Chapter 3
Dye Sensitized Solar Cell fabrication: Methods and optimization to realize high power conversion efficiency for low power applications

This chapter deals with optimization of device fabrication methodology to prepare small area (0.15 cm$^2$ - 1 cm$^2$) and large area (5 cm$^2$) DSSCs. The detailed device fabrication protocol is illustrated which includes the preparation of doctor-blade pastes for working electrode (photo-anode), post-treatments on working electrode, preparation of dye solution, counter electrode, electrolyte and sealed assembly of photo-electrodes. Using DSSC fabrication protocol optimized in our lab we demonstrated a power conversion efficiency of 10% on small area (0.15 cm$^2$) and 6% on large area (5 cm$^2$). Finally, the use of sealed large area DSSCs for low power applications such as pedometer, calculator and mobile charging is demonstrated.
3.1 Introduction

Dye sensitized solar cells (DSSC) have attracted widespread attention because of their high efficiency at low production cost[1]. The low temperature chemical processability of DSSCs offer a great advantage in terms of ease of fabrication and cost as compared to the high temperature vacuum processed thin film solar cell. The DSSC consists of multiple components viz. transparent conducting substrates, mesoporous metal oxide film, dye, electrolyte with several additives and platinum coated counter electrode. This multi-component architecture of DSSC imposes an inherent complexity in device optimization as the functionalities of these components are interdependent. For instance higher concentration of lithium ions[2] in electrolyte is found to increase the rate of electron injection in TiO$_2$ conduction band leading to higher $J_{sc}$ however it also lowers the conduction band edge of TiO$_2$ leading to lower $V_{oc}$. Therefore in order to obtain maximum power conversion efficiency it is important to carefully optimize each component of DSSC.

This chapter elaborates detailed DSSC fabrication protocol developed in our laboratory after optimization of various parameters pertaining to the DSSC architecture. We further demonstrate that the sealed large area (5cm$^2$) DSSCs fabricated in our lab can be utilized for small power applications such as solar powered pedometer, calculator and cell phone charger.

3.2 Fabrication of DSSC

3.2.1 Transparent Conducting Oxide (TCO) substrates

Transparent conducting oxide (TCO) substrate is one of the crucial components of the DSSC device architecture as its transparency ensures efficient absorption of solar spectrum by the sensitizer and its high conductivity allows efficient transport of electrons to the outer circuit. For past three decades the most popular TCOs have been Tin doped Indium Oxide (ITO), Fluorine doped Tin Oxide (FTO) and Zinc Oxide (ZnO). However ITO and ZnO suffer from poor chemical and thermal stabilities[3]. Therefore FTO has been a preferred substrate for DSSC fabrication because of its high temperature (< 550°C) and chemical stability.
Generally high transparency and low sheet resistance are the ideal conditions for use of TCOs as substrates in DSSC. However in order to obtain low sheet resistance in FTO coated glass, higher thickness of FTO on glass is required which in turn hampers overall transparency of substrate. Therefore we selected optimal values of sheet resistance and transparency in order to obtain maximum device performance. The FTO substrates with sheet resistance of 10-15 Ω/□ and transparency > 80% were purchased from Solaronix, Switzerland.

3.2.2 Cleaning protocol of FTO substrates

The FTO substrates were cut into 2.5x1.5 cm rectangular pieces. It is important to clean FTO substrates to remove organic/inorganic surface contaminants so as to improve the wettability of chemical precursors or doctor blade paste used in DSSC fabrication. The cleaning protocol followed included,

- Ultra-sonication of FTO substrates in soap solution for 15 min.
- Cleaning and subsequent ultra-sonication of substrate in deionized water for 15 min.
- Cleaning and subsequent ultra-sonication of substrates in anhydrous ethanol for 15 min.
- The substrates were then heated at 450°C for 30 min to remove any remaining organic impurities on the FTO surface.

3.2.3 Preparation of counter-electrode

The role of counter electrode in DSSC is also considered to be vital as efficient reduction of the oxidized electrolyte species (I$_3^-$) to I$^-$ is important to complete the photo-electrochemical reaction. However at the bare FTO surface the rate of I$_3^-$ reduction is low which limits the electrolyte regeneration within cell and hence it results in high recombination and lower photovoltaic efficiency. Therefore a catalyst is generally deposited on the surface of FTO counter electrode which accelerates the rate of electrolyte regeneration. Among various electro-catalyst$^{[4]}$ platinum is considered to be the most preferred candidate due to its high catalytic activity towards reduction of tri-iodide species in electrolyte. We used Pt-coated FTO as counter electrode for the DSSCs fabricated in our laboratory. In order to prepare Pt-FTO, a single drop of 7mM solution of H$_2$PtCl$_6$ in isopropanol was put on the
cleaned FTO and allowed it to spread uniformly. After drying at ambient conditions the drop casted FTO was heated at 450°C for 15 min which thermally reduces the platinum on FTO substrate. Figure 3.1 (b) and (c) shows the SEM images of the bare FTO and Pt-FTO electrodes. It can be clearly seen that thermal decomposition of H₂PtCl₆ on cleaned FTO fives islands of ‘platinum’ in the range of 200-500nm.

**Figure 3.1:** (a) Drop casting of H₂PtCl₆ on FTO for counter electrode preparation, (b) and (c) FESEM of only FTO and Pt coated FTO.

### 3.2.4 Preparation of the electrolyte solution:

We used iodide/tri-iodide redox couple as the electrolyte for DSSCs fabricated in our laboratory. The redox electrolyte is chosen in such a way that the electrolyte redox potential should be energetically above the sensitizer HOMO level so that the electrolyte can regenerate oxidized sensitizer molecule by donating electrons. We have used N719 as sensitizer for the DSSCs fabricated in our lab. I⁻/I₃⁻ redox couple is most suited for N719 sensitizer as its redox potential \(^{[5]}\) (0.35 V vs. NHE) is well above the N719 HOMO (1.12V vs. NHE) which is sufficient to effectively transfer the electrons from redox couple to oxidized sensitizer.

The typical composition of the I⁻/I₃⁻ redox couple was 0.05M LiI, 0.05M I₂, 1M 1-propyl-2,3-dimethyl-imidazolium iodide (DMPII), and 0.5M 4-tertbutylpyridine (TBP) in acetonitrile/valeronitrile solution (v/v 1:1). The DMPII and LiI in
electrolyte are sources of iodide ions and I\(_2\) is necessary to produce the redox couple with them. The TBP in electrolyte helps to improve \(V_{oc}\) by positively shifting the conduction band edge of TiO\(_2\) and also by reducing the dark current\([6]\).

3.2.5 **Preparation of the sensitizer dye solution:**

The sensitizer in DSSC is the key light harvesting component which absorbs the incident sunlight and converts it in the usable electricity. Therefore the sensitizer to be used in DSSC should have high molar extinction coefficient in visible region, energetically negative LUMO level with respect to conduction band edge of TiO\(_2\) and energetically positive HOMO level with respect to the redox potential of electrolyte. Due to these stringent conditions on HOMO-LUMO levels of sensitizers only a few among several proposed organo-metallic and organic sensitizers could actually demonstrate high photovoltaic conversion efficiency\([7]\). For the research included in this thesis we chose one of the most successful sensitizer Di-tetrabutylammonium \(\text{cis-}
\)bis(isoniocyanoato)bis(2,2\text{'}bipyridyl4,4\text{'}dicarboxylato)ruthenium(II) which is commonly called N719 dye. **Figure 3.2 (a)** shows the UV-Visible absorbance curve of N719 dye with absorption extending up to 650nm in visible region. **Figure 3.2(b)** shows the structure of N719 dye molecule. Importantly the N719 dye also possess high molar extinction coefficient\([8]\) of 14000 mol\(^{-1}\) cm\(^{-1}\).

![Figure 3.2:](image)

**Figure 3.2:** (a) The UV-Visible absorbance of N719 dye (b) Chemical structure of N719 dye where Bu\(_4\)N\(^+\) corresponds to the tetrabutylammonium group.
The N719 dye was purchased from Solaronix, Switzerland and used without further purification. The 0.5mM dye solution was prepared in 1:1 (vol/vol) mixed solution of tert-butyl alcohol and acetonitrile.

3.2.6 Preparation of the bottom compact layer on photo-anode (working electrode):

The DSSC architecture consists of mesoporous TiO$_2$ photo-active layer whose higher surface area as compared to non-porous film facilitates the sensitizer adsorption and hence give high photo-currents. However the mesoporous nature of TiO$_2$ photoactive layer also leaves unmasked regions on FTO substrate which can act as islands of recombination ($2e^- + I_3^- \rightarrow 3I^-$) between injected photo-electrons in FTO and the tri-iodide ($I_3^-$) species in the electrolyte$^{[9]}$. It is critical to avoid this recombination in order to obtain high photovoltaic efficiency. One of the key solutions to this problem is to deposit the highly dense metal oxide layer which blocks the direct contact of electrolyte with the FTO. Though various metal oxides$^{[10]}$ can be used as blocking layer but for TiO$_2$ based mesoporous film a compact layer of TiO$_2$ is generally preferred because of possible ohmic contact and improved adhesion between mesoporous TiO$_2$ and the compact layer.

The pre-requisite sol for blocking layer was prepared by mixing the Titanium tetra-isopropoxide (TIP) (1 mL) with ethanol (5 mL) and acetic acid (0.5 mL). Washed and annealed FTOs were masked except the coating area with the help of scotch tape. The prepared sol was spin coated on masked FTOs at 3000 rpm for 30 sec. The substrates were dried under ambient conditions and then heated at 450$^\circ$C for 30 min which forms a 40-50nm thick TiO$_2$ bottom compact layer.

3.2.7 Preparation of the (photo anode) working electrode of DSSC

In order to prepare the metal oxide based mesoporous photo anodes it is important to prepare a slurry/paste of metal oxide nanoparticles which on coating on the FTO substrate gives un-cracked and uniform films of desired thickness. The quality of mesoporous metal oxide coating on FTO depends on the ingredients within the paste which control the metal oxide nanoparticle aggregation, the extent of porosity and transparency as well as rate of drying to obtain crack-less films. Various paste making protocols$^{[11]}$ exists in literature which can be followed.
depending on the specific experimental constraints such as low temperature for flexible substrates or high temperature processed metal substrates etc.

During the initial trials of DSSC fabrication we followed formulation\textsuperscript{[12]} which involved commercially available P25-TiO\textsubscript{2} based paste with water/alcohol mixture as solvent, Poly-ethylene glycol as binder and Triton-X 100 as surfactant. This protocol could deliver power conversion efficiency up to 5-6\% on small area of 0.25cm\textsuperscript{2}. However this paste formulation suffered from the drawbacks such as non-uniform thickness of film and TiO\textsubscript{2} nanoparticle aggregates within the film which made it difficult to push efficiency beyond 6\%. In the later years we changed the paste formulation so that the pastes could also be screen printed. The new formulation was based on ethanol as solvent, \(\alpha\)-terpeniol as surfactant and ethyl cellulose as binder\textsuperscript{[13]}. This formulation could effectively avoid the TiO\textsubscript{2} nanoparticle aggregation and hence DSSCs with power conversion efficiencies up to 8-9\% could be fabricated. In the following sections we give detailed procedure of paste making and device fabrication which lead to high photovoltaic efficiency up to 9\%.

**Preparation of TiO\textsubscript{2} nanoparticle based pastes for doctor blading:**

It has been established by several researchers that the particle size of TiO\textsubscript{2} greatly influences the photovoltaic conversion efficiency\textsuperscript{[14]}. Though smaller particle size can give high surface area for dye adsorption but it also increases the density of inter-particle joints as well as density of trap states. Thus DSSCs fabricated with TiO\textsubscript{2} particles less than 15nm diameter give low photovoltaic efficiency due to low mean free path and low diffusion coefficient of charge carriers\textsuperscript{[14d]}. For particle size greater than 30-40nm though the electron scattering effects due to inter-particle joints are less but larger particle size leads to low surface area and hence low dye adsorption. Also the scattering of incident light by larger particles at FTO interface leads to lower photo-currents and photo-voltaic efficiency. Therefore the optimum particle size for high efficiency DSSC is found to be 15-25nm. We used anatase TiO\textsubscript{2} nanopowder with average particle size of 21 nm as supplied by Sigma-Aldrich. The formulation was developed based on report by Seigo Ito\textsuperscript{[13]} et al.

The ingredients in the paste are TiO\textsubscript{2} nanopowder (particle size ~21nm, Sigma Aldrich), ethyl cellulose (Sigma-Aldrich), alpha terpineol (ACROS) absolute
ethanol, and de-ionized water. The steps involved in the paste preparation and corresponding explanations are given below,

1. **6g of TiO$_2$ powder and 1 ml acetic acid is mixed homogeneously in agate mortar for 15 mins.**
2. **1 ml of de-ionized water is added to paste in step 1 and mixed homogeneously for 1 min. This step is repeated 5 times.**
3. **1 ml of absolute is added to paste in step 2 and mixed homogeneously for 1 min. This step is repeated 15 times.**
4. **1 ml of acetic acid is added to paste in step 3 and mixed homogeneously for 5 min.**
5. **2.5 ml of absolute is added to paste in step 4 and mixed homogeneously for 1 min. This step is repeated 6 times.**
6. The paste is transferred to a beaker and 100ml of absolute ethanol is added to it. This dispersion is stirred using magnetic stirrer for 2 hours.
7. The dispersion in step 6 is then sonicated using ultrasonic horn with intervals of 5 seconds sonication and 5 seconds rest for 30 such cycles.
8. **22 ml of $\alpha$-terpineol is added to solution in step 7.**
9. Solution in step 8 is stirred on magnetic stirrer for 20 mins and then ultrasonicated using probe sonicator with intervals of 5 seconds sonication and 5 seconds rest for 30 such cycles.
10. Separately a solution of 3g of ethyl cellulose in 30 ml ethanol is prepared.
11. The ethyl cellulose solution in step 10 is added to nanoparticle dispersion in step 9.
12. The dispersion in step 11 is then sonicated using ultrasonic horn with intervals of 5 seconds sonication and 5 seconds rest for 30 such cycles.
13. Finally the ethanol in the dispersion in step 12 is evaporated using rotary evaporator so that a smooth paste is obtained.
Preparation of thin mesoporous films of TiO$_2$ on FTO:

The washed and annealed FTOs were masked with scotch tape on both sides to keep $1\text{cm} \times 2\text{cm}$ rectangular area unmasked. A small amount of the TiO$_2$ paste was put on one edge of FTO and spread along its length using a glass rod or a glass slide as shown in Figure 3.3. The 40 micron thicker scotch tape provides an area for paste to dry to a particular thickness and also maintains the masked area cleaned which can be later used for making contacts while testing the DSSCs. After one coat of TiO$_2$ paste on FTO the scotch tapes were removed and the TiO$_2$ film was dried at 150$^0\text{C}$ for 10 min. Above procedure was repeated 4-5 times so as to achieve the desired optimum thickness to get maximum photovoltaic efficiency. The effect of thickness of TiO$_2$ paste on photovoltaic efficiency is demonstrated in the following sections.

![Figure 3.3: Visuals of TiO$_2$ doctor blade technique used to coat a single layer. The process is repeated 5-6 times to achieve the desired thickness of 12-14\(\mu\text{m}\).](image)

After the 4-5 coatings and subsequent drying, the TiO$_2$ coated FTOs were heated slowly to 500$^0\text{C}$ to remove the organic components in the film and to improve the inter-particle necking/connectivity. A slow heating procedure was followed to avoid the formation of cracks in the film. The heating steps involved were 200$^0\text{C}$ (10 min), 325$^0\text{C}$ (5 min), 375$^0\text{C}$ (5min) 450$^0\text{C}$ (15 min) and 500$^0\text{C}$ (15 min).

Post-TiCl$_4$ treatment of the TiO$_2$ coated FTOs: The prepared TiO$_2$ coated FTOs were then treated with aqueous TiCl$_4$ treatment so as to improve the inter-particle necking and to improvise the dye loading by surface roughening. The desired
TiCl$_4$ solution was prepared by drop wise addition of 0.55 mL of TiCl$_4$ in 100mL ice of de-ionized water. The ice was later melted under ambient conditions and stirred to form a homogeneous aqueous TiCl$_4$ solution. The TiO$_2$ coated FTOs were dipped in TiCl$_4$ solution and heated at 70\(^{\circ}\)C for 30 min. Later the TiCl$_4$ treated films were washed with de-ionized water and ethanol. TiCl$_4$ treatment of TiO$_2$ nanoparticle coated FTO forms an amorphous layer\[15\] (less than 2 nm) of TiO$_2$ which can be converted to crystalline form by annealing the TiCl$_4$ treated films at 500\(^{\circ}\)C. The heating protocol followed was, 200\(^{\circ}\)C (10 min), 325\(^{\circ}\)C (5 min), 375\(^{\circ}\)C (5min) 450\(^{\circ}\)C (15 min) and 500\(^{\circ}\)C (15 min).

**Sensitization of TiCl$_4$ treated films with N719 dye solution:**

The TiCl$_4$ treated films were put in N719 dye solution prepared as described in the sec. 3.2.5. Importantly before dipping, the films were kept at 70\(^{\circ}\)C so as to minimize the adsorption of water on TiO$_2$ coated FTOs. Films were soaked in dye solution for 24 hrs to ensure the chemisorptions of monolayer of dye on TiO$_2$ surface. After 24 hrs of dye loading the films were washed with absolute ethanol to remove excessive un-adsorbed dye. As shown in Figure 3.4 the color of TiO$_2$ coated FTO film changed from white to crimson color which is characteristic of adsorbed dye on TiO$_2$.

![Figure 3.4: Visuals of the TiO$_2$ films without and with dye sensitization](image)

**3.2.8 Temporary assembly of working electrode and counter electrode as DSSC and photovoltaic measurements**

In order to evaluate the performance of working electrode we initially followed the temporary assembly of working electrode which gave stable performance for the
duration of measurement. The area of dye sensitized working electrode was limited to 5 mm × 5mm (area = 0.25 cm²) while TiO₂ film on remaining area was scratched. The bare FTO on working electrode was masked with the cello tape of thickness 40 microns which prevents the direct contact of electrolyte with FTO and also acts as spacer between working electrode and counter electrode. A small amount of electrolyte was injected between the working and counter electrodes using a syringe. The DSSC prepared from sandwich assembly of working electrode and counter electrode is shown in Figure 3.5. The JV curves were measured using Newport solar simulator attached to Keithley IV meter.

![Step 1](image1.png) ![Step 2](image2.png) ![Step 3](image3.png) ![Step 4](image4.png) ![Step 5](image5.png) ![Step 6](image6.png)

**Figure 3.5:** Photographs of various steps followed for the temporary assembly of DSSC to evaluate the photovoltaic performance

### 3.3 Results and Discussion

#### 3.3.1 Influence of the TiCl₄ treatment

The TiCl₄ treatment is considered to be one of the most crucial steps in the preparation of DSSC. In order to demonstrate the effect of post TiCl₄ treatment on performance of DSSC we made devices with and without TiCl₄ treatment and tested them for photovoltaic performance under AM 1.5 conditions. **Figure 3.6** shows the JV curves of the DSSCs made without (black) and with (red) TiCl₄ treatment. It can
be clearly seen that the TiCl₄ treatment remarkably improved the photocurrent density from 10.5mA/cm² to 12.7mA/cm² with very slight decrease of 20mV in open circuit potential. This improvement in photocurrent density resulted in improvement photovoltaic efficiency from 5.4% to 6.4%.

![Figure 3.6: The JV curves of DSSC prepared with and without TiCl₄ treatment.](image)

The reason for improvement in the efficiency of DSSC with TiCl₄ treatment can be assigned to various factors such as (a) increased surface roughness due to additional deposition of TiO₂ layer over the doctor bladed TiO₂ nanoparticle film which in turn leads to improved dye loading and improved photocurrents\(^\text{[15c]}\), (b) downshift of TiO₂ conduction band edge which can improvise the rate of electron transfer from excited dye molecule to TiO₂ conduction band resulting in improved quantum efficiency and photo-currents\(^\text{[16]}\), (c) increased charge transport and hence carrier diffusion coefficient within the mesoporous film due TiCl₄ mediated improved inter-particle connectivity\(^\text{[17]}\).

### 3.3.2 Effect of TiO₂ film thickness on photovoltaic efficiency of DSSC

The thickness of TiO₂ electrode plays a crucial role in photovoltaic efficiency of DSSC which in turn depends on the number of doctor blade coatings of TiO₂ paste on FTO\(^\text{[13]}\). In order to establish the optimum thickness of DSSC electrode made from the paste made in our lab, we prepared DSSC working electrodes with different numbers of coatings as described in section 3.2.6. The thickness of electrode was
measured after the TiCl$_4$ treatment with the help of Veeco Dektak 150 thickness profiler.

We studied the photovoltaic parameters of DSSCs with varied thickness using JV measurements under simulated AM 1.5 radiations. Figure 3.7 (a) shows the JV curves of the DSSCs with working electrode thickness varying from 5μm to 15.5μm. We have separately plotted the variation of $J_{sc}$, $V_{oc}$ and efficiency in Figure 3.7 (b), (c) and (d) respectively. It can be clearly seen that the thickness of mesoporous TiO$_2$ layer on FTO has profound effect on short circuit current density.

![JV curves of DSSCs with different TiO$_2$ layer thickness and variation of $V_{oc}$, $J_{sc}$ and efficiency with thickness.](image)

Figure 3.7: (a) JV curves of DSSCs with different TiO$_2$ layer thickness and variation of (b) $V_{oc}$, (c) $J_{sc}$ and (d) efficiency with thickness.

The $J_{sc}$ of DSSC is found to increase dramatically from 10.6mA/cm$^2$ to 13.1mA/cm$^2$ for TiO$_2$ electrode thickness increasing from 5.8μm to 8.6μm. However for further increase in thickness the short circuit current density is seen to achieve a plateau. It can be seen from Figure 3.7 (c) that the maximum photocurrent density is observed for thickness 13.8μm. The increase in $J_{sc}$ with thickness is mainly attributed to the higher surface area being made available for dye adsorption. The increased dye
adsorption with increased thickness of the TiO$_2$ film was verified by another independent set of experiment in which the sensitized TiO$_2$ films were subjected to KOH treatment for desorption of adsorbed dye molecules and the amount of adsorbed dye was quantified using UV-Vis absorption spectroscopy$^{[12]}$. Particularly 1 cm$^2$ of the N719 sensitized TiO$_2$ films were dipped in 7.5 ml of 1mM KOH aqueous solution for 4 hrs to ensure complete desorption of the dye molecules. **Figure 3.8 (a)** shows the UV-Vis absorption spectrum of the desorbed dye solutions.

**Figure 3.8:** (a) UV-Vis absorbance of desorbed dye solution from TiO$_2$ films of different thickness (b) number of adsorbed dye molecules vs. thickness of TiO$_2$ film

The amount of adsorbed dye in films of thickness ranging from 4µm to 16µm was found out using Beer Lambert’s Law which can be stated as

$$A = \varepsilon \ell c$$

Where $\varepsilon$ = Molar absorptivity in M$^{-1}$cm$^{-1}$= 14$\times$10$^3$ M$^{-1}$cm$^{-1}$ for N719

$\ell$ = Length of solution = Length of cuvette = 1 cm

$c$ = concentration of solution in M

The absorption of dye solution at 500nm was used in the calculations. The Beer Lambert’s Law thus gives the concentration of dye molecules in mM/cm$^2$ which can be converted to number of molecules/cm$^2$ by multiplying it with Avogadro’s number. The graph of no. of molecules adsorbed per cm$^2$ vs. the thickness of TiO$_2$ film is plotted in the **Figure 3.8 (b)** which clearly establishes the linear trend between the amount of dye adsorbed per unit area and the thickness of TiO$_2$ film. Therefore this
linear trend between the dye adsorption and thickness explains the initial increase in short circuit current density with thickness of the TiO$_2$ film up to 15$\mu$m. However for thickness higher than 15$\mu$m the $J_{sc}$ achieves a plateau and then starts decreasing for thickness of TiO$_2$ films beyond 20$\mu$m which can be attributed to the diffusion limited recombination along the thickness of working electrode$^{[18]}$.

Figure 3.7(b) shows the variation of open circuit voltage with thickness of the TiO$_2$ film. It can be seen that the $V_{oc}$ of film decreases with increase in the thickness of TiO$_2$ film. The rate of recombination within DSSC is one of the main factors which controls the $V_{oc}$ of the DSSC which can be mathematically expressed as the relation$^{[19]}$,

$$V_{oc} = \frac{kT}{q} \left( \frac{n}{n_0} \right)$$

(3.1)

where $n$ and $n_0$ correspond to the concentration of free electrons in semiconductor conduction band under illumination and equilibrium concentration of free electrons under dark. Therefore for increased rate of recombination within DSSC, the equilibrium concentration of free electrons under dark increases which leads to lower open circuit potential. For the higher thickness of TiO$_2$ films the probability of recombination between photo-injected electron in conduction band of TiO$_2$ and oxidized electrolyte species increases due to increased path-length through which photo-injected electrons have to diffuse to reach FTO electrode. The increase in recombination rate of TiO$_2$ with film thickness was also supported by an independent transient experiment which measures the recombination lifetime of charge carriers in DSSC through small perturbation open circuit potential decay measurements. The details about the transient voltage measurements are given in Chapter 4. Figure 3.9 shows the transient photovoltage decay lifetime measurements carried out under different illumination conditions to give a range of open circuit potential values. It can be clearly seen that the 13.8$\mu$m film shows maximum lifetime as compared to other electrodes of higher or lower thickness. This increased recombination lead to lower open circuit voltage in DSSCs with thicker TiO$_2$ mesoporous film.
The opposite trends in $V_{oc}$ (decreasing) and $J_{sc}$ (increasing) as a function of working electrode thickness can explain the optimum observed in the graph of efficiency vs. thickness in Figure 3.7(d). The working electrode with mesoporous TiO$_2$ layer of thickness 13.8 μm showed maximum photovoltaic performance with $V_{oc} = 0.71$ V, $J_{sc} = 14.01$ mA/cm$^2$, Fill Factor = 61.3% and efficiency = 6.4%. For further increase in mesoporous TiO$_2$ film thickness beyond 14 μm the efficiency was found to decrease due to both decreased $V_{oc}$ and $J_{sc}$ as compared to 13.8 μm film. Therefore for all the later experiments related to DSSCs we generally kept the working electrode thickness in the rage of 13-14 μm.

### 3.3.3 Double layer architecture for high efficiency DSSC: Importance of transparent mesoporous TiO$_2$ layer with light scattering over layer

Overall power conversion efficiency of DSSC can be improved with increase in short circuit current density $J_{sc}$ which can be expressed as\(^{[20]}\),

$$J_{sc} = \Phi_{ET} \int qF(\lambda)[1 - r(\lambda)] \text{LHE}(\lambda) d\lambda$$

(3.2)

where $\Phi_{ET}$ is electron transfer yield (averaged over wavelength) which is a function of yield of electron injection and the charge collection efficiency; $F(\lambda)$ is incident photon flux density at wavelength $\lambda$; $r(\lambda)$ is the incident light loss at the
FTO-TiO$_2$ interface; $LHE(\lambda)$ is the light harvesting efficiency at wavelength $\lambda$. The parameter $r(\lambda)$ which therefore corresponds to loss of incident light before being completely utilized for photovoltaic action is an important parameter to increase the short circuit current density.

The DSSC architecture consists of TCO substrate (FTO) on which a 13-14μm thick mesoporous layer of metal oxide (TiO$_2$) is present. The optical properties of this TiO$_2$-FTO interface are important for light management within DSSC to obtain high photovoltaic conversion efficiency. Transparency of FTO for visible light is generally in the range of 70-80% therefore nearly 10-20% of visible radiations are lost at FTO coated glass substrate. As TiO$_2$ is a high band gap material (3.3 eV) then in principle its layer on FTO should be transparent and it should allow at least 70-80% of incident light to enter within DSSC. However agglomeration of TiO$_2$ nanoparticles during synthesis process or paste making gives scattering nature to the mesoporous TiO$_2$ overlayer on FTO which further adds to the loss of incident visible light radiations at the FTO-TiO$_2$ interface. According to the Lorenz-Mie-Debye theory$^{[21]}$ and Anderson localization of light$^{[22]}$, when the size of agglomerates of TiO$_2$ nanoparticles is in the range of wavelength of visible light then it results in the resonant scattering in the visible region. Therefore if the mesoporous TiO$_2$ film deposited on glass is scattering then it results in the loss of incident radiations (i.e. high $r(\lambda)$ in equation (3.2)) thereby resulting in low photovoltaic efficiency.

In order to obtain transparent but mesoporous TiO$_2$ layer we developed a solvothermal protocol of synthesis of TiO$_2$ nanoparticles which resulted in a very stable dispersion of 10-12 nm TiO$_2$ nanoparticles. The doctor blade paste made from this stable dispersion of nano-particles resulted in high transparency and uniformity. The experimental procedure to make highly dispersible TiO$_2$ nanoparticles by solvothermal method is described below.

**Synthesis of highly dispersed TiO$_2$ nano-particles:** We mixed 10 mL of Titanium-tetra-isopropoxide (TIP) in 150mL of absolute ethanol to obtain pale yellow solution without any precipitation. The utensils used for mixing TIP and ethanol were properly dried to avoid the precipitation of TIP. 2 ml of concentrated HCl (35% in water) was added to above solution under stirring. 5 ml of deionized water was
added drop-wise to above acidic solution of TIP under stirring. The final solution was transferred to Teflon lined stainless-steel autoclave and heated at 190°C for 12 hours. After completion of reaction the supernatant solution was discarded and the precipitate was re-dispersed in 80ml ethanol. Importantly the final colloidal dispersion was found to be stable for at least a period of one week. One of the possible reason for stable dispersion of the solvothermally synthesized TiO\textsubscript{2} is the presence of acid in the synthesis which functionalize the TiO\textsubscript{2} nanoparticle surface and provide a zeta potential of 30-40mV which is sufficient for a stable dispersion.

![Figure 3.10](image)

**Figure 3.10:** (a) XRD of the solvothermally synthesized TiO\textsubscript{2} nanoparticles (b) DRS of TiO\textsubscript{2} films on glass made from P25 (opaque film) and solvothermally synthesized TiO\textsubscript{2} nanoparticles (transparent film) (c) and (d) shows the SEM of opaque film made from P25 nanoparticles and transparent film made from solvothermal TiO\textsubscript{2} nanoparticles. Inset of figures (c) and (d) shows the actual photographs of opaque and transparent films.

The anatase phase of solvothermally synthesized TiO\textsubscript{2} was confirmed from the X-ray diffraction of the dried TiO\textsubscript{2} product as shown in **Figure 3.10 (a)** The average particle size of the TiO\textsubscript{2} nanoparticles was calculated to be 15nm by using Debye-Scherrer formula for the most intense (101) peak in x-ray diffraction. We prepared
the doctor blade paste using the dispersion of solvothermally prepared TiO$_2$ nanoparticles. The weight of TiO$_2$ nanoparticles per mL of dispersion was first calculated by gravimetric measurements of solution and dry powder. Accordingly the volume of solution which contained 6g of TiO$_2$ was measured and the paste making protocol as described in section 3.2.7 was followed.

We prepared the doctor blade films with P25-TiO$_2$ or solvothermal TiO$_2$ pastes and compared them for the transparency. Figure 3.10 (b) shows the Diffused Reflectance Spectrum (DRS) and actual photographs of the doctor blade films made with P25-TiO$_2$ and solvothermal TiO$_2$ paste. It can be clearly seen from the DRS that the film made with agglomerated TiO$_2$ paste shows reflectance in the range of 50-60% whereas the films made with solvothermal TiO$_2$ paste showed reflectance in the range of 10-20%. The visual appearance of undyed TiO$_2$ films made with solvothermal TiO$_2$ paste is also shown in the insets of Figure 3.10 (c) and (d) which clearly proves the superior transparency of the solvothermally made TiO$_2$ paste. As shown in the SEM in Figure 3.10 (c) the origin of opaqueness of the P25-TiO$_2$ based films lies in the agglomerated assemblies of the P25-TiO$_2$ nanoparticles formed within the film after doctor blade coating. The sizes of these agglomerates are in the rage of 300 nm to 2μm which is sufficient to resonantly scatter the visible light according to Lorenz-Mie-Debye theory and Anderson localization of light$^{[21-22]}$. However the SEM image of doctor blade film made with solvothermal TiO$_2$ nanoparticle is highly uniform and without presence of any submicron or micron sized agglomerates. This clearly avoids the unwanted scattering of visible radiation at the Glass/FTO interface giving transparent/translucent nature to the film.

**Need for double layer architecture:** According to equation (3.2) if the light harvesting efficiency (LHE) i.e. the fraction of light of a particular wavelength absorbed by the sensitizer is improved then than can result an improvement in $J_{sc}$. As shown in Figure 3.11 the absorbance maxima of sensitizer dye, N719 is in the wavelength range of 400-550 nm. This implies that the N719 sensitizer can yield maximum IPCE in the wavelength rage of 400-500nm. However, beyond 550 nm the N719 sensitizer absorption coefficient decreases i.e. higher absorption length is required to fully absorb the incident light of wavelength greater than 550nm. Therefore, it is necessary to increase the path-length of light within the film so that
the dye can efficiently absorb the incident photons of wavelengths greater than 550 nm.

![Absorbance Spectrum of N719 dye](image1.png)

**Figure 3.11:** (left) UV-vis absorbance spectrum of N719 dye showing weak absorbance in 550-700 nm region and (right) translucent nature of dye loaded TiO₂ film showing ‘loss of incident radiations’ through transmittance.

The transparent nature of TiO₂ films avoids the loss of radiations at glass/FTO interface however it can be disadvantageous as it allows the unabsorbed light to transmit through the cell (**Figure 3.12 (a)**) which also contributes to the loss of photo-voltaic efficiency. Therefore a scattering over layer of TiO₂ paste which contains submicron size particles is deposited on the top of transparent TiO₂ paste which scatters the light back into the active TiO₂ layer as shown in **Figure 3.12 (b)**.

![Schematic explaining the need of double layer architecture](image2.png)

**Figure 3.12:** Schematic explaining the need of double layer architecture.
This double layer structure increases the path length of light within the film thereby leading to maximum absorption of incident light and hence increases in photo-current density as shown in the following schematic.

Though various metal oxides (e.g. ZnO, ZrO₂, SrO₂, Nb₂O₅ etc.) [23] based nanostructures have been employed as scattering layers in DSSC, the most efficient scattering layer has been TiO₂ as it can play duel role of back scattering the light into the film as well as help to adsorb dye molecules to generate additional photo-current. We therefore synthesized nano-particles assembled submicron to micron sized TiO₂ spheres with diameter in the range of 300nm-2μm as per the report by N.G. Park [24] et al. In order to prepare nanoparticle assembled TiO₂ spheres 2 mmol of titanium-isopropoxide (TIP) was mixed in 20 mL of absolute ethanol. 4 mmol of tetrabutylammoniumhydroxide was added to above solution in drop wise manner. This mixture was then transferred to Teflon lined stainless steel autoclave and heated at 220°C for 10hrs. The supernatant was discarded and the precipitate was washed with absolute ethanol.

![Figure: 3.13](image)

Figure: 3.13 (a) XRD of TiO₂ spheres prepared for light scattering layer in double layer DSSC architecture, (b), (c) and (d) shows the SEM of spheres at different scales.
The anatase phase of nanoparticle assembled TiO$_2$ spheres was confirmed by x-ray diffraction Figure 3.13 (a) whereas the spherical morphology was confirmed by the SEM images as shown in the Figure 3.13 (b). It can be clearly seen that the TiO$_2$ spheres are formed from the assembly of the TiO$_2$ nano-particles. The doctor blade paste for this TiO$_2$ sphere powder was made according to the experimental procedure given in section 3.2.7. The double layer architecture was prepared with 9μm transparent TiO$_2$ layer and 5μm scattering TiO$_2$ layer. Figure 3.14 shows the photovoltaic efficiency of the double layer architecture which clearly shows an enhancement of 0.7% as compared to single layer architecture. The main contribution to increase in efficiency is the enhanced photo-current density by ~1.5mA/cm$^2$ in the case of double layer architecture as compared to single layer architecture which can be attributed to the increased path-length of light within the cell leading to improved photocurrents. Therefore a photo-voltaic efficiency of 8.12% could be demonstrated on the 0.25 cm$^2$ active area using double layer (transparent TiO$_2$ + scattering TiO$_2$) architecture.

![Figure 3.14 and Table 3.1: The JV curves for DSSCs with single layer and double layer architecture. Table 3.1 shows the corresponding photovoltaic parameters.](image-url)
3.3.4 Sealing of DSSCs in order to obtain stable photovoltaic performance

During the initial stage of research we followed the temporary assembly of working and counter electrode in order to check the efficiency and do the related opto-electronic characterizations. However the long term stability studies were not feasible with the temporary assembly due to the volatile nature of the solvents used to prepare DSSC electrolytes. Therefore we developed a protocol to seal the DSSCs to obtain stable opto-electronic performance from them.

The dye sensitized photo-electrodes consisting of N719 dye loaded TiO2 films on FTO were prepared according to the procedure given in section 3.2.7 and section 3.3.3. For sealed devices we generally kept the active area of 1cm × 1cm on FTO substrate of size 2.5cm × 1.5cm. In order to prepare the counter electrode we took another FTO of dimensions 2.5cm × 1.5cm and drilled two holes of diameter 0.5mm at the two opposite corners of square 1cm × 1cm as shown in the photograph in Figure 3.15 (a).

![Figure 3.15: Steps involved in DSSC sealing (Note PF corresponds ‘Protective film’ on sealant which is removed in step (e) after the sealant ‘Surlyn’ is adhered to FTO)](image)

---

Onkar S. Game 95 Savitribai Phule Pune University
The deposition of platinum catalyst on FTO was done according to the procedure given in section 3.2.3. In order to seal the working electrode and counter electrode we used a polymeric sealant which sticks the two substrates upon heating. The polymeric sealant ‘Meltonix PF 1170-25’ was purchased from Solaronix. The Meltonix PF 25 has a thin protective film (PF) on the top which offers the efficient sealing to both electrodes. A square frame with the open area slightly larger than 1 cm× 1cm and width 0.6 cm of the Meltonix sealant was placed on the top of sensitized TiO$_2$ square of dimension 1cm×1cm with its non protected part on the FTO as shown in Figure 3.15 (b) and (c). The TiO$_2$ coated FTO along with the Meltonix sealant was heated under a hot press at 120°C for 40 sec which makes the sealant to stick to FTO surface Figure 3.15 (d). For this heating step the PF part of the sealant was placed on the heater and also the care was taken to avoid the trapping of air bubbles within the meltonix sealant. Now the protective film on meltonix was removed with a forceps as shown in Figure 3.15(e). The counter electrode was place on the top of working electrode such that the two drilled holes fall on the two corners of the sensitized TiO$_2$ coated FTO as shown in Figure 3.15 (f).

The two electrode assembly with meltonix sandwiched between them was again heated on a hot plate at 120°C under application of some pressure for 60 sec as shown in Figure 3.15 (g). During this step of heating under pressure the counter electrode was kept in direct contact with hot plate to avoid damage to the adsorbed dye on FTO. The care was taken to avoid trapped air bubbles between the meltonix and counter electrode. The electrolyte prepared according to procedure in section 3.2.4 was injected using micro-pipette through one of the hole drilled in the counter electrode. The holes were then sealed using a micro-slide coated with Meltonix. Finally silver paste was applied on the ends of working and counter electrodes for further measurements. Figure 3.15 (l) shows the photograph of final sealed device.

Using the sealing process described above we fabricated small area (0.15cm$^2$) and large area (1 cm$^2$) DSSCs with the double layer architecture. An outstanding power conversion efficiency of 10% was demonstrated on the small area (0.15 cm$^2$) sealed DSSCs without black mask over the cell. The same device with masking showed a power conversion efficiency of 9% as shown in Figure 3.16 (a) and (b). Higher efficiency in case of unmasked DSSC in Figure 3.16(a) than masked DSSC.
in Figure 3.16(b) can be attributed to the light piping effect\(^{25}\) through the edges of the DSSC which guides extra light into the active area of cell thereby giving higher efficiency than the masked DSSC. Importantly both the efficiencies reported here were independently certified at Indian Institute of Technology, Bombay, Powai (See Appendix-I).

\[ V_{oc} = 0.75V \]
\[ J_{sc} = 18.08 \text{ mA/cm}^2 \]
\[ FF = 73.5\% \]
\[ Efficiency = 10\% \]

\[ V_{oc} = 0.75V \]
\[ J_{sc} = 16.20 \text{ mA/cm}^2 \]
\[ FF = 74.3\% \]
\[ Efficiency = 9\% \]

**Figure 3.16:** JV curves of the champion device demonstrating efficiency of 10\% in unmasked configuration (a) and 9\% in masked configuration (b).
We evaluated the stability of the sealed devices by checking the efficiencies of fabricated DSSCs after every few days through the period of a month. Importantly the sealed DSSCs showed excellent stability over the period of one month as shown in the Figure 3.17.

**Figure 3.17:** (left) Graph showing the stability of sealed DSSC over a period of month (right) the connections made to the cross-assembly of sealed DSSC for efficient charge collection.
3.3.5 Development of large area DSSCs for low power applications:

The active area of DSSCs prepared in the previous section was only \(0.25 \text{ cm}^2\) which is good enough to test performance of a new material system on device scale. For real life applications of photo-voltaics one needs DSSC with active areas larger than \(0.25 \text{ cm}^2\) however fabrication of which has several technical challenges in terms of design and process. In this section we review some of the known designs for large area DSSC fabrication and also describe the technical challenges involved in the transition from small area to large area DSSC.

![Figure 3.18: (left) Example of a single square cell large area configuration\([26]\) (right) JV curve of DSSC with single square cell architecture which shows very low fill factor due to ohmic losses\([26]\)
Images are reprinted with permission from reference [26].](image)

One of the main challenges of scaling up the active area of DSSC is to efficiently collect the electrons from the working electrode as well as counter electrode. For large area DSSCs the electrons/holes have to travel considerable distance through FTO to reach the collecting wires. As the resistivity of FTO is \(10^2\) times less than the resistivity of a typical metal, even a path length of 3.5 cm offers high resistance to the flow of charges which adds to the series resistance of DSSC and thus substantially decreasing the fill factor/efficiency. For instance E. Ramaswamy\([26]\) et al. prepared a large area (12 cm\(^2\)) DSSC of dimension 3.5 cm×3.5 cm as shown in Figure 3.18. Such single cell architecture showed a fill factor of only 26% under 1 Sun illumination which can be attributed to the large ohmic losses due to inefficient collection at working as well as counter electrode.
Above example clearly shows the importance of effective collection of charge collection at working and counter electrodes. Therefore researchers have identified various designs\cite{27} to fabricate large area DSSC which are broadly classified in two categories as series connection design and parallel connection design. The series connection design is generally followed for the high voltage applications whereas the parallel connection design is used for high current applications. In this study we have developed a protocol to fabricate a single strip DSSC which can be connected in series or parallel assemblies to get desired voltage and current.

**Materials and Methods:**

The large area (~ 4-5 cm$^2$) DSSC were prepared on FTO substrates (3.5cm × 8 cm) using doctor blade technique with commercially available TiO$_2$ paste (Dyesol T90) as shown in Figure 3.3. The working electrode dimensions were 1 cm × 5 cm. The doctor bladed films were first dried at 120$^0$C overnight and then heated at 450$^0$C for 1 hour and then slowly heated to 500$^0$C in the steps 200$^0$C (10 min), 325$^0$C (5 min), 375$^0$C (5 min) 450$^0$C (15 min) and 500$^0$C (15 min). The TiCl$_4$ post treatment and heating was carried out on the cells in order to enhance the inter particle connectivity and dye adsorption. The cells were then soaked in the dye solution (N719 0.5mM) overnight for dye adsorption on TiO$_2$ nano-particles. The counter electrodes were prepared by thermal decomposition of H$_2$PtCl$_6$ on FTO (3.5cm × 8 cm). Two holes were also drilled within the counter electrode for injecting electrolyte within TiO$_2$. Silver contacts were thermally evaporated on both the working electrode (dye loaded TiO$_2$) and the counter electrode (platinised FTO). The working electrode and counter electrode were then sealed using Surlyn (Solaronix) sealant by heating the electrodes at 120$^0$C under the application of some pressure.

**Results and Discussion:**

One of the most important strategy to efficiency collect the charge carriers from working and counter electrode is to deposit silver contacts around the dye sensitized TiO$_2$ film as well as around the area of counter electrode facing TiO$_2$ film. The silver was chosen because of its low resistivity of $1.6 \times 10^{-8} \Omega m$ which is almost $10^2$-$10^3$ times lower than resistivity of FTO. Figure 3.19 illustrates device architecture used in this study.
Figure 3.19: The schematic of single strip large area (5cm$^2$) DSSC fabricated in this study. The active rectangular strip dimensions were 5cm×1cm.

In order to evaluate the effect of silver contacts on DSSC performance another set of DSSCs were assembled without thermally evaporated silver contacts on both the electrodes. Figure 3.20 shows the effect of thermally evaporated silver on performance of DSSC. The DSSC without any silver collection electrodes deposited showed lowest efficiency due to poor collection of charges as reflected in lowest value of fill factor (29%).

Figure 3.20: (a) JV curves of DSSCs with and without thermally evaporated silver on either electrode. (b) Comparative JV curves of DSSCs immediate after fabrication and after two months.
With the silver contacts on working electrodes the collection of photo-generated electrons at working electrode is efficient which results in higher shunt resistance and hence fill factor of 40% but insufficient hole collection at counter electrode results in comparatively lower fill factor. The DSSC with silver collection electrodes deposited on working as well as counter electrodes resulted in efficient charge carrier collection at both electrodes giving maximum fill factor of 60% with a power conversion efficiency of 5%. The sealing process was optimised to prepare DSSCs with high stability. The solar cells were found to be stable for several months. As shown in Figure 3.20(b) the efficiency of the fabricated solar cells showed a stability of 90-95% even after two months.

![Figure 3.21](image)

**Figure 3.21:** (a) **DSSC operated calculator:** 2 cells in series Voc: 1.4 V, Isc: 50 mA (b) **DSSC operated pedometer:** 4 cells with 2 series & 2 Parallel combination Voc.: 1.4 V & Isc = 100mA (c) **DSSC based Solar Water Splitting Setup:** 14 cells with 7 parallel and 7 series: Voc = 5V Isc = 350mA (d) hydrogen bubbles formed at Platinum electrode due to water splitting by DSSC module

The fabricated DSSCs were then used for some low powered applications such as calculator, pedometer and electrochemical water splitting using DSSC module as shown in Figure 3.21.
We further assembled 14 DSSCs in series onto a farmer’s hat in order to get the total open circuit potential of 10V and a maximum potential ($V_{\text{max}}$) of 5V. The short circuit current of this series assembly was around 50mA with maximum output current ($I_{\text{max}}$) of 30mA. This solar cell assembled farmers hat we could demonstrate the charging of a cell phone battery under the natural sunlight as shown in the Figure 3.22.

![Figure 3.22: DSSC assembled Farmer’s hat: 14 cells in series. $V_{\text{oc}} = 9.8$V $I_{\text{sc}} = 50$ mA Inset on right top shows the charging signal appearing on cell phone screen.]

### 3.4 Conclusion:

In this study several DSSC fabrication parameters such as TiO$_2$ paste making, electrode thickness, double layer architecture, electrolyte composition, electrode assembly and sealing procedure etc. were optimized. We successfully developed a protocol for fabrication of small area ($0.15$ cm$^2$) DSSC and demonstrated an outstanding power conversion efficiency of 10% on unmasked cell and 9% on the masked cell. Stable photovoltaic performance of sealed DSSCs up to the period of one month was also demonstrated.
The issue of efficient charge collection encountered during the transition from small area (0.15cm$^2$) to large area (5cm$^2$) DSSCs was resolved successfully by depositing silver collection electrodes on both working and counter electrode. A dramatic improvement in the fill factor was observed for large area DSSCs with the silver grids deposited on both electrodes (FF~60%) over the DSSCs without silver grid on either electrodes (FF~29%). The sealed 5cm$^2$ active area DSSCs showed 90-95% stability over the period two months. Further these sealed DSSCs were used for low power applications such as calculator, pedometer and electrochemical water splitting for H$_2$ generation. We also assembled these solar cells on a farmer’s hat to demonstrate the charging of a cell phone battery under the sunlight.

3.5 References:


