.42</td>
</tr>
</tbody>
</table>
2B.6.3 Stability test of DSSC

It is fact that the solar cell working parameters in real conditions are quite differ than those maintained in laboratory. In working condition, solar cells are exposed to variable light, heat and humidity. Moreover, initial efficiency of the DSSC can’t be accounted for its absolute performance. Absolute performance of the DSSC mostly depends upon the stability of dye molecule used as sensitizer. There are many dyes which are photochromic and degrade as a function of time which leads to dwindled performance over time. In order to make dye a commercially potential counterpart, it is desirable to study the stability of DSSC in real condition. This section discusses the performance of DSSC subjected to actual atmosphere in open terrace. The performance of this DSSC was monitored as function of time (Figure 2B.30).

![Graph](image)

**Figure 2B.30** Photovoltaic parameters of device (SK3 dye) measured under the illumination of sun light for 600 hr. η: Power conversion efficiency, FF: Fill factor, \( J_{sc} \): Short-circuit photo current density, \( V_{oc} \): Open-circuit voltage

The DSSC under investigation was set on the terrace for 25 days and its performance was measured using simulated sunlight. We have acquired short circuit current density
(J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency (\eta).

**Figure 2B.30** reveals that the performance of the DSSC remains intact up to a greater extent after 600 hour real time measurements. Looking to the photovoltage, we have found that there is little i.e. 30-40 mV loss has been observed at initial but found constant afterwards. This may be originated from dye desorption of loosely bound molecules leading to recombination and loss in $V_{oc}$. Photocurrent shows 0.8-1.0 mA/cm$^2$ decrement from its initial value. Decrease in fill factor has been observed after a week but it retained its original value at the end of the measurements. The overall power conversion efficiency has been slight down from 7.1% to 6.8% giving overall $\sim$4% reduction in the photovoltaic performance.

### 2B.8 Conclusion

This Chapter 2B dictates the characterizations of various DSSC fabricated from the dyes discussed in Chapter 2A. We have discussed various characterization techniques such as $I-V$ curves, Incident photon to current conversion efficiency (IPCE), Electrochemical Impedance Spectroscopy (EIS), Tafel polarization technique and Intensity modulated spectroscopy. These techniques are discussed in details along with underlying principles and set up for measurements. We have also given the equations to determine the photovoltaic and electron transfer parameters. Later this discussion turns to characterizations of DSSC sensitized with our dyes. Section 2B.3 reveals the fabrication technique of dye solar cell in details. Section 2B.4 depicts the fabrication of DSSC from the anthracene based primitive molecule. This DSSC was characterized by using IV, EIS and Tafel polarization techniques. This dye shows poor performance in DSSC which was attributed to the lower surface coverage by dye molecules. Section 2B.5 deals with the carboxy anchored hemicyanine dyes (HC1, HC2 and HC3)
sensitized DSSC fabrication and characterizations. These dyes carries different chain on their backbone i.e. hexyl chain on HC3, butyl chain on HC2 and ethyl chain on HC1. We have found that there is marked effect of chain length in the dye skeleton on the performance of the solar cell. This has been attributed to the fact that as the chain length increases, recombination of the injected electron is suppressed. This leads to enhanced photocurrent and photovoltage leading to increase in overall performance of DSSC. The order of PCE follows the trend as hexyl chain>butyl chain>ethyl chain. This fact has been supported by various experimental and theoretical observations. Section 2B.6 explains the characterizations of DSSC from the dyes INS 1 and INS 2 containing the –SO3H as anchoring group. The design of these dyes varies only at para position on donor atom. INS 1 dye carries p-OH group on donor atom while INS 2 dye carries p-OMe. DSSC were characterized by using I-V, EIS and Tafel measurements. We have found that there is remarkable difference in the performance of these dyes even though there is little difference in their molecular skeleton. INS 1 dye with p-OH is having better performance than INS 2 dye. We have also measured the polarity of these dyes onto TiO2 surface and found that the INS 1 is more polar than INS 2. Further theoretical calculations suggest that the dipole moment of INS 1 is in the direction of excited state electron flow while that of INS 2 is opposite. Hence, conclusion was drawn that the p-OH group enhances the excited state dipole due to the ionization ability if –OH leading to enhanced injection and faster dye regeneration. Section 2B.7 deals with the fabrication and characterization of DSSC sensitized with alkyl substituted carbazole dye. These dyes carried hexyl chain on the carbazole donor moiety but are differ in acceptor unit. SK2 dye is having rhodanine-3-acetic acid acceptor while SK3 dye is having cyano acrylic acid as acceptor unit. We have found that the performance of SK3 dye is far better than SK3 dye in terms of photocurrent
and photovoltage. This difference has been attributed to the placement of HOMO level in SK2 dye which is extended up to acceptor unit leading to recombination of injected electron. While in SK3 dye both the levels are well separated giving high dipole moment to excited state and efficient charge injection capacity. Moreover, SK3 dye is also outperforming than standard dye N719 in our set up. This may be attributed to the molar absorptive difference in both dyes. We have also carried out the stability test for SK3 dye sensitized solar cell in open atmosphere under direct sun light. There is ~4% reduction in performance was observed after 600 hour stress. We have concluded that the SK3 dye is a potential competitor in the commercialization of DSSC since it has been synthesized using facile organic reactions which can be easily scaled up for bulk production.
2B.9 References


