CHAPTER-4

OPTIMIZING STEPS AND OVERCOMING CHALLENGES OF DSSC FABRICATION

4.1 Coating method: conventional doctor blade vs spin coating method

The transparent layer and reflective layer were coated by both the conventional doctor's blade method and the spin coating method. Pictures of different layers coated by conventional methods are shown in Fig.22. Both transparent and reflective layers coated by conventional methods are found to be non-uniform. Nonuniformity of layers resulted in poor quality of film. After sintering, many cracks and flakes were present most of the time in films of anode. Peeling off TiO_2 nanoparticles in the form of filmwas observed, which is shown in Fig.24. (a). Also, repeatability of film thickness is not possible with the conventional doctor's blade method.

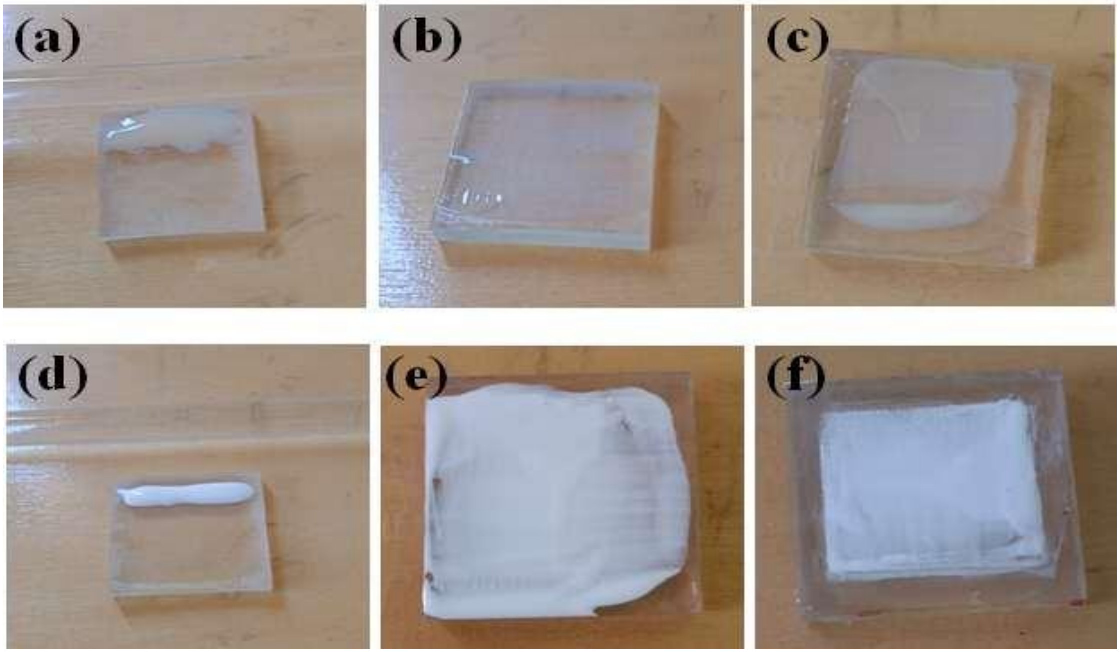

Fig.22: Images of anode layers coated by doctor's blade method: (a), (b) & (c) transparent layer, (d), (e) & (f) reflective layer coating

Transparent and reflective layers were also coated by a spin coating method. Images of coatings are shown in Fig.23. Both transparent and reflective layers coated by the spin coating method resulted in uniform thickness coating on FTO. Uniform coating by spin coating method gave a strongly adhered film of TiO_2 nanoparticles on FTO. Also, after the sintering of layers, no peeling off layers was observed. Images of TiO_2 nanoparticle film after sintering are shown in Fig 24.b. Repeatability of film thickness of both transparent layer and reflective layer are possible in the spin coating method. The repeatability of the thickness of different layers is crucial to the study the effect of any one parameter on the performance of DSSC.

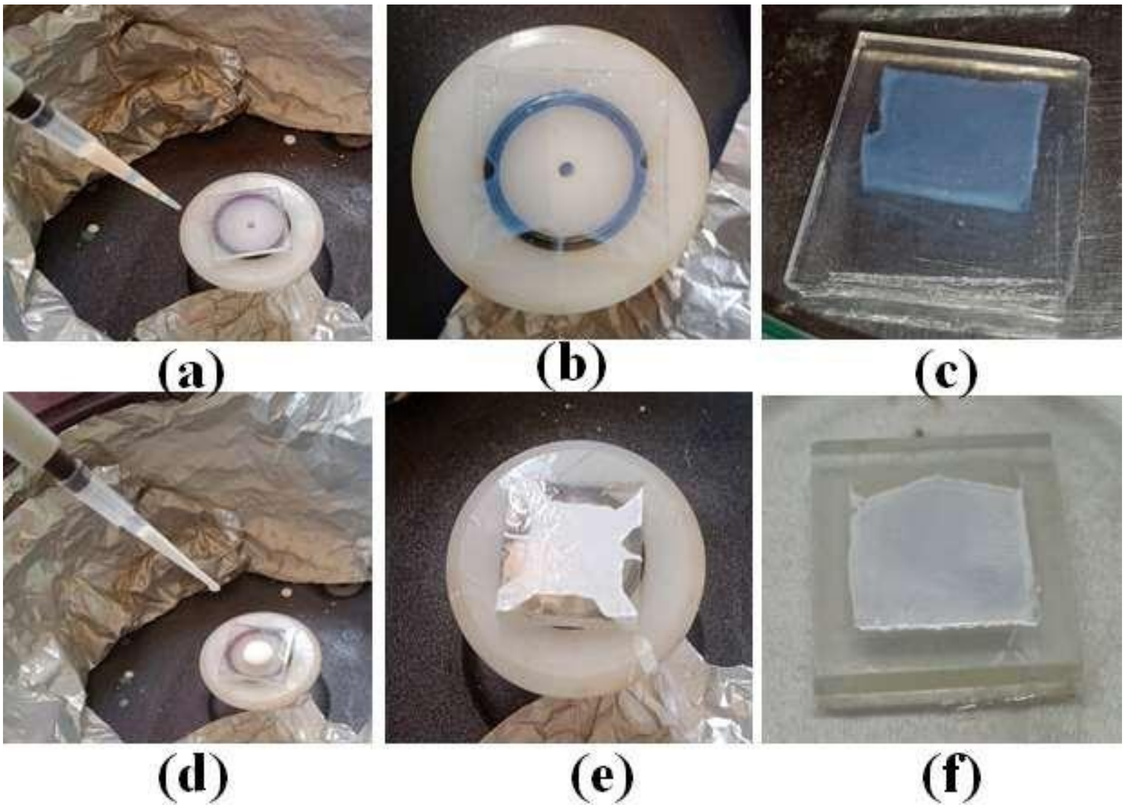

Fig.23: Images of anode layers coated by spin coating method: (a), (b) & (c) transparent layer and (d), (e) & (f) reflective layer

For DSSC fabrication, spin coating method is a less preferred film coating method than doctor's blade method in literature. Results obtained from this work suggest that the spin coating method should be preferred over the conventional doctor's blade coating method.

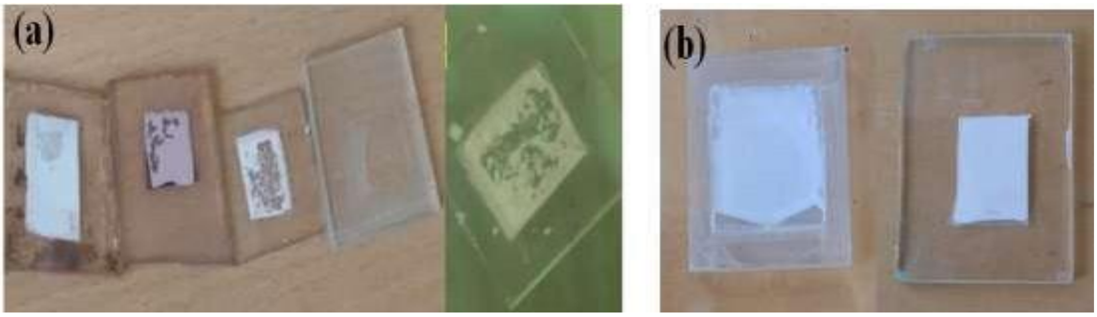

Fig.24: Images of TiO_2 nanoparticles film after sintering: (a) by doctor's blade method and (b) by the spin coating method

4.2 Compact layer coating

4.2.1 $TiCl_4$ vs TTIP as the compact layer coating material

An aqueous solution of $TiCl_4$ is mostly reported in the literature to coat compact layers in DSSC fabrication. However, preparation of an aqueous. solution of $TiCl_4$ is difficult and is also harmful. As $TiCl_4$ is very reactive upon coming in contact with even less humid air, it forms dense white clouds of TiO_2 and HCl vapors. That's why handling $TiCl_4$ is difficult and so is preparing an aqueous solution of it. $TiCl_4$ must be kept in a deep freezer to reduce its reactive nature and the number of fumes coming out of it. Distilled water must be ice cold before preparing an aqueous solution of $TiCl_4$. Also, environmental air should be free of any water vapors. Even after taking all precautions, heavy fumes of TiO_2 and HCl coming out of $TiCl_4$ are difficult to handle as well as very harmful to health. The use of an aqueous solution of $TiCl_4$ to coat a compact layer is suggested because another product of its reaction (HCl) is in vapor form. Thus, unlike other precursors of titania (i.e. TTIP and TTIB), sintering at high temperatures can be avoided to remove heavy carbon compounds. Also, coating the aqueous solution of $TiCl_4$ is mainly done by drop cast orsoaking method, which is non-uniform and non-repeatable. A much simpler compact coating material is suggested in this work using TTIP.

TTIP is much less reactive as compared to $TiCl_4$ and therefore much easier to handle even in a heavy humid environment. The preparation of TTIP compact layer material is detailed in the experimental section of this work. Coating of the compact layer using TTIP solution is done using a simpler spin coating method followed by sintering at 450˚C for 30 minutes. Images of pre- and post-compact layer coating using an aqueous solution of $TiCl_4$ and TTIP solution are shown in Fig. 25.

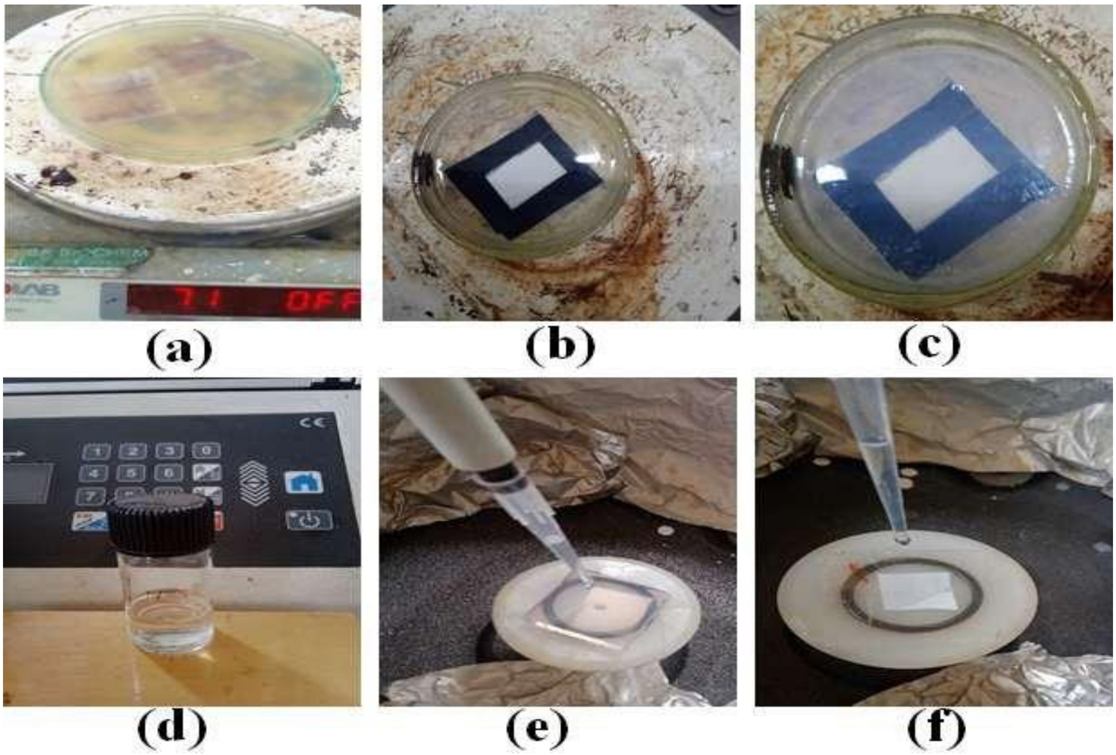

Fig: 25: Images of Compact layer coating: (a) Pre coat, (b) Post coat, (c) post coat after 30 min of compact layer using $TiCl_4$ solution, (d) TTIP solution, (e) pre and (f) post coat of compact layer using TTIP solution

4.2.2 Need for compact layer

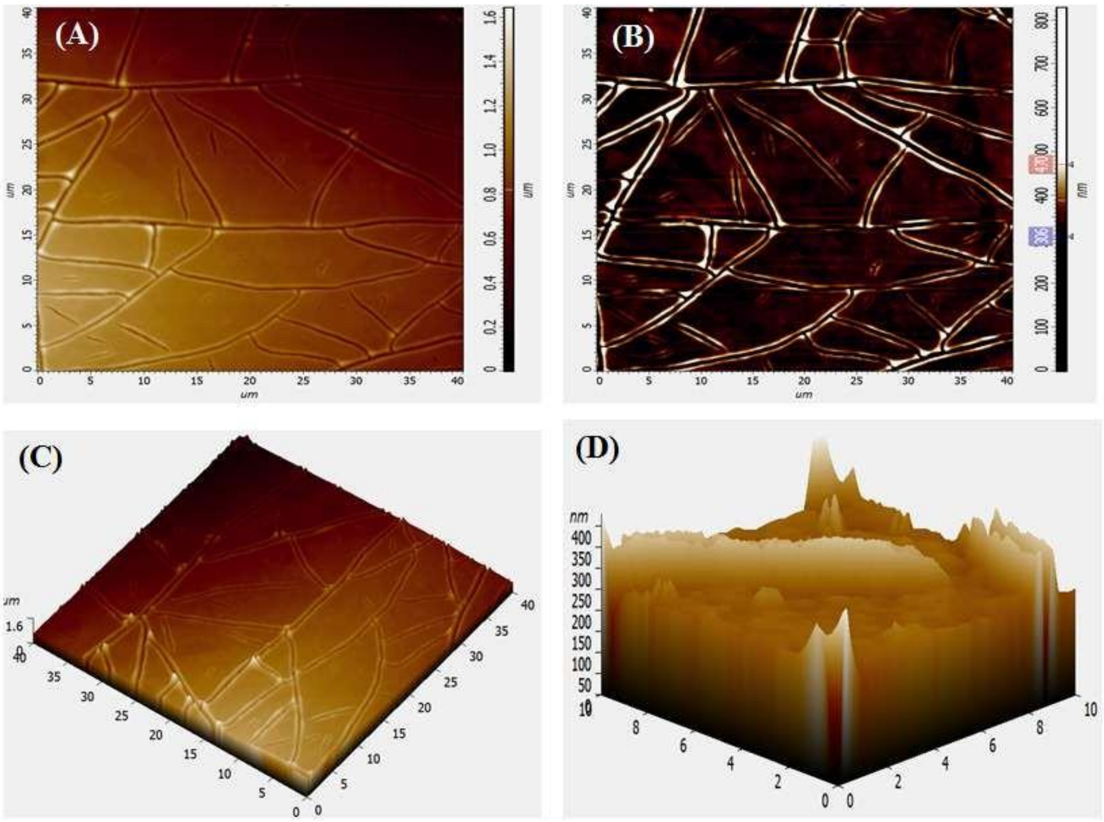

Fig.26: AFM Images of compact layer on Anode: (A) µm scale, (B) nm scale, (C) µm scale showing cracks in compact layer & (D) 3D pie view

The effect of no compact layer, only pre (or post) compact layer, and both compact layers on % of solar cells is discussed in this section and is shown in Fig.27. No compact layer resulted in only ~14% of functioning solar cells. Solar cells having only pre- or post-compact layers resulted in ~77% and ~44% times functioning solar cells. Solar cells having both pre- and post-compact layers resulted in ~97% times functioning solar cells. Many thin layers are present in DSSC ranging from compact layer to platinum layer, each layer has its significance. Two compact layers are there in DSSC, pre-compact is coated at the FTO, and post-compact is coated over the reflective layer. Pre compact layer is to avoid the direct contact of electrolyte with the FTO to avoid the short circuit. Post compact layer was not coated during the early phase of cell fabrication and observation was that several times the cell did not work. Many reasons were thought of as to why the cell was not working. To know about this AFM of the pre-compact layer was done and cracks were noticed in AFM images (Fig.26). Cracks were the reason for the short circuit. After knowing this post compact layer was coated so that the cracks could be filled to avoid the short circuit. Hence pre- and post-compact layer coatings are crucial steps to avoid any short circuit in fabricated solar cells.

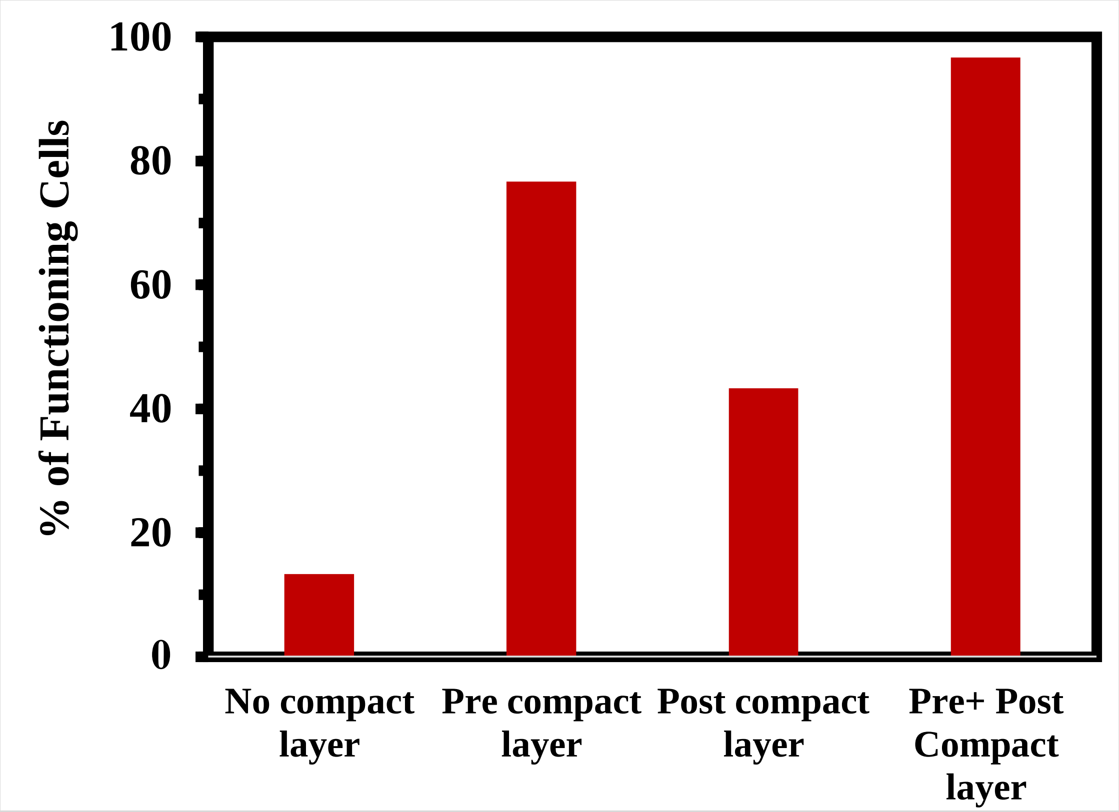

Fig.27: Bar graph displaying % of functioning solar cells w.r.t compact layer coating

4.3 Challenge of dye desorption and addressing this challenge

4.3.1 Dye desorption from anode

Sugar dissolves in water and so does the salt, we know that salt and sugar have solubility towards water. Similar phenomena taking place between the dye and the electrolyte were observed. When the electrolyte was poured over the anode before the JV test of the DSSC, the color of the anode changed from dark red to light pink, which is shown in Fig.28.b. Dye molecules are soluble in electrolyte, that’s why upon addition of (electrolyte which has no dye molecules in it), electrolyte dissolves dye from anode into it, until chemical potential at both surfaces become equal.

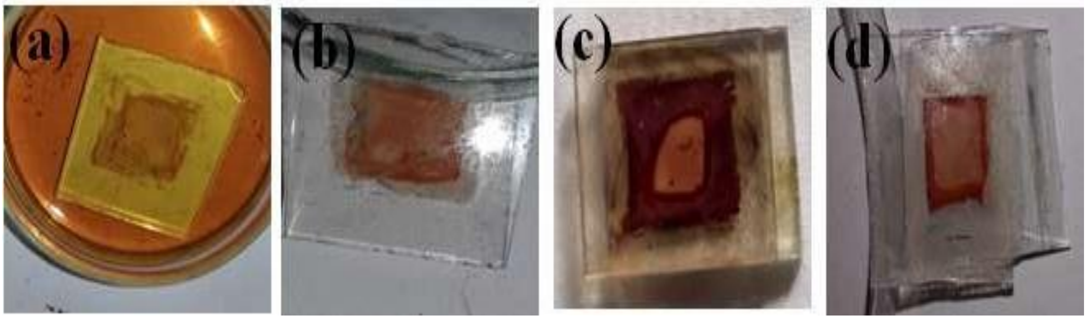

Fig.28: Dye desorption images: (a) & (b) in the anode and (c) & (d)in the DSSC assembly

4.3.2 Performance decrement due to dye desorption

Desorption of dye from anode is a very fast process. Within approximately 2 minutes of electrolyte addition in cell assembly, dye starts to desorb from anode to electrolyte till the concentration of dye at the anode is in equilibrium with the concentration of dye in an electrolyte. Dye-sensitized solar cell efficiency decreases from 3.2 % to 0.5 % in a fraction of a minute. Short circuit current (Jsc) and fill factor (FF) decrease drastically as Jsc and FF depend on the amount of dye adsorbed at the anode. Open circuit voltage (Voc) also decreases significantly. Drop in Voc is approximately 0.15 V from 0.63 V to 0.48 V. Dye desorption challenge is less reported in the literature, even when dye desorption is evident in DSSC and reduces the efficiency of DSSC up to 84.4 %. The dye desorption problem needs to be addressed. A convenient and effective solution is suggested and discussed in the following section 4.3.3.

4.3.3 Addition of dye in electrolyte to stop dye desorption

4 anodes were prepared and soaked in 0.55 mM dye solution for sufficient time. Electrolytes with 0 mg/ ml (no dye), 0.36 mg/ml, 0.66 mg/ml, and 1.32 mg/ml dye concentration were prepared. Dye adsorbed anodes were soaked in above prepared electrolytes for 5 minutes. 0 mg/ml dye conc. electrolyte (no dye) dissolved dye in it to balance dye conc. at the anode and in an electrolyte, which is shown in Fig. 29.a.

A Color change of the anode confirms dye dissolution from the anode to the electrolyte. No dye desorption from the anode was observed for the electrolyte with 0.36 mg/ml dye conc. as shown in fig. 29.b by the color of the anode before addingthe electrolyte and after adding the electrolyte. Some more dye adsorptionon anode was observed in the case of electrolytes with 0.66 mg/ml and 1.32 mg/ml dye conc. as shown in fig. 29.c and fig. 29.d. Dye desorption was only observed in electrolytes with 0 dye molecule in it and no further dye desorption was observed when conc. of dye in electrolyte was increased from 0 to 0.36 mg/ml. So, 0.36 mg/ml dye conc. is optimum conc. of dye which should be present in electrolytes. Further increasing dye conc. in the electrolyte will not help in enhancing the efficiency of DSSC as dye addition also decreases the conductivity of the electrolyte.

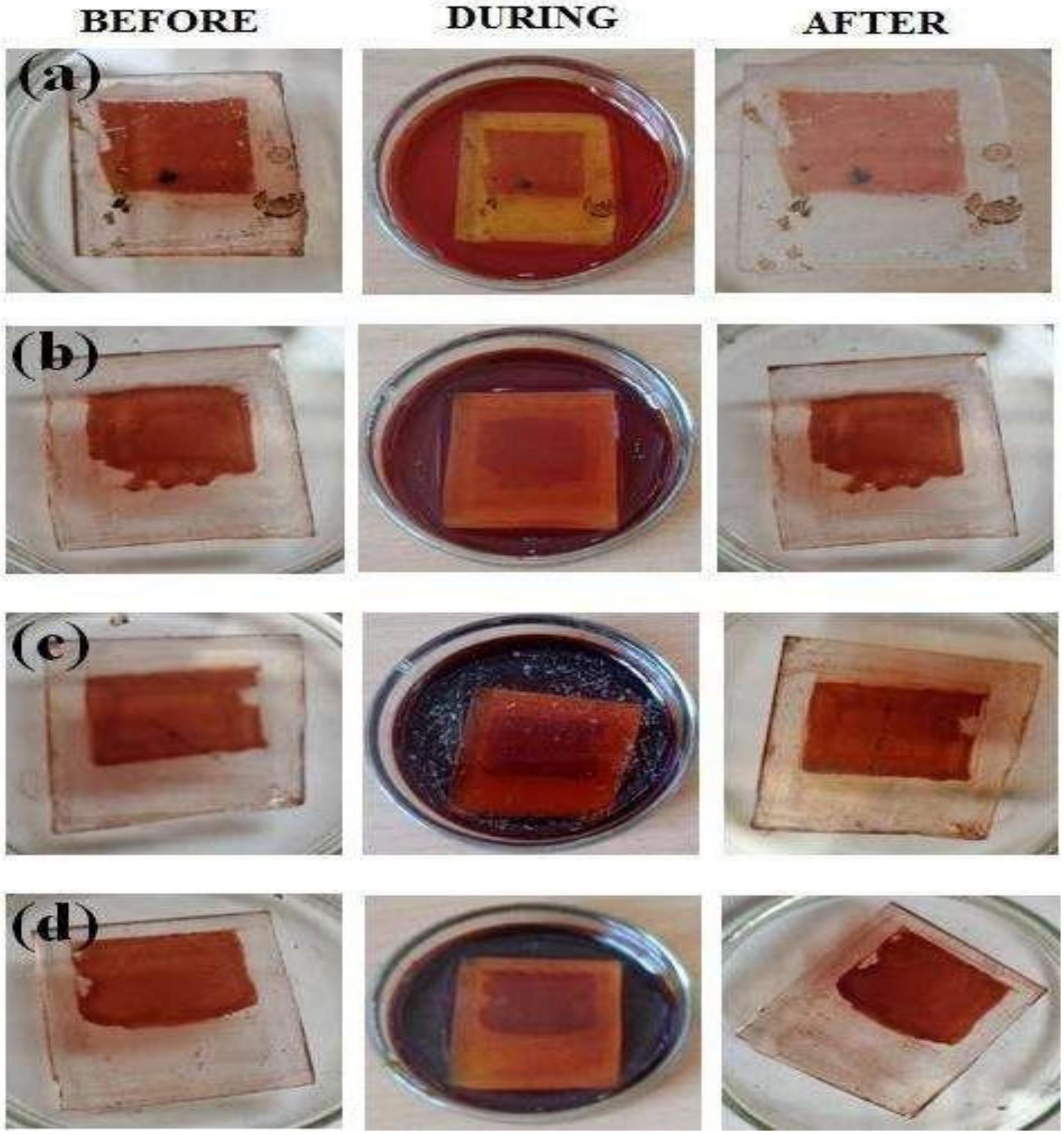

Fig.29: Images of anode before the addition of electrolyte, during electrolyte addition, and after electrolyte addition: for (a) 0, (b) 0.36 mg/ml, (c) 0.66 mg/ml, and (d) 1.32 mg/ml dye conc. in electrolyte.

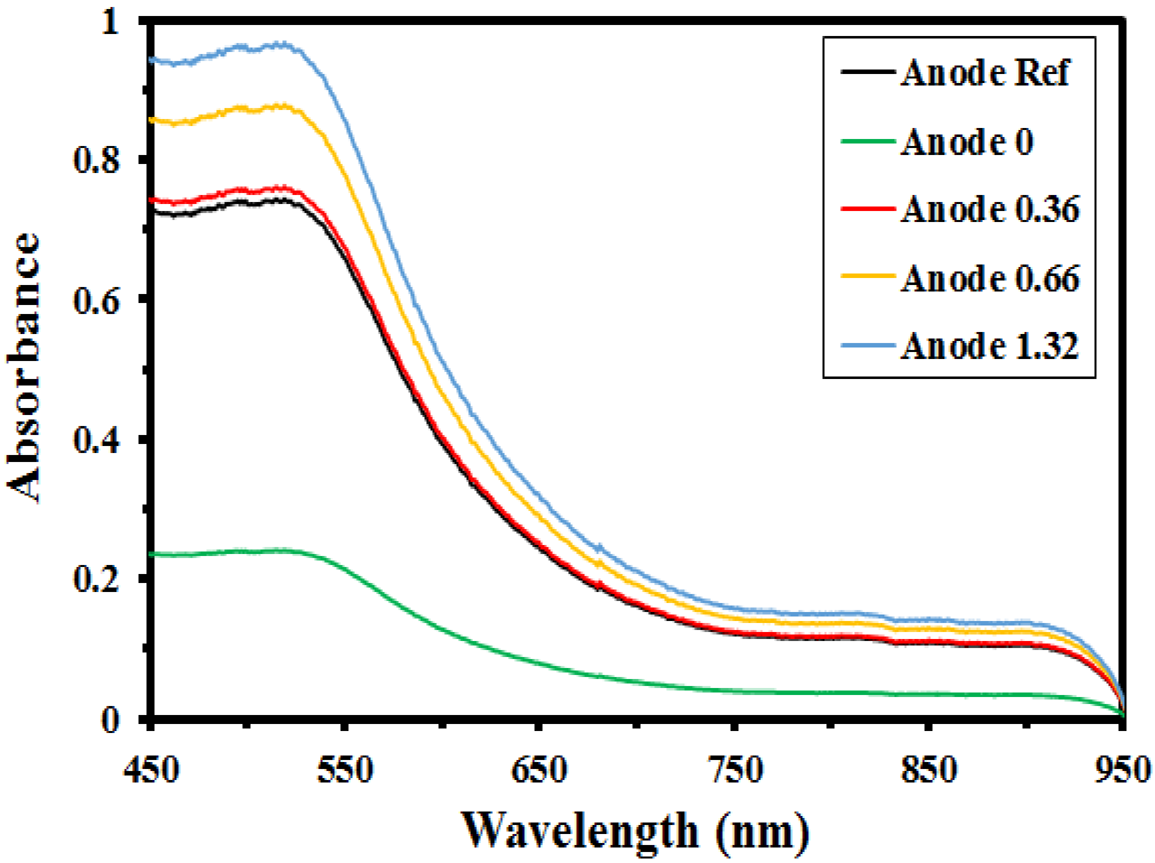

Fig.30: UV-Vis absorbance curve of anode dipped in electrolyte with different conc. of dye in it

JV plot of DSSC before dye desorption, after dye desorption, DSSC fabricated using 0.36 mg/ml and 0.66 mg/ml dye conc. of electrolyte is plotted and is shown in Fig.31. Sudden drop in efficiency of DSSC after dye desorption is also confirmed from the JV plot in the following Fig.31. No dye desorption of DSSC fabricated using 0.36 mg/ml dye conc. electrolyte (labeled as 0.36 DSSC) is further confirmed by a similar JV curve of DSSC before dye desorption. Also, it is confirmed from the JV plot of DSSC fabricated using 0.66 mg/ml dye conc. electrolyte (labeled as

0.66 DSSC) and table, that adding more dye to electrolyte will further decrease the efficiency of DSSC. Adding more dye to electrolyte after reaching optimum dye conc. to stop dye desorption, will only hinder the electron transfer process and slow the electron transfer rate. Dye molecules are heavy metal-carbon compounds, which will create inertia for electron moment and decrease the conductivity of electrolytes. And in turn, decrease the efficiency of DSSC. Therefore, dye should be added to electrolyte only to stop dye desorption at optimum conditions. Efficiency (η), Short circuit current (Jsc), Open Circuit voltage (Voc), and fill factor (FF) data for above mentioned cases are listed in the table. 1.

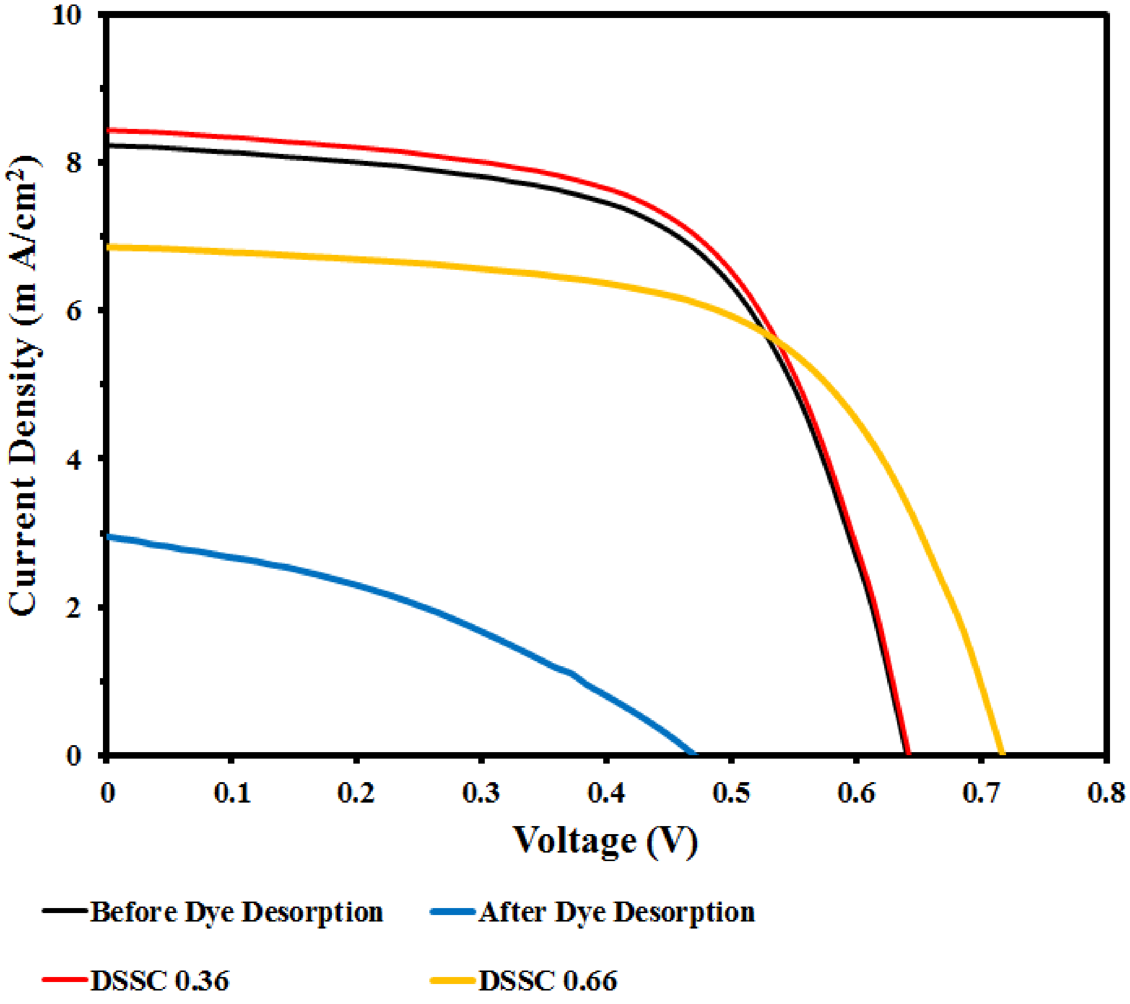

Fig.31: JV plot of DSSC before dye desorption, after dye desorption, DSSC fabricated using 0.36 mg/ml and 0.66 mg/ml dye conc. of electrolyte

Table 1: Jsc, Voc, FF, and η for the different conditions of DSSC

Cell type	**Jsc (mA/cm^2)**	**Voc (V)**	**FF**	**η**
Before Dye Desorption	8.2	0.63	0.62	3.2
After Dye Desorption	2.9	0.48	0.36	0.5
DSSC 0.36	8.4	0.65	0.60	3.3
DSSC 0.66	6.9	0.71	0.62	3.0

4.4 AFM Images Different layers

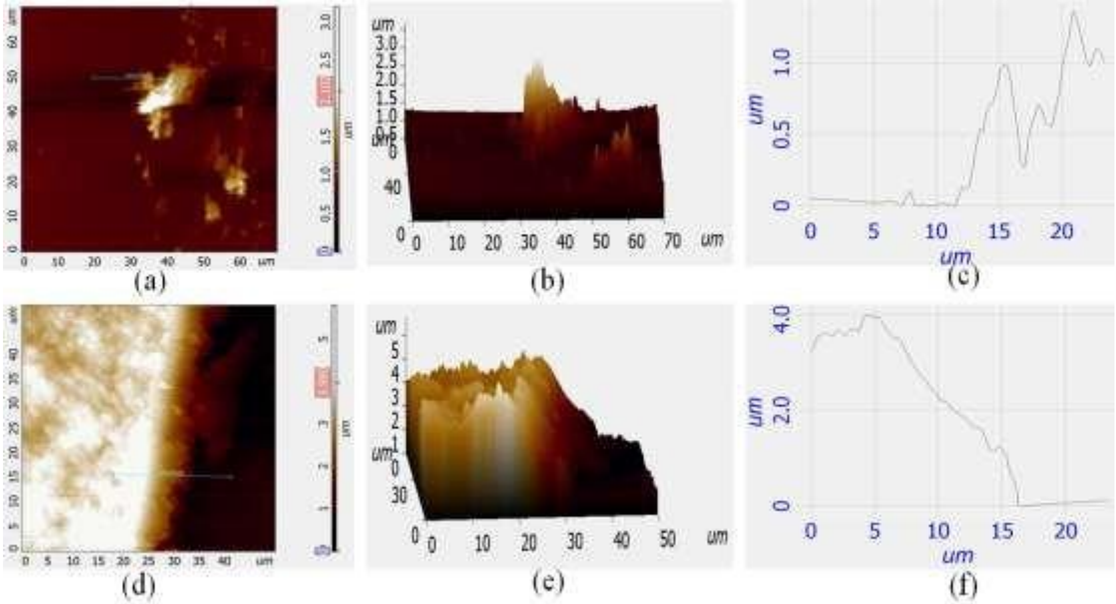

Fig.32.: AFM images of anode layers: (a), (b) 3D view & (c) topography profile of transparent layer and (d), (e) 3D view of & (f) topography profile of the reflective layer

The average thickness of the transparent layer is around 1.5 to 2 μm, which is observed from the AFM image of Fig.32. (a), (b) & (c). Similarly, the average thickness of the reflective layer is around 4μm, which is observed in AFM images of Fig. 32. (d), (e) & (f).

4.5 Effect of thickness of transparent layer in anode

The transparent layer plays an important role in DSSC as this is the area to which dye particles will get adhered. The higher the thickness of the layer the higher will be the particles of dye present in the cell. The amount of dye affects the efficiency as dye molecules are responsible for electron- hole pair generation. However, higher thickness can't ensure higher efficiency because increasing the thickness will make mass transfer limiting during the soaking of the dye and the transport of electrons. Therefore, to study the effect of the thickness of the transparent layer on theperformance of DSSC, three DSSCs were fabricated with varying no. of transparent layers. Transparent layers were coated with the same material using the spin coating method at 2000 RPM to coat 2, 3, or 4 layers. AFM images of transparent layers are shown in section 4.4 in Fig.32. JV plot of DSSC with 2, 3, and 4 transparent layers is shown in Fig.33. Jsc, Voc, FF and η values of 2-, 3- and 4-layer DSSC is listed in Table 2. DSSC with 3 transparent layers gave maximum efficiency of 3.2 %, whereas DSSC with 2 and 4 transparent layers gave efficiency of 3.1% and 2.6 %,respectively. 3.13 % and 18.75 % decrement in efficiency were observed with 2- and 4-layers w.r.t 3 layers. Jsc (8.6 mA/cm^2) for 2-layer DSSC is higher than Jsc (8.2 mA/cm^2) for 3-layer DSSC. This is because there is less resistance to the flow of electrons in 2 layers than in 3 layers of transparent TiO_2. Also, dye molecules reached most inner TiO_2 film because of the lesser thickness of 2 layers than 3 layers. Voc of 2 layers (0.57 V) is lower than Voc of 3 layers DSSC. This is attributed to the fact that more dye is present in 3 layers of DSSC. Jsc, Voc, FF, and η values for 2, 3, and 4 layers of DSSC are listed in the table. Jsc (6 mA/cm^2) of 4 layers DSSC is lower than Jsc of 3 layers DSSC due to additional resistance offered by an extra 1 layer of TiO_2 nanoparticles. The rate of flow of electrons will be the least in the case of 4 layers, so Jsc is lowest in this case. Also, in a 4-layer DSSC case, dye molecules won't be able to reach the inner most TiO_2 nanoparticles. This again reconfirms lower Jsc. Voc (0.71V) of 4 layers DSSC is highest because of more dye present, in turn, which will generate more electron-hole pairs. Fill factors of 2, 3, and 4 layers DSSC are 0.63, 0.62, and 0.61. The highest fill factor of 2 layers ofDSSC is due to the highest rate of flow of electrons in 2 layers as comparedto 3 and 4 layers of DSSC. 3 layers (i.e. ~6-7.5μm thick transparent layer)of DSSC gave an optimum performance in our case.

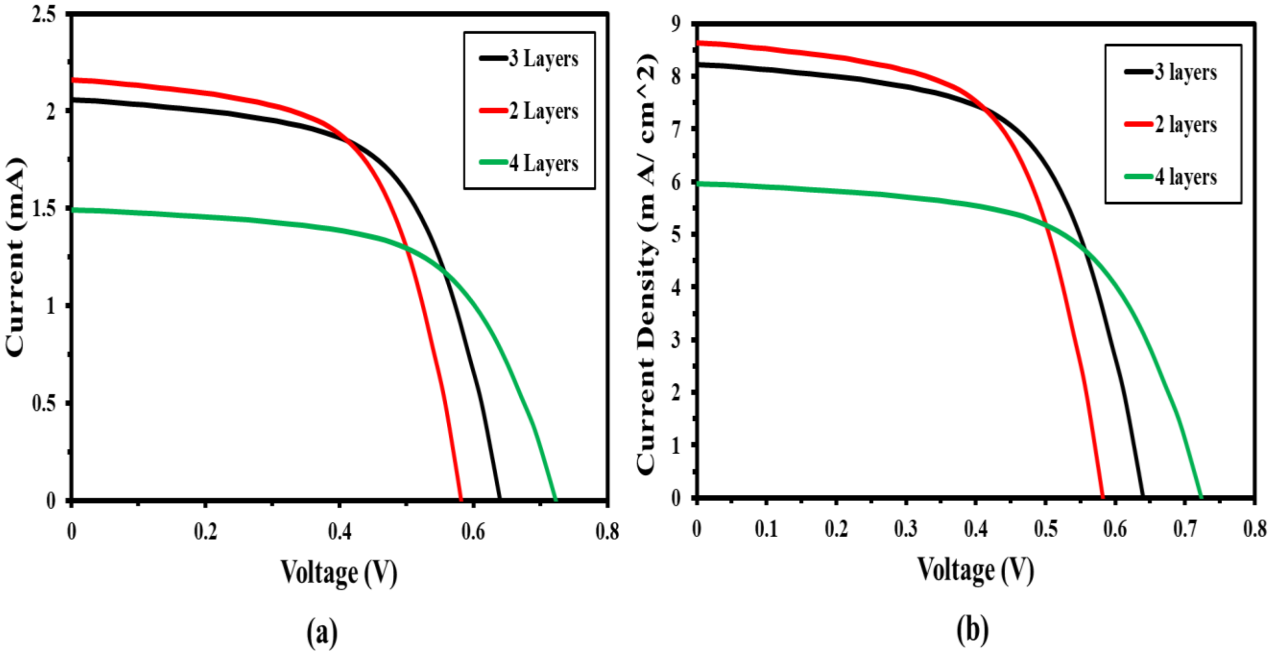

Fig. 33: (a) IV, (b) JV plot of DSSC fabricated with 2µm, 4µm and 6µm thick transparent layer

Table 2: Jsc, Voc, FF, and η of DSSC with 2µm, 4µm, and 6µm thick transparent layer

Thickness of Transparent Layer	Jsc (mA/cm^2)	Voc (V)	FF	η
2 Layers	8.6	0.57	0.63	3.1
3 Layers	8.2	0.63	0.62	3.2
4 Layers	6.0	0.71	0.61	2.6

4.6 Temperature effect on performance of dye-sensitized solar cell

Temperature of anode before dye soaking, and temperature of cell assembly before electrolyte filling are very crucial steps to optimize DSSC performance. At these steps, moisture from the environment can degrade the dye present at the anode. In turn, the efficiency of DSSC dropped drastically. So, to avoid any moisture interaction between the anode and cell assembly, temperatures should be adjusted accordingly.

4.6.1 Temperature range of anode before dye soaking

The temperature of the anode before dye soaking is a very crucial parameter in fabricating dye sensitized solar cell. The anode should be kept at a higher temperature so that moisture present in the atmosphere does not degrade the dye adsorbed on the anode. The temperature of the anode should be adjusted according to the humid condition of the cell fabricating place. Anode at lower temperature can easily absorb moisture and degrade dye at anode. Hence efficiency of DSSC drastically reduces due to dye degradation. The efficiency of DSSC was reduced to 85-90% due to dye degradation. It is confirmed that moisture affects the performance of DSSC, as the cell fabricated in the lab is exposed to the environment so certain steps can be taken to avoid such conditions. One step can be to fabricate cells under an inert environment, and another is to keep the temperature at a limit where neither layer gets deformed, nor the moisture can get absorbed into the layers of DSSC. Before soaking in dye,a post-compact layer over the DSSC is coated and this process is done at 450°C. Therefore, high temperature limit can be taken up to 450°c. Now the question is the lower limit of temperature, it can be decided by knowing the boiling point of water and dew point temperature of ambient. The boiling point of water at 1 atm is known to be around 100°C. As water is a wetting liquid i.e. it wets the surface with which it is in contact. so lower limit of temperature should be more than 100°C. Heating of the anode is done inside the furnace and cell assembly is done outside the furnace, so there will be a drop in temperature once it is taken out of the furnace. Therefore, temperature should be fairly above 100°C. With all these in mind, experiments of dye soaking were carried out at different temperatures and the range of temperature was observed from 100°C to 150°C.

4.6.2 Temperature of cell assembly during electrolyte filling

The temperature of the cell assembly becomes very important if it is not kept in an inert environment as there are holes at the cathode to fill the electrolyte. These holes make the cell susceptible to moisture which can degrade dye and in turn, ultimately result in a decrease in the efficiency of DSSC. The temperature of the cell assembly was kept at and above 50°C to avoid contact with the moisture. However, the temperature of the cell assembly can’t be kept very high because of the use of volatile electrolytes and EVA sheets for sealing the cell. Keeping the temperature too high may cause the evaporation of electrolytes and the EVA sheet to reach above its glass transition temperature. During the electrolyte filling and cell assembling process, extra care should be given by keeping the cell assembly temperature above 50°C to avoid dye degradation.

4.7 J-V and P-V curves of reference DSSC

JV and PV plot of optimized DSSC is shown in Fig.34. 3.2 % efficiency was obtained with optimized DSSC. The current density of 8.2 mA/cm^2, Open circuit voltage of 0.63 V, Fill factor of 0.62, and maximum power density of 3.22 mW/cm^2 were obtained for optimized DSSC.

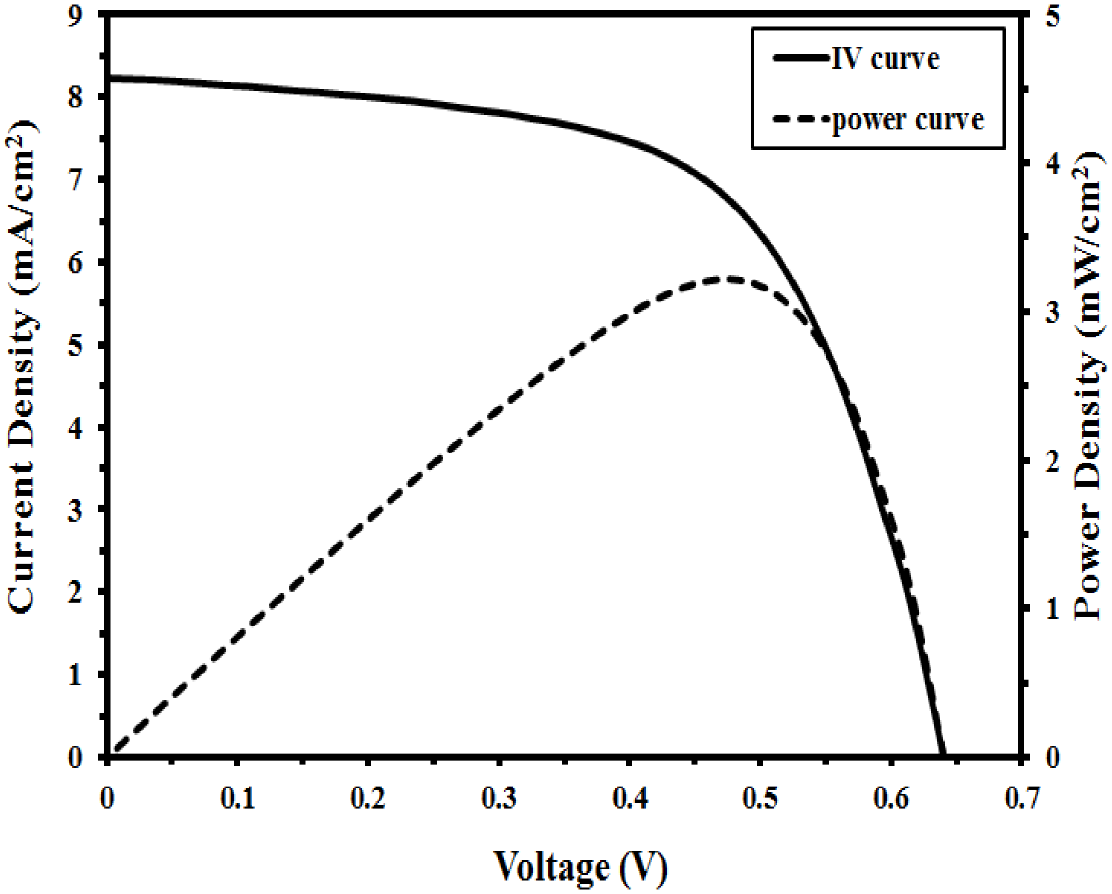

Fig. 34: JV and PV plot of standard DSSC

4.8 Conclusions

In this chapter, DSSC fabrication challenges were addressed. Spin coated method is preferred over conventional doctor's blade method for compact, transparent, and reflective layer coating on FTO. Uniformity and repeatability of films are achieved by spin coating method which stops peeling off films after sintering. TTIP solution showed easy handling as compared to aq. $TiCl_4$ solutions for compact layer coating material. Pre and post compact layer coating ensures that there is no path left for electrolyte to directly come in contact with FTO surface. In turn, which ensures no short circuit and functioning solar cells. Dye desorption from anode continues till chemical potential of dye is equal at anode and in electrolyte, which reduces cell efficiency from 3.2 % to 0.5 %. To address this issue, dye was added in electrolyte (Optimum conc. 0.36 mg/ml) which stopped dye desorption completely. Transparent layer is main current producing layer is DSSC and its thickness plays important role. Too thick layer will decrease current as electron flow will get more resistance even though more dye molecules are attached.

Less no. of dye molecule will generate less no. of electron-hole pairs in too thin layer. The optimum thickness of transparent layer was found to be 6 to 7.5 μm. Lastly to avoid any dye degradation from moisture present in environment, anode temperature should before dye soaking should be above 100˚C. Also, during cell assembly, temperature should be above 100˚C to avoid any moisture interaction with dye. A DSSC was fabricated with 3.2 % efficiency, 8.2 mA/cm^2 Jsc, 0.63 V Voc and 0.62 FF.Maximum power density of DSSC with 3.2 % efficiency is 3.22 mW/cm^2 at 0.49 V.