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Fabrication and characterization of dye sensitized solar cells: A photographic guide

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This paper presents the detailed fabrication procedure of dye-sensitized solar cells. The characterization techniques used for evaluating solar cell performance have also been described. The photographs of the fabrication process and characterization systems have been provided wherever necessary. Important fabrication steps which have not been provided in detail in the scientific literature have been presented for clarity. Proper characterization methodology has been provided to correctly evaluate the performance of solar cells. The general procedures and techniques presented here can also be used for fabricating efficient perovskite solar cells. Present work can be used as a guide for fabricating and characterizing high efficiency dye sensitized solar cells, and will be very useful for the researchers engaged in solar cell research work.

Keywords: Dye-sensitized solar cell, Fabrication, Thin film solar cell, Photographic guide

1 Introduction

Dye-sensitized solar cell (DSSC) is an emerging PV technology and belongs to the thin film solar cell group. In the conventional *p-n* junction solar cells, light absorption and charge transport take place in the same material (silicon, for example). However, in DSSC these two processes are differentiated and occur in different media. The light is absorbed by a dye (hence the name dye-sensitized) adsorbed on to titanium dioxide (TiO_2) nanoparticles (NPs) and the electrons and holes are transported through TiO_2 and the electrolyte, respectively. A schematic of the DSSC structure[1] is shown in Fig. 1.

The working principle of a typical DSSC is illustrated in Fig. 2. TiO_2 is a wide band gap semiconductor and absorbs only the wavelengths below 400 nm; in other words, it is transparent to visible and near infra-red (NIR) light. This allows the dye molecules to harvest a broadband region of the solar spectrum. The incident light photons are absorbed by the sensitizing dye molecules and get excited from the ground state S to a higher energy state S^* (Eq. (1)). The excited dye molecules inject electrons to the conduction band of TiO_2 and are left in an oxidized state S^+ (Eq. (2)). The electrons are transported via nano-TiO_2 network and fluorine doped tin oxide (FTO) substrate (anode), and finally through the external circuit before reaching the counter electrode (cathode). The electron reduces the tri-iodide (I_3^-) to iodide (I^-) in the electrolyte, at the counter electrode (Eq. (3)). The cycle of regeneration is completed by reduction of oxidized dye molecules by the iodide in the electrolyte (Eq. (4)).

$$S + h\nu \rightarrow S^* \text{ Photon absorption} \qquad \ldots (1)$$

$$S^* \rightarrow S^+ + e^- \text{ Electron injection} \qquad \ldots (2)$$

$$I_3^- + 2e^- \rightarrow 3I^- \text{ Reduction of tri-iodide} \qquad \ldots (3)$$

$$2S^+ + 3I^- \rightarrow 2S + I_3^- \text{ Regeneration of dye} \qquad \ldots (4)$$

As shown in Fig. 2, theoretical maximum voltage that can be obtained from DSSC is dependent upon the Fermi level of TiO_2 and the redox potential of tri-iodide/iodide electrolyte solution. The dye molecules return back to their original ground state, or in other words, get regenerated after completion of a working

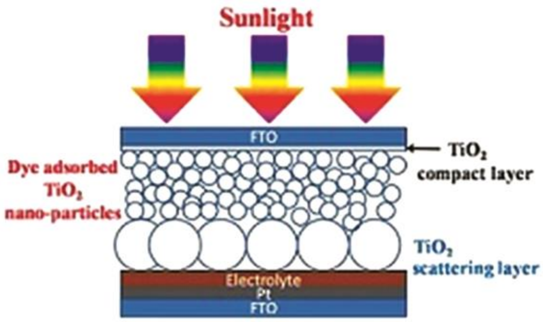

Fig. 1 — A schematic structure of a typical dye-sensitized solar cell.

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*Corresponding author (E-mail: vamsi@ces.iitd.ac.in) cycle following the photon absorption. Thus, there is no permanent change in the state of dye molecules and the involved chemicals are not consumed in the operating process of DSSC.

A typical dye-sensitized solar cell (DSSC) is composed of a photo-anode and a counter electrode (cathode). The photo-anode is made up of a mesoporous TiO_2 layer which is infiltrated by the dye molecules. Other metal oxides, like like zinc oxide (ZnO), tin oxide (SnO_2), nickel oxide (NiO) and niobium pentoxide (Nb_2O_5) are also used for making DSSC photo-anodes; but, the best performance is achieved with TiO_2, therefore, we have used only TiO_2 based photo-anodes in the present work[2-6].

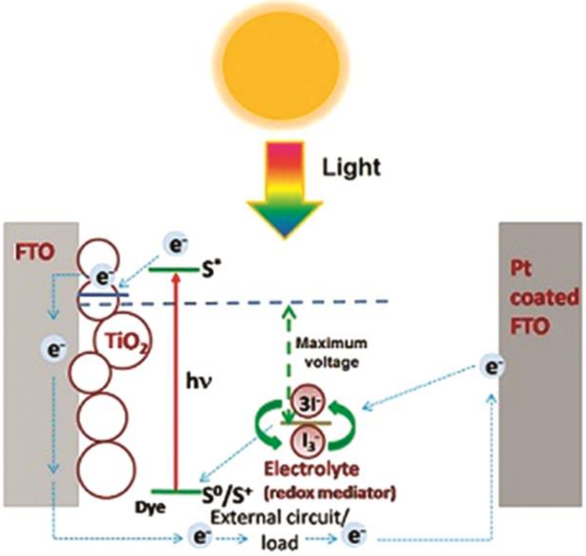

Fig. 2 — Schematic illustrating the working principle of a DSSC. The electrons are injected from excited dye molecules to the TiO_2 layer. The oxidized dye molecules in turn oxidize the electrolyte redox mediator. The electrolyte mediator is reduced at the cathode by electrons which flow through the external circuit.

A mesoporous TiO_2 layer can be deposited on FTO substrates by doctor blade (DB), screen printing (SP) and spray deposition (SPD) techniques[7,8]. These three are the broad categories of fabrication methods and slight variations of these techniques may be followed by different laboratories. DB method is the easiest to adopt and can be performed with simple laboratory tools, without utilizing any special apparatus. We describe the DB method, with photographic support, in the following sections.

2 Experimental Details

2.1 TiO_2 film fabrication by doctor blade method

In this section, we present the detailed fabrication procedure of fabricating TiO_2 films by the DB method. The photographs of the fabrication steps are also provided for a better understanding of the procedure. Fluorine doped tin oxide (FTO) glass substrates are used for fabricating TiO_2 films. FTO glasses are cut into pieces of 1 inch×1 inch with the help of a glass cutter. The FTO pieces are then cleaned using soap water, de-ionized (DI) water and propanol in an ultrasonic bath. A compact layer of TiO_2 is then deposited on the cleaned FTO substrates by spray pyrolysis of an ethanolic solution of di-iso-propoxy titanium-bis(acetylacetone) (Sigma Aldrich) at 450 °C. The spray apparatus and nozzle shown in Fig. 3 are used for depositing the compact layer. Figure 4 shows the photograph and scanning electron micrograph (SEM) of a FTO substrate coated with TiO_2 compact

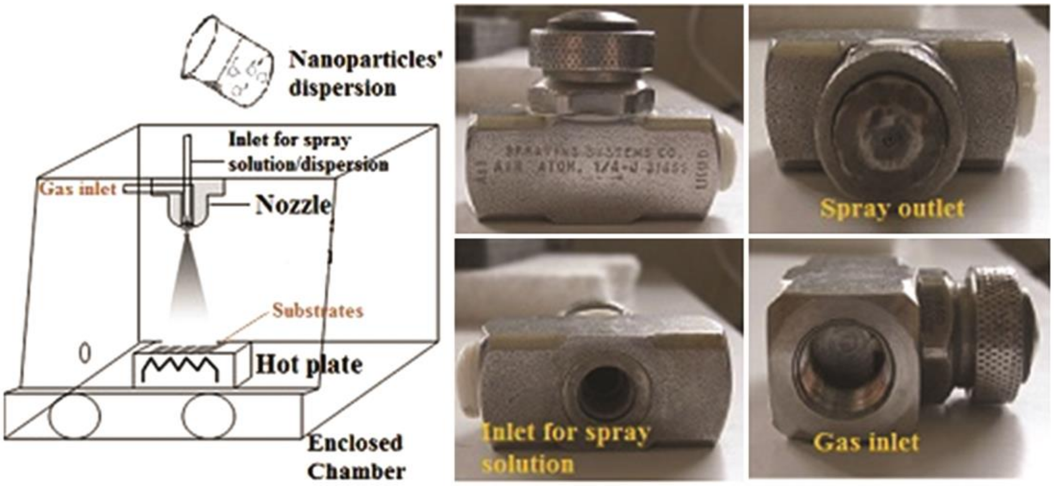

Fig. 3 — A schematic of the spray apparatus used to deposit compact TiO_2 films. The photographs depict the solution and gas inlets, and also the spray outlet of the nozzle.

layer. The compact layer coated area can be easily seen with unaided eye. The compact layer helps in preventing the recombination of electrons flowing through FTO and ions present in the electrolyte at the FTO-electrolyte interface.

The FTO substrate is kept on a flat surface and an area of 1 cm×1 cm is defined by scotch tape (Fig. 5(a,b)). The TiO_2 commercial paste (Dyesol 18-NR-T, average particle size ~20 nm) is applied using a small spatula as shown in Fig. 5(c). The paste is spread on the defined area using a glass rod (Fig. 5(d)). The rod is pressed against the scotch tape and quickly moved in a downward direction (Fig. 5(e)). This fills the area between the scotch tape layers with the TiO_2 paste and results in the formation of TiO_2 film in the area defined by the tape layers. The glass rod should be held firmly and moved quickly to ensure that nearly equal force/pressure is applied throughout the length of the rod. This will result in smooth and uniform films. If the pressure applied is not uniform, the resulting films will have uneven texture and significant variations in film thickness at different points will be obtained. This coating step can be perfected after a few initial tries.

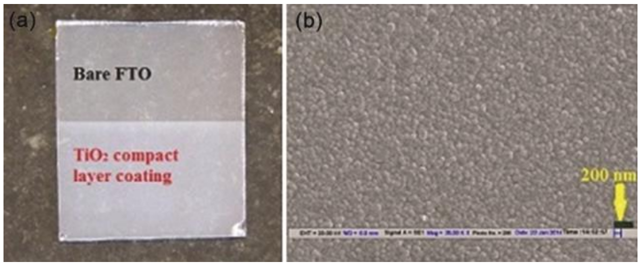

Fig. 4 — (a) Digital photograph of FTO substrate spray coated with TiO_2 compact layer. (b) Scanning electron micrograph of the compact layer.

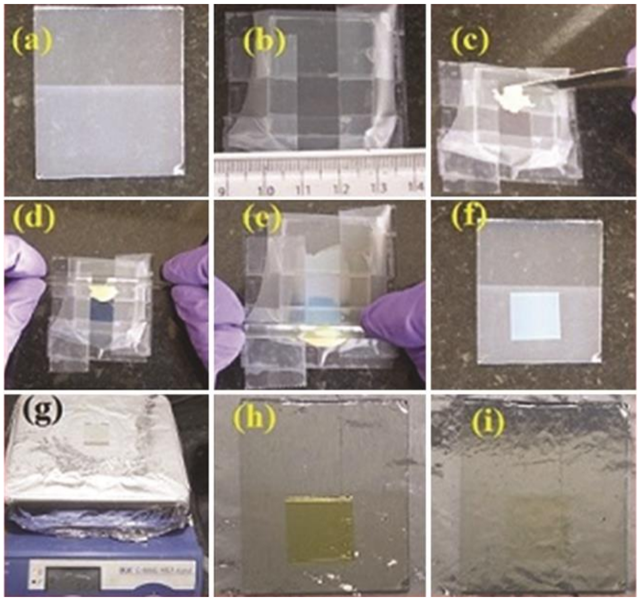

Fig. 5 — (a) Compact TiO_2 layer coated FTO substrate is kept on a flat substrate. (b) Scotch tape is applied to define the deposition area, and (c) TiO_2 paste is put using a spatula. (d), (e) and (f) A glass rod is used for evenly spreading the paste on FTO and a smooth film is obtained. (g) The deposited film is placed on a hot plate for annealing. (h) and (i) The initially yellowish film changes to colorless transparent film after completion of the heating process.

After the deposition, the scotch tape is removed to obtain a uniform film as shown in Fig. 5(f). The film is placed on a hot plate and slowly heated as shown in Fig. 5(g). The film appears to be yellowish due to the presence of organic binders in the paste (Fig. 5(h)). Initially, the film is dried at 50 °C for 10 min and subsequently the temperature is raised to 125 °C. The temperature is then raised in steps of 75 °C every 5 min. A sudden increase in temperature may damage the film due to thermal shock. The step heating is crucial to obtain a crack-free film. The temperature is maintained at 500 °C for 30 min and afterwards the heating is stopped and the film is allowed to cool down to room temperature. It can be seen that the film loses its yellow color and turns almost transparent as seen in Fig. 5(i). Figure 6 shows the SEM image of a mesoporous TiO_2 layer deposited by the DB method. In contrast to the tight bound structure of compact TiO_2 layer (Fig. 4(b)), the porous structure of TiO_2 film prepared by the DB method is evident from Fig. 6.

Apart from the commercial paste, a paste of TiO_2 NPs can be prepared in the laboratory also. The details of paste fabrication are given in the paper by Ito *et al.*[7]. Alternatively, about 0.5 g of TiO_2 NPs (synthesized in lab or procured commercially) can be mixed with 2.5 mL of terpineol and 1 mL of ethyl cellulose solution

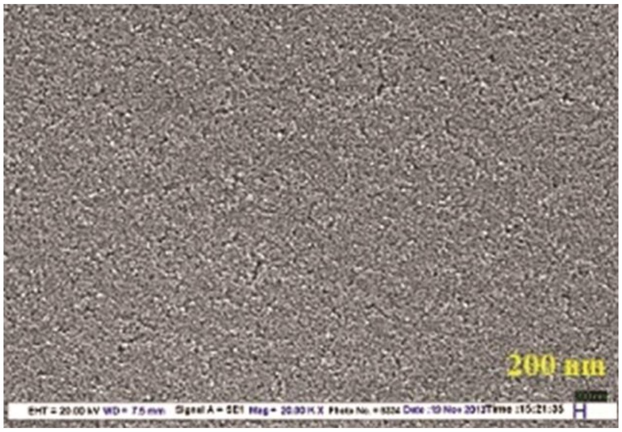

Fig. 6 — Scanning electron micrograph of mesoporous TiO_2 layer deposited by a doctor blade method using commercial paste (Dyesol 18-NR-T).

(50 mg/ml ethanolic solution) and grinded thoroughly in a mortar-pestle. The resulting paste can be used to deposit meso-TiO_2 films in the same manner as that described above for commercial paste.

A scattering layer of large TiO_2 particles (Dyesol WER2-O) is deposited using DB method on top of the meso-TiO_2 layer (Fig. 7(a,b)). This layer helps in trapping more light and provides enhanced photocurrent[7]. After deposition of scattering layer, the film is again heated up to 500 °C (Fig. 7(c)). When the film cools down to the room temperature, it is placed in a 40 mM titanium tetrachloride ($TiCl_4$) aqueous solution at 70 °C for 30 min (Fig. 7(d) and (e)). Afterwards, the film is rinsed with DI water and heated again at 500 °C for 15 min (Fig. 7(f)). This completes the fabrication of a bi-layer TiO_2 structure on FTO substrates. The film is now ready for further processing to make a DSSC photoanode which is described in the next section.

2.2 Preparation of a DSSC photoanode

The TiO_2 films, fabricated by the method described in the previous section, are dipped in a dye solution. Typically, about 20 mL of 0.3 mM dye solution in ethanol is taken for a film of area ~1 cm^2. In the present work, we have used N719 dye (Di-tetrabutyl-ammonium cis-bis(isothiocyanato) bis (2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II)) procured from Sapala Organics, Hyderabad, India. The film is dipped in the dye solution for 18-20 h. These are the optimized parameters for obtaining best DSSC performance. Figure 8 shows the color change of TiO_2 film after dipping in N719 dye solution for 20 h. The back side of the film shows a dark maroon coloration due to the dye molecules adsorbed in mesoporous TiO_2 layer. The top side of the film shows only a minor change in coloration because the dye molecules are not adsorbed in large numbers in the scattering layer. This happens because the scattering layer consists of large TiO_2 particles (~400 nm) and its surface area is much less than that of the highly porous meso-TiO_2 layer.

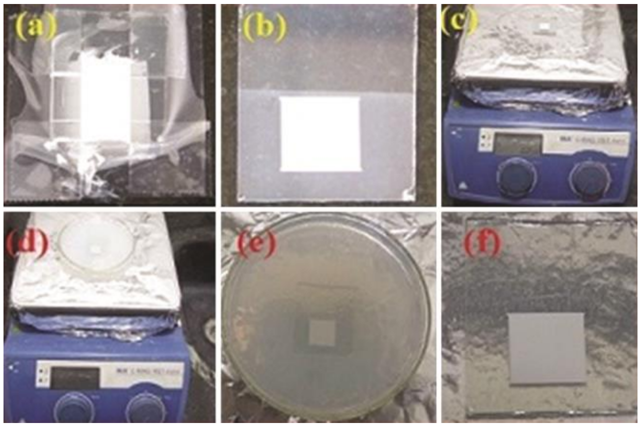

Fig. 7 — (a) and (b) A scattering layer of large TiO_2 particles is deposited by the doctor blade method on top of meso-TiO_2 layer. (c) The film is annealed at 500 °C for 30 min. (d) and (e) Afterwards, the film is placed in a $TiCl_4$ solution at 70 °C for 30 min. (f) The film is rinsed with DI water and finally heated again at 500 °C for 15 min.

After the dipping process, the dye molecules are adsorbed on to the surface of TiO_2 particles and the TiO_2 film is said to be 'sensitized' with the dye molecules. The film is taken out from the dye solution and rinsed thoroughly with ethanol to remove any aggregated dye molecules on the film surface. Alternatively, the film can be dipped in acetonitrile for 1 min to remove the aggregated dye molecules. The film is then dried in air for a few minutes. After drying, the photoanode is ready for use.

2.3 Assembly of DSSC

A DSSC consists of a photoanode and a counter electrode, with electrolyte in between (Fig. 1). The fabrication of TiO_2 film and preparation of photoanode is the most important step, and is generally a lengthy process that has been described in detail in the previous sections. The counter electrode used in the present work is platinum (Pt) coated FTO substrate. The counter electrode can be prepared by platinizing a FTO glass piece by putting a few drops of Platisol (Solaronix) on it and annealing it at 450 °C for 10 min. Platisol is a solution of H_2PtCl_6 (chloroplatinic acid) in propanol. The other method is sputter deposition of Pt on FTO substrates. About 100 nm of Pt is sputter coated to result in reflective Pt films on FTO (Fig. 9(b)). Counter electrodes prepared by both the techniques can be used. Here, we have used sputter coated counter electrodes of Pt.

The dye-sensitized TiO_2 film is covered on three sides by a transparent tape (Fig. 9(a)). The tape is applied by slightly covering the films; this results in an

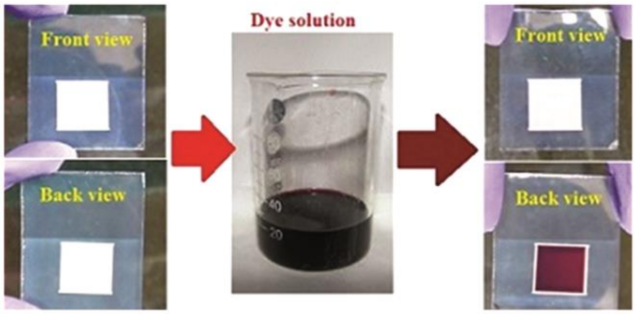

Fig. 8 — TiO_2 film is dipped in dye solution to obtain dye-sensitized film.

effective area of about 0.9 cm×0.9 cm. This is done in order to prevent a direct contact between anode and cathode (counter electrode), which will otherwise electrically short the device. A few drops of electrolyte are dropped on the dye-sensitized TiO_2 film as shown in Fig. 9(c). The electrolyte consists of 0.1M Lithium iodide (LiI), 0.05M I_2, 0.5M tert-butylpyridine (TBP) and 0.6 M 1-propyl-2,3-dimethyl imidazolium iodide (DMPII) in acetonitrile. Finally, a sandwich configuration is made using the photoelectrode and the counter electrode as shown in Fig. 9(d). The two electrodes are clamped together using binder clips. This completes the fabrication and assembly procedure of a typical DSSC. The device is now ready for testing.

A complete sealed cell can also be fabricated in a similar fashion as described above. The difference is that a counter electrode with a pre-drilled hole is used and a plastic spacer-cum-sealant, namely Surlyn, is used instead of tape. The electrolyte is injected through the hole in the counter electrode. The hole is then sealed with a cover glass slide and Surlyn. The detailed procedure for sealed cell fabrication and synthesis of various types of TiO_2 nanoparticles and pastes can also be seen from the paper by Ito *et al.*[7].

2.4 Characterization of DSSCs

The basic solar cell characterization techniques are current density-voltage (*J*-*V*) and incident photon to current conversion efficiency (IPCE) measurements. The *J*-*V* measurement is also referred to as the *I*-*V* (current-voltage) measurement. IPCE is also known as external quantum efficiency (EQE) or spectral response (SR) measurement.

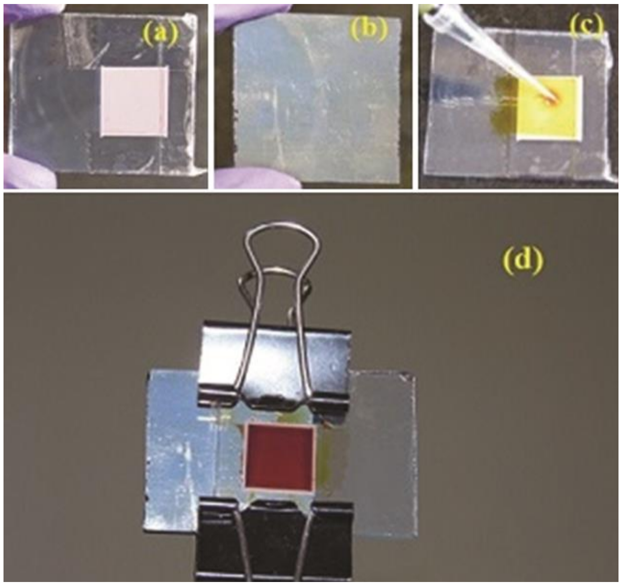

Fig. 9 — (a) Dye-sensitized TiO_2 photoanode with tape on three sides. (b) Sputter deposited platinum on FTO glass. (c) Electrolyte being dropped on the photoanode. (d) A complete sandwich-type configuration of a typical DSSC.

2.4.1 I-V measurement

For evaluating the *I*-*V* characteristics of DSSCs, a solar simulator (Sol3A, Oriel Newport, USA) along with a computer controlled source-meter (Keithley 2440) has been used. The cell is connected as shown in the Fig. 10. The two positive and the two negative probes are shorted and connected to crocodile pins to obtain one positive and one negative connection. All the four parameters, open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), fill factor (FF) and power conversion efficiency (PCE) are automatically evaluated and shown on the computer screen. A black colored mask with dimensions ~0.8 cm×0.8 cm is used while making the measurements. This has been done in order to define an active area of ~0.64 cm^2 for the DSSCs. If the masking is not done, the efficiency may be overestimated as scattered light may also contribute to the photocurrent, apart from the normally incident light from the simulator. Use of a proper mask also ensures that devices fabricated in different batches can be fairly compared. The *I*-*V* curve of the cell fabricated and assembled, as shown in previous sections, is shown in Fig. 11. The important photovoltaic parameters are also shown for clarity.

2.4.2 IPCE measurement

IPCE or the external quantum efficiency (EQE) is the percentage of incident photons that are converted to electric current (collected charge carriers), when the cell is operated under short circuit conditions. The term

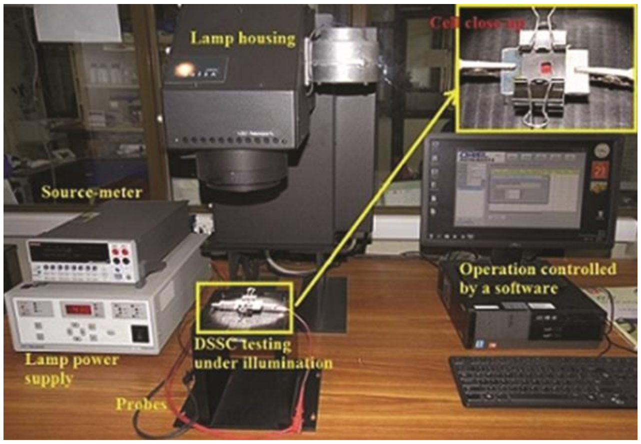

Fig. 10 — Current-voltage measurement setup comprising of a solar simulator, source-meter and computer controlled software. The close-up of a masked DSSC under test is also shown.

‘external’ implies that the effects of optical losses like transmission and reflection are included in the measurement. Internal QE (IQE) is the percentage of absorbed photons that are converted to electric current. IQE excludes the effects of optical losses and tells only about the fraction of absorbed photons being converted to electricity. Quantum efficiency is usually expressed as a spectral measurement (as a function of wavelength or photon energy). Since DSSCs absorb some wavelengths more effectively than others, spectral measurements of QE can yield valuable information about the quality of the solar cell material (dye sensitized photoanode) and its ability to absorb a particular portion of the solar spectrum.

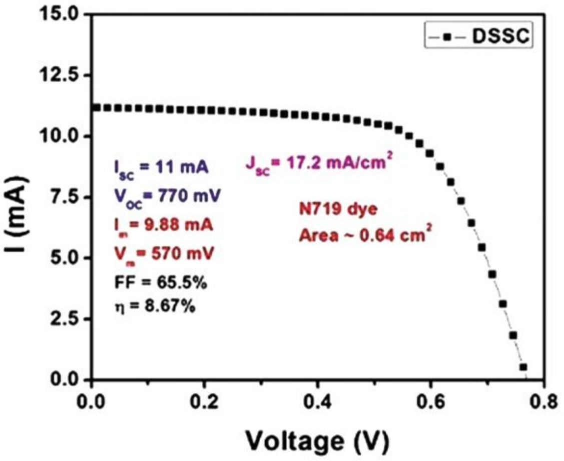

Fig. 11 — *I-V* curve of the DSSC shown in Fig. 9 measured using the setup shown in Fig. 10.

To measure the EQE of a given cell, it is compared to a reference cell whose EQE and spectral response (SR) are previously known. Quantum efficiency measurement system (ReRa SpeQuest, Netherlands) is used for recording incident photon to current conversion efficiency (IPCE) spectra of DSSCs. The system consists of a halogen lamp and a 150 W xenon lamp. The incident monochromatic light is chopped at 20 Hz and the signals are acquired using a lock-in amplifier (Anfatec eLockIn203, Germany). IPCE measurements of all DSSCs are performed with a halogen bias light of ~0.1 Sun intensity. The bias light is necessary to fill the trap states of TiO_2, so that the charge carriers generated by the monochromatic illumination can be effectively collected by the detection electronics of the instrument[9,10].

The IPCE spectra have been recorded at a relatively high chopping frequency of 20 Hz. Due to some limitations of the system hardware, the chopping frequency could not be set at 1–2 Hz or the DC mode, which is the required frequency setting for measuring the IPCE spectra of DSSCs. A higher chopping frequency reduces the IPCE spectrum[9,10]. Nevertheless, if the same chopping frequency is used for measuring all the DSSCs, a comparison between the devices can be made.

The IPCE measurement setup used for recording the IPCE spectra is shown in Fig. 12. The spectrum of a reference detector is first measured for calibration. Afterwards, the masked DSSC is connected and arranged as shown in Figs 12 and 13. The cell is

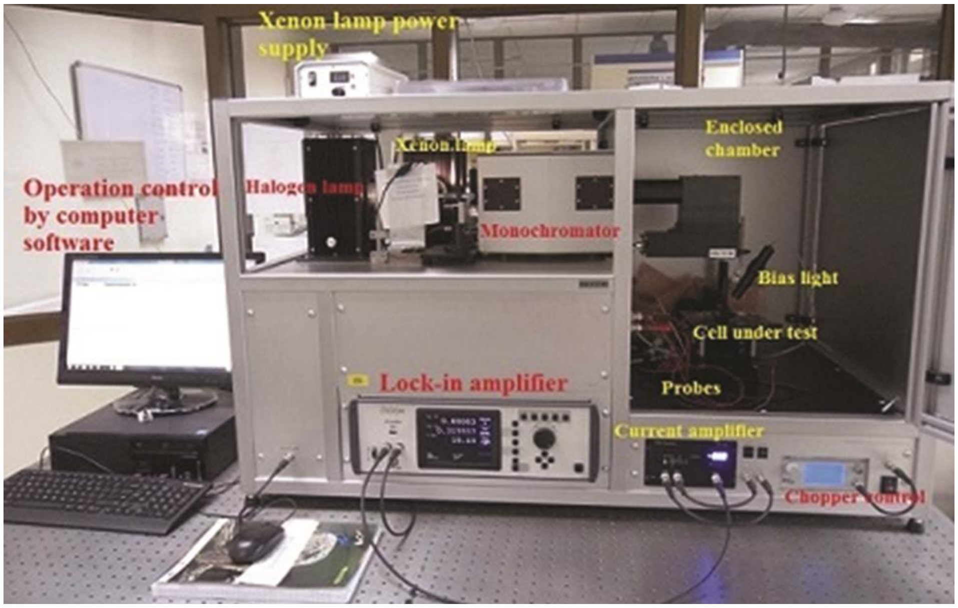

Fig. 12 — A photograph of IPCE measurement system showing its important components.

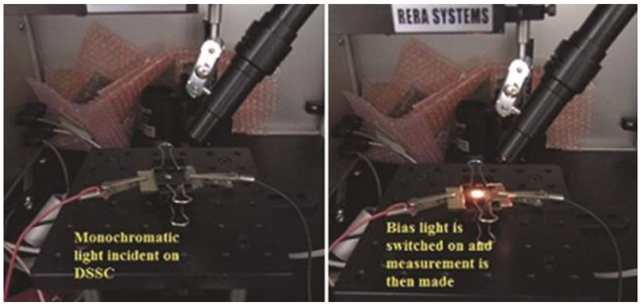

Fig. 13 — Monochromatic light and bias light incident on DSSC during measurement.

adjusted so that the monochromatic illumination falls on it and bias light is turned on. The IPCE spectrum is then recorded by the instrument using a computer program and displayed on the computer screen.

Figure 14 shows the IPCE spectrum of the DSSC, whose *I*-*V* curve is shown in Fig. 11. The photocurrent density calculated by integrating the IPCE spectrum is ~10 mA/cm^2. It is expected since the chopping frequency used is 20 Hz, which is much higher than the frequency required for measuring DSSCs[9,10].

3 Discussion

The process parameters described above have been optimized over a period of more than two years and, if followed properly, can easily result in DSSCs with efficiencies greater than 7%. The compact layer has been shown to result in an increased V_{OC} and better meso-TiO_2 film contact with FTO substrate and should be considered an important part of the DSSC fabrication process[11]. Also, the $TiCl_4$ post treatment of a complete bilayer TiO_2 film is an essential step which not only improves the adhesion and integrity of the film, but also passivates the surface defects of TiO_2. This improves the electron transport process and increases effective electron lifetimes in DSSC[12,13].

The procedures described above can also be used for fabricating efficient perovskite solar cells (PSCs) which are a highly active area of research at present[14,15]. The PSCs employ a very thin layer of meso-TiO_2, typically 150-300 nm compared to ~10 µm for DSSCs, which can be easily deposited by spin-coating technique after suitably diluting the TiO_2 paste in ethanol. The compact layer deposition and $TiCl_4$ treatment procedures remain the same as in the case of DSSCs. Thus prepared FTO substrates can subsequently be used for perovskite deposition.

While characterizing a DSSC, or any other excitonic solar cell like organic/polymer solar cell and perovskite solar cell, it is very important that a proper mask be used during *I*-*V* and IPCE measurements. In *I*-*V* measurements, a proper masking is of utmost importance if the measured efficiency is to accurately estimate the actual device efficiency[16]. The chances of error due to stray and scattered light are very high when a mask is not used. For IPCE measurements, the chopping frequency and bias light should be proper. A standard protocol for measurements is necessary, if a fair comparison between literature values and the values obtained in the lab is to be made.

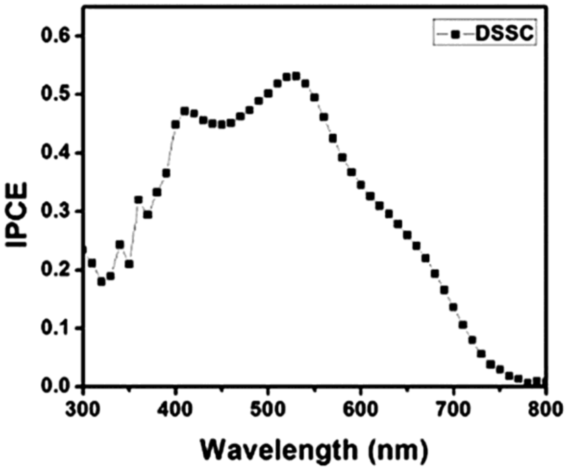

Fig. 14 — IPCE spectrum of the DSSC, whose *I*-*V* curve is shown in Fig. 11.

4 Conclusions

We have presented a detailed procedure for fabrication and characterization of high efficiency DSSCs. The fabrication and characterization steps are also presented in photographs for easy visualization. Some important points to be considered while fabricating and characterizing a DSSC are also discussed. It is expected that students and researchers, at all levels, will benefit from this photographic guide and will adopt a standard protocol for characterization of solar cells. The present work aims to promote DSSC research in the country by providing a step-by-step reference guide that will enable the researchers to fabricate high efficiency DSSCs in their own laboratories.

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