



Third-Generation Photovoltaics: Dye-Sensitized Solar Cells (DSSC)

Abdul Hai Alami[✉], Shamma Alasad[✉], Haya Aljaghoub[✉], Mohamad Ayoub[✉], Adnan Alashkar[✉], Ayman Mdallal[✉], and Ranem Hasan[✉]

Abstract

The investment in new PV technologies is important and is done by exploiting novel materials, materials processing, and manufacturing techniques to achieve performance levels that supersede those attained by classical counterparts. This chapter covers the unique materials and procedures utilized to produce dye-sensitized solar cells of the third-generation technologies. The chapter also includes a do-it-yourself project to provide the reader with a chance to build and test a dye-sensitized solar cell.

1 Introduction

Third-generation photovoltaics technologies have emerged recently to replace conventional silicon-based ones. Using alternative materials and processing technologies is important to explore higher device efficiencies at lower costs. The manufacturing technologies, however, will utilize thin-film (second-generation deposition) techniques with minimal

modifications. The main goal remains to minimize the cost per Watt peak, in addition to using nontoxic and abundant materials, just like the traditional Si-based solar cells, and second-generation thin-film technologies (Conibeer 2007).

According to findings from a study conducted by the National Renewable Energy Laboratory on the top efficient cells in the renewable energy industry, there are three main varieties of third-generation solar cells (and their modified variants): (i) Dye-sensitized solar cells (DSSC), (ii) Organic photovoltaics (OPV), and (iii) Perovskite solar cells (PSC). The variants are enhancements for the above three, such as monolithic, organic tandem, copper zinc tin sulfide (CZTSS), and quantum dot cells.

With the independence from silicon and its processing equipment and technologies, chemical companies such as the Canadian giant DuPont entered the PV materials market. They focused on allocating some of their product lines to be suitable and compatible with equipment and processes to produce third-generation solar PV cells, especially OPV. What the NREL-reported results lacked was the association of output power or efficiency with the associated costs of producing the cells. Figure 1 shows this association for all three PV generations, with first generation cells having high production cost and consistent, but low efficiency. Second-generation technologies have low cost and low efficiency. The technologies that have the best promise are third generation which reside in the low cost/high efficiency quadrant (CleanEnergyWIKI 2022).

The first gray area in the graph of Fig. 1 is the thermodynamic limit (theoretical limit) which cannot be exceeded. It is similar to the Carnot cycle efficiency limit. The second gray area represents the single bandgap limit for a single heterojunction cell. To have more than one bandgap means to build and test a tandem solar cell, where the light absorbers are arranged in a layered way, with the one with a bigger bandgap being placed at the top.

A. H. Alami (✉) · H. Aljaghoub · M. Ayoub · A. Mdallal · R. Hasan
University of Sharjah, Sharjah, United Arab Emirates
e-mail: aalalami@sharjah.ac.ae

H. Aljaghoub
e-mail: haljaghoub@sharjah.ac.ae

M. Ayoub
e-mail: mohamad.ayoub@sharjah.ac.ae

A. Mdallal
e-mail: ayman.mdallal@sharjah.ac.ae

S. Alasad · A. Alashkar
American University of Sharjah, Sharjah, United Arab Emirates
e-mail: g00070854@aus.edu

A. Alashkar
e-mail: b00028197@alumni.aus.edu

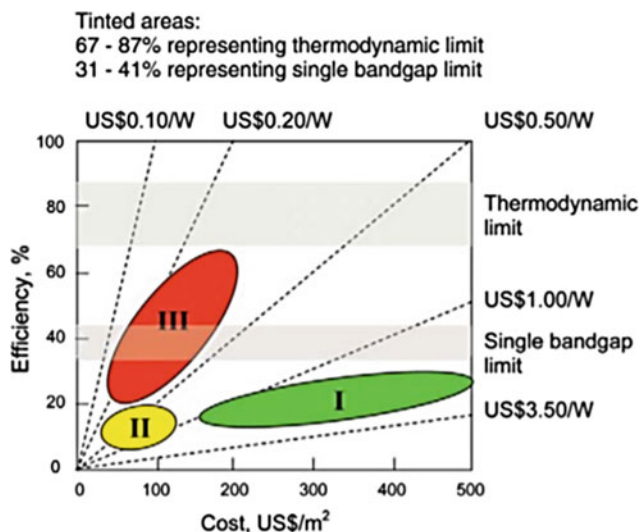


Fig. 1 Cost-efficiency graph, where costs are modules per peak W (CleanEnergyWIKI 2022)

1.1 Roll-To-Roll (R2R) Manufacturing

Thus, the main goal of developing third-generation photovoltaics is to reduce the cost and provide consistent efficiency. This should be done via manufacturing processes amenable to mass production, or what is known as roll-to-roll (R2R). If this is done, the PV modules can be printed in ways similar to how newspapers or magazines were printed decades ago. Instead of the Cyan, Magenta, Yellow, and Black (CMYK) colors, active precursors are used through nozzles and slots on temperature-controlled substrates and different processing conditions. It is said that if the PV rolls are produced at 60 km/hr, then one year would be enough to produce PV modules to cover the world energy needs.

The major problems that preclude these technologies from achieving their desired status include their limited lifetime and compatibility, since these solar cells are not guaranteed to last for 25 years as their silicon counterpart. Also, most of the technologies require a strictly pristine and controlled environment (i.e., in a Glovebox), which means that their operation in their real environment cannot be predicted. It is, however, interesting to mention that it is possible that third-generation solar cells may achieve efficiencies higher than the 31–41% power efficiency range established by the Shockley–Queisser limit, since their bandgap can be tuned and manipulated, which keeps the door open for R&D work to allow their performance and economics to be truly competitive.

1.2 Third-Generation PV Cell Structure

Third-generation photovoltaics can be considered as electrochemical devices. This is a main difference between them and the strictly solid-state silicon solar cells, as shown in Fig. 2. For third-generation photovoltaics, there are two mechanisms of charge transfer after the charge generation due to incident solar radiation. The first mechanism occurs after incident radiation produces the electron/hole pairs and electrons are guided to the external circuit directly. The second mechanism involves a series of redox reactions at the surface of the photoanode and the electrolyte as well as at the interface between the electrolyte and the counter-electrode that will receive the electron after it passes through the external load.

From a manufacturing point of view and as will be seen later, most third-generation photovoltaic materials are built upon a transparent glass substrate. This substrate allows subsequent strata of active materials to be deposited on a smooth and perfectly straight base. Titanium dioxide (TiO_2) or titania is another common denominator for all third-generation technologies. Titania is a very porous material upon which active materials can intercalate and attach. Also, to make the transparent photoanode conductive, a transparent conductive oxide (TCO) layer is added. This layer is composed of indium-tin oxide (ITO) or fluorine-doped tin oxide (FTO) and deposited on the nonconductive glass. Such oxides have sheet resistance less than $30 \Omega/\text{square}$ and reflectivity of around 10%. Making such layers more transparent and more conductive requires a strict balance of two opposing factors. To be more conductive, an opaque metal is ideal, but this takes the transmission down to zero, and thus, an optimization has to be made.

2 Dye-Sensitized Solar Cells (DSSCs)

From a manufacturing standpoint, the most straightforward third-generation solar cell technology is the dye-sensitized solar cells. There is a biomimetic aspect to how light interacts with the solar materials that is similar to photosynthetic activities in plants and some aquatic creatures. The titanium dioxide in the photoanode is “sensitized” when a dye is introduced to shift the material’s absorbance from the UV “Ultraviolet” to the visible spectrum range. Figure 3 shows the absorbance of TiO_2 under UV radiation, which happens in a strictly narrow range. Since the target range is around 500–600 nm, a dye is added to the titania to allow this shift and utilization of incident solar radiation.

Fig. 2 **a** General structure of a solid-state silicon photovoltaic technologies and **b** photo-electrochemical third-generation technologies

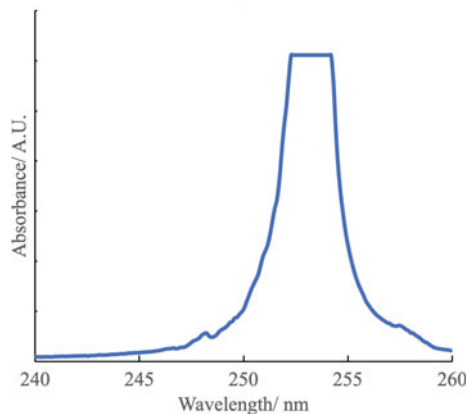
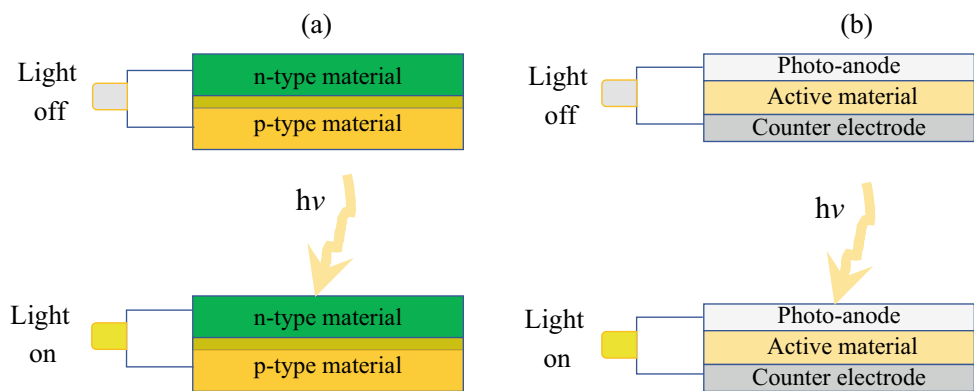


Fig. 3 Titanium dioxide (TiO_2) absorbance in the UV range

Dyes are ligands, which are ions or neutral molecules that function as Lewis bases (electron pair donors) and bond to a central metal atom or ion, also behaves as a Lewis acid (electron pair acceptor). A covalent bond is formed with the central atom using ligands consisting of at least one donor atom with an electron pair. Ligands allow for the production or consumption of electrons in the ionic state and can attach to the surface of the TiO_2 material and allow for the shift in its absorbance from UV to Vis as will be detailed later. When a semiconductor is sensitized, sensitizers are adsorbed on its surface. They are responsible for the absorption of visible light, which results in the subsequent injection of excited electrons into the conduction band of the semiconductor electrodes.

2.1 Grätzel Cell

These biomimetic devices are a major shift from conventional silicon solar cells and were produced in 1992 by Michael Grätzel at the Ecole Polytechnique in Switzerland (O'Regan and Grätzel 1991). There was no boron or phosphorus doped Si p-n junction present in this cell. The result is a photo-electrochemical cell, which functions similarly to

a photosynthetic plant cell. Since the Grätzel cell is so cheap and simple to produce, it has attracted a lot of interest and served as a foundation for further research.

The cell structure is based on the following main components:

1. Photoelectrode (photoanode)
2. Electrolyte (reduction/oxidation)
3. Dye (in the heart of the cell)
4. Counter-electrode.

The operation at a glance:

In a dye-sensitized solar cell, the dye is the engine that drives the device (operates like chlorophyll in a photosynthetic plant cell). The dye is often an organometallic complex based on ruthenium, but other natural sensitizers can be used; however, they bear lower efficiencies. In order to capture photons, the dye is essential (by generating excitons), i.e., when a photon hits the dye, an electron is excited from the ground state (HOMO) into the first excited state (LUMO), leaving behind a hole. For the semiconducting layer, titania is not the only option as zinc oxide (ZnO) and tin oxide (SnO_2) can also be used. TiO_2 is the most prominent one for use in cell manufacture because of its ultra-porosity, which provides anchoring locations for dyes as well as ample area for redox reactions to take place.

2.2 DSSC Cell Structure

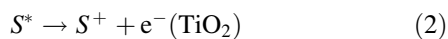
The cell building takes place over a lime soda glass substrate. Although it is a nonconductive material, it allows solar radiation to pass into the active material. Once the light hits the active material (TiO_2), it will start to produce electrons. In order to collect the electrons, it is necessary to apply a transparent conductive oxide (TCO) to the glass in the form of indium-tin oxide (ITO) or fluorine-doped tin oxide (FTO) so that charge can be conducted. ITO is transparent, conductive, and has sheet resistance of $30 \Omega/\text{square}$, while

the fluorine doping reduces the sheet resistance further to 15 Ω /square. The counter-electrode (Al, Au, Ag, etc.) is put on top of the TiO_2 , and in between the electrolyte is injected which helps to close the circuit electrochemically. The dye operates like chlorophyll in a photosynthetic cell. Dyes could be natural sensitizers or synthetic. Ruthenium-based organometallic synthetic dye is often used and is responsible for harvesting the photons and generating excitons (electron/hole pairs). Figure 4 shows the cell structure.

Once a photon hits the dye, an electron will be excited from the ground state, which is located in the highest occupied molecular orbital (HOMO) and will move into the lowest unoccupied molecular orbital (LUMO), producing excitons and leaving behind a hole. The most significant thing in DSSC is that the generation of e^- and h^+ are occurring in two different locations. As will be seen later in this chapter, the substrate and enhancer selections have a significant impact on the resulting voltage levels in practice.

3 Operating Mechanism

The TCO-coated electrode (e.g., SnO_2 /glass) consists of a nanocrystalline oxide semiconductor thin-film electrode (TiO_2 or ZnO), a sensitizer (dye) is adsorbed on the surface of the TiO_2 electrode, and the TiO_2 electrode absorbs the incoming photons, causing a transition from the ground state (S) to the excited state (S^*). An electron moves from the sensitizer's HOMO to its LUMO during photoexcitation. Here are the equations for how the oxidation of the sensitizer molecule occurs, as a consequence of the of the propulsion of the excited charge carriers from the valence band to the conduction band of the TiO_2 layer (photo-electrode). The redox ions are contained inside the electrolyte.



Electrons are not only transferred from singlet states, where all electrons are paired, but also from triplet states that include two unpaired electrons. This is due to the high energy states. Next, the injected electrons permeate through

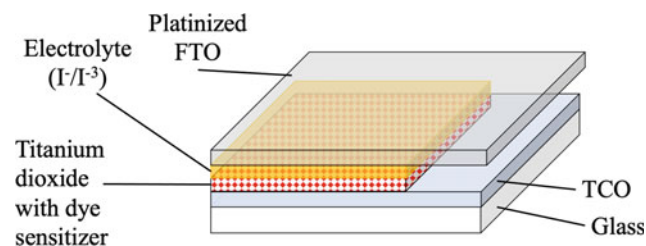


Fig. 4 Simplified DSSC cell structure

the TiO_2 electrode to the transparent conducting oxide (TCO) electrode. The ground state of the oxidized sensitizer is regenerated when it is reduced by the I^- ions that are present in the electrolyte, and the I^- ions themselves are oxidized into I_3^- ions during this process. Because of this, I_3^- ions move toward the opposite electrode, where they are reduced to I^- ions. Figure 5 depicts the operation of DSSC under illumination.

4 Energy Levels and Recombination Prevention

If the hole and the excited electron are not separated by two different and separate media, then recombination will occur. Keep in mind that the anode, composed of nanostructured titania (TiO_2), serves as the electron transport layer (ETL) and receives the excited electrons. Titania is a mesoporous material that is annealed to be in its anatase structure (rather than rutile), and the pore structure of titania ranges from 2 to 50 nm in size. The titania matrix receives dye molecules, where ligands bond to titania. Electrons can then transfer quickly from the LUMO of dye molecules to the lower energy of titania conduction band. Figure 6 below displays a typical energy diagram.

The hole should be directed to the opposite side of the cell (the cathode). This is also referred to as the hole transport layer (HTL). An iodide/triiodide (I^-/I_3^-) redox couple was used in the first Grätzel cell. The iodide would regenerate the oxidized dye molecules and the resulting oxidized species (triiodide) are transported to the cathode via diffusion, where they are reduced back into iodide. Since diffusion is a physical phenomenon, it is sensitive to the density,

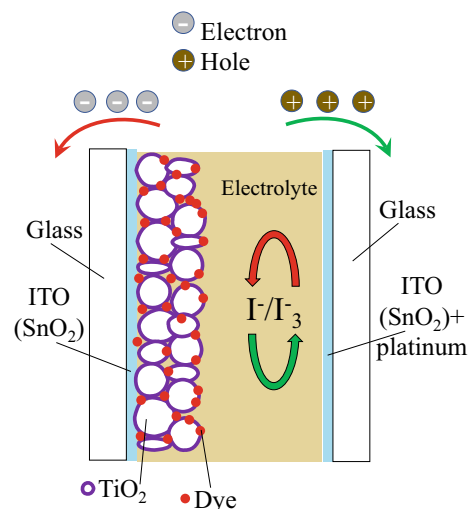


Fig. 5 Dye-sensitized solar cells principle of operation

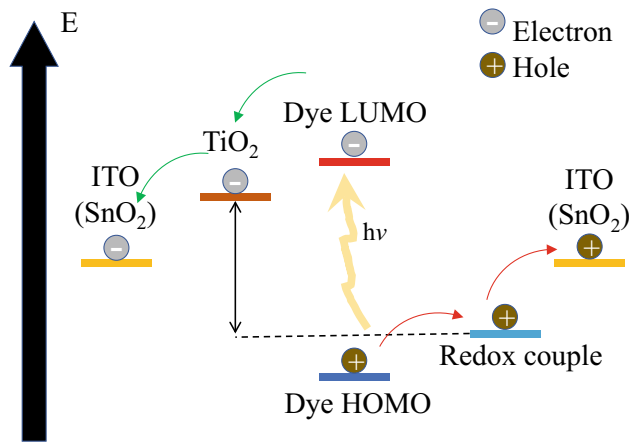


Fig. 6 Dye-sensitized solar cell's typical energy diagram

concentration, and viscosity of the electrolyte (solute/solvent ratio and type).

5 Generated Voltage

The open-circuit voltage in DSSC depends on the interaction between different material layers and their work functions under illumination. The effective voltage obtained is measured between redox couple and dye LUMO, and hence, any enhancements of this voltage have to happen at this interface. The difference in energy that exists between the Fermi energy of the electrons in TiO_2 , and the redox potential of the liquid electrolyte is what determines the maximal photovoltage that may be achieved. TiO_2 's conduction band and the HOMO level of the hole transport layer (HTL) material combine to provide the highest possible voltage for a solid-state device. The practical voltage values depend on many factors such as the type of material used. The maximum V_{oc} obtained is 0.7 V, and the maximum efficiency is 11% (13% in 2022). In cells that utilize Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) and poly(4-undecyl-2,20-bithiophene) (P3PUT), the photovoltage is differed by 0.7 V, although their HOMO levels are 1 eV apart.

Recombination is the leading cause for fewer electrons to perform the desired work. It also reduces the anode's voltage and Fermi energy of electrons. Furthermore, the less holes that reach the cathode, the more energy the electrons will gain at the cathode. This adversely affects the photovoltage, measured from the difference between two electrodes.

Grätzel cells still have not reached their full industrial potential, but improvements to their three main components (Dye, ETL, HTL) as well as increased reliability and a longer lifespan will help get them there. These factors are discussed the following sections.

6 Space Charge and the Electric Field

In silicon solar cells that utilize p-n junctions, the active junction is formed when electronic charge carriers from different components balance out, creating a space-charge region. In the space-charge layer, the electric field effectively separates the photogenerated charges.

In third-generation PV and in DSSC in particular, there are no space-charge effects as there is no long-range continuum of host material. The titania has individual particles with nano-dimension size (~ 20 nm), which is not thick enough to produce a space-charge layer. Also, cations at the counter charges of I^-/I_3^- redox couple in electrolytes act as a filter for electrons in the electrode, which results in the absence of a potential gradient in the electrode. The first step in the process of charge separation is completed when electrons are injected into the semiconductor (titania) and holes are injected into the electrolyte.

7 Depletion Zone/Charge Separation

Contrary to conventional PV cells, where the charge carrier separation happens under the influence of a built-in electric field, the charge separation in DSSC happens due to the chemical interface and energy level differences between the different layers. For example, once the electrons are generated in the sensitizer media, they are transferred into the TiO_2 layer and subsequently into the transparent conductive oxide layer (i.e., ITO). Moreover, the consequently generated holes are transferred via the I^-/I_3^- electrolyte and finally to the counter-electrode. A similar phenomenon can be found in the photosynthesis process in plants, where a synthesizer (chlorophyll) generates charge carriers that are transferred via a membrane in the living organism.

For all solar cells, the following equation may be used to determine their individual efficiency (%) in transforming solar energy into electricity:

$$\eta(\%) = \frac{J_{sc} [A \cdot m^{-2}] \times V_{oc} [V] \times FF}{I_0 [W/m^{-2}]} \times 100 \quad (3)$$

where I_0 is photon flux (100 mW cm^{-2} for Air Mass 1.5G (AM 1.5 G)), J_{sc} is the short-circuit current density (at no voltage) when under illumination, V_{oc} represents the open-circuit voltage, and FF is the fill factor.

8 Open Circuit Voltage Considerations

The energy gap between the Fermi level and the TiO_2 electrode is used to measure the open-circuit voltage of the cell (which is located near the conduction band potential or

E_{CB}) and the redox potential of the I^-/I_3^- in the electrolyte. See Fig. 7 for an illustration of where the voltage is measured. The yellow stripes indicate a voltage measurement point. Redox couples have an energy separation of (ΔE_1), which is taken into account as the driving force for electron injection. Therefore, I^- oxidation results in the regeneration of the dye-cation. The HOMO has to be highly positive than the I^-/I_3^- tendency to gain/lose electrons in order to receive electrons efficiently. The value of ΔE_2 represents the difference between these two values. For improved DSSCs with TiO_2 and I^-/I_3^- , ΔE_1 and ΔE_2 are around 0.2 and 0.5 eV, respectively.

Both the E_{CB} value of the TiO_2 electrode and the redox potential in the electrolyte are strongly dependent on the nature and concentration of the electrolyte components and are generally between -0.5 and 0.4 V against normal hydrogen electrode (NHE), respectively. Currently, optimized DSSCs show V_{oc} in the range of 0.75 – 0.85 V, whereas the greatest V_{oc} achieved for DSSCs with a TiO_2 electrode and the I^-/I_3^- redox medium is typically around 0.9 V.

9 Short Circuit Current Considerations

The short-circuit current density J_{SC} is determined by the product of the charge injection efficiency φ_{inj} , the charge collection efficiency η_c , and the light harvesting efficiency (LHE) which is given by the following formula:

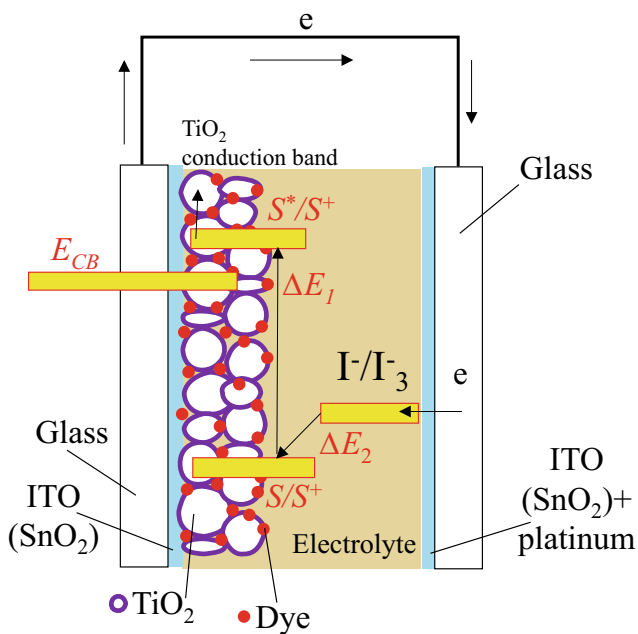


Fig. 7 A typical DSSC construction with voltage reference points highlighted in yellow

$$LHE = 1 - T = 1 - 10^{-A} \quad (4)$$

where T represents radiant transmission and A represents radiant absorption. The LHE is obtained by determining the electrodes effective absorption coefficient. TiO_2 electrode thickness, adsorbed dye concentration, and sensitizer extinction coefficient each have a contribution.

The photo response range of the cell is set by its bandgap (HOMO–LUMO difference). The higher the bandgap, the better in order to allow higher energy to go to the cell. In order to take advantage of a larger spectrum of solar radiation, it is necessary to have a narrow HOMO–LUMO energy gap. The LUMO must be more negative compared with E_{CB} to have high φ_{inj} .

10 Surface Area Considerations

High LHE is obtained when incident photons are completely absorbed by the sensitizer. TiO_2 nanoparticles offer a huge surface area for dye molecules to adhere. In fact, TiO_2 electrodes have a surface area that is almost a thousand times bigger than their apparent surface area, as measured by a roughness factor (r_f). In other words, the actual surface area of a TiO_2 film measuring 1 cm^2 with a thickness of 10 μm is 1000 cm^2 . This also means that if the r_f of the nanoporous TiO_2 film is high, the dye adsorption will be very high (by a quantity of the order of 10^{-7} mol cm^{-2}), resulting in almost complete absorbance at the dye spectrum absorption's peak wavelength.

11 Charge Collection Efficiency

Electron diffusion length (L) is used to determine charge collecting efficiency:

$$L = \sqrt{D[m^2/s] \cdot \tau[s]} \quad (5)$$

where D is the diffusion coefficient for electrons in nano-sized pores in semiconductor electrodes, and τ represents the electron lifetime in the electrode, which is measured by the rate of recombination at the interface between the electrode, dye, and electrolyte.

Due to the different nature of liquid-based and solid-state DSSC, the diffusion length of the electrons with them varies accordingly. As to capture the generated electrons, their diffusion length must be higher than the cell's materials thickness. For liquid-based DSSC, the diffusion length is in the tens of micrometers; in an optimized DSSC, the resultant collection efficiency would be bordering 100%. However, in solid-state DSSC, the diffusion length is shorter, which is

why they require more efficient sensitizers to make up for any potential collection losses.

12 The Fill Factor

The fill factor (FF) is affected by the solar cell's shunt and series resistances. In addition to charge recombination at the TCO/electrolyte interface, interfacial charge recombination contributes to the shunt resistance. Shunt resistance should be decreased, which is achieved by finding materials that are better compatible with each other. The electrolyte thickness may be decreased, the concentration can be increased, and the surface area of the platinum counter-electrode can be increased to in order to decrease the series resistance. The FF may also be connected to the rate of potential-dependent electron transfer or transport when exposed to light.

13 Components of DSSC

To construct a functioning DSSC, the following components should be present, and their interactions optimized:

1. TCO Electrode
2. Nanocrystalline TiO_2 Photoelectrode
3. TiO_2 nanoparticle
4. Ru-complex photosensitizer
5. Redox electrolyte
6. Counter-electrode
7. Sealing materials, used to eliminate leakage of electrolyte and solvent evaporation. For example, co-polymers such as Surlyn Du Pont, which is a mixture of ethylene and acrylic acid, are used.

13.1 TCO Electrode

Substrates for TiO_2 photoelectrodes typically consist of TCO-coated glass. High solar cell performance is achieved by ensuring the TCO substrate has a high conductivity (low sheet resistance) and transmittance (transparency). Sintering of the TiO_2 electrode typically takes place between 450° and 550°C ; therefore, the conductivity should be temperature independent up to these temperature extremities. The TCO resistance is measured by the four-point probe technique. A multimeter is a handy tool to know which surface has the TCO deposition, and it can also be used to estimate the resistance between the two multimeter probes knowing the distance between them. This procedure carries many sources of errors, and thus, a four-probe setup like the one shown in Fig. 8 has a pre-set distance (x) between the probes and

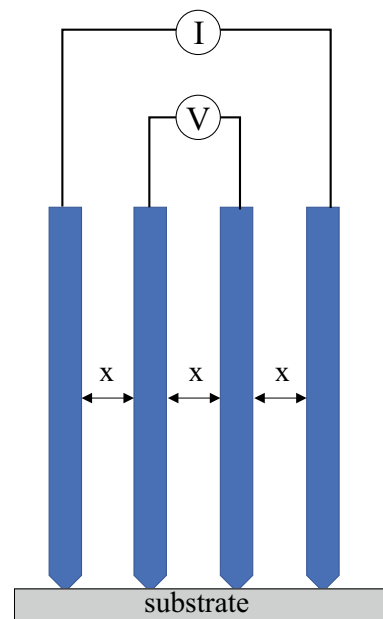


Fig. 8 Four-probe test to determine the sheet resistance of glass with TCO

offers separate voltage and current readings to enhance the accuracy.

Indium-tin oxide (ITO) is the most common TCO material. Despite its low resistance at room temperature, ITO has a poor thermal stability of resistance. Nippon Sheet Glass Co. and other manufacturers employ FTO (fluorine-doped SnO_2) as the TCO substrate for DSSC. (nsg.com), or Asahi Glass Co. Ltd. (agc.com) that produce glass with sheet resistance in the range of $R = 8\text{--}10 \Omega/\text{square}$. Plastic DSSCs may employ ITO-coated poly(ethylene terephthalate) (PET) or poly(ethylene naphthalate) (PEN) as a substrate if TiO_2 electrode preparation can be done at temperatures under 200°C .

13.2 Nanocrystalline TiO_2 Photo-Electrode

In this and any other electrochemical system, the essential function of an electrode is to offer adequate surface area for dye adsorption, which is why porous electrodes are preferred over their counterparts, to transport all injected electrons to TCO, and to enable redox reaction to take place. Electrodes have to be transparent in order for visible and near-infrared radiation to pass through (wavelengths between ~ 380 and 1000 nm). The absorption coefficients of the sensitizers dictate the required penetration depth for the photons to be absorbed, which is why the porosity of the electrode (measure of the present surface area) and its thickness are important parameters (while taking into account the diffusion length of electrons).

For typical cells, the best thickness of porous electrodes is 10–20 μm . Electrodes utilize commercial nanocrystalline TiO_2 , such as P25 Degussa/anatase (see sigmaaldrich.com) and ST-21 from Ishihara Sango Kaisha Ltd. (see <https://www.iskweb.co.jp>). TiO_2 has to be in nanoparticles form with maximum particle size of 20 nm that can be obtained from the hydrolysis of Ti (IV) alkoxides. It is necessary to exercise control over the hydrolysis and condensation kinetics in order to generate monodispersed particles of the required size. Acetic acid (or acetyl acetonate) treatments are carried out on titanium alkoxides to obtain colloids with relatively large porosity-induced surface area density, with values reaching 200 m^2/g . However, an adverse effect is witnessed on the particle size, where a reduction up to a diameter of 7 nm was present.

13.3 Preparation of the TiO_2 Electrode

To begin the process of preparing the TiO_2 electrode, initially a TCO substrate is covered with the TiO_2 paste employing screen printing, spin coating, or doctor blading and then heated at temperature in the range of 450–550 $^\circ\text{C}$ to transform the TiO_2 into the desired porous anatase structure. The target thickness of the TiO_2 is around 10 μm , which requires multiple runs in the spin coater or doctor blading. In screen printing, film thickness can be controlled by (i) proper paste composition selection (i.e., TiO_2 nanoparticles wt % in the paste), (ii) screen mesh size, and (iii) printing repetition. It is also important that the TiO_2 film is porous enough to enable the electrolyte holding the redox ions to permeate it, allowing the redox ions to access all the adsorbed dyes and diffuse again to the counter-electrode. Some enhancements to film production such as the addition of a polymer (polyethylene glycol (PEG) and ethyl cellulose (EC) into the TiO_2 paste control the porosity of 50–70% in the sintering process. Adding surfactants also helps enhance the surface adhesion and can be fired away during sintering operation.

13.4 Adsorption Properties of Dyes

Dye is added to enhance the sensitivity of the cell and absorption of longer wavelengths. This is true for all types of dyes, natural and synthetic. The former can consist of either chlorophyll (green) or anthocyanin (red), and the latter uses Ru-complex sensitizer. Being adsorbed onto the TiO_2 surface, it aids in the initial processes of photon absorption and the subsequent injection of electrons. Grätzel's typical Ru-complex sensitizers' chemical structure is seen in Fig. 9a, and their absorption (solid lines) and transmission (dashed lines) properties are illustrated in Fig. 9b (Nazeeruddin et al. 2004).

The metal-to-ligand charge-transfer (MLCT) transition is responsible for these dyes' absorption in the visible and near-IR ranges. The d-orbital of the Ru metal and the π^* of the ligand provide the basis for the HOMO and the LUMO, respectively. The absorption characteristic of the complex is shifted toward the red because the NCS ligand accepts electrons from iodide ions and causes a negative HOMO level shift.

Among the visible wavelengths of light, blue has the greatest frequency while red has the lowest. A redshift occurs when an object moves away and the light is stretched to lower frequencies and longer wavelengths. On the other hand, a blueshift occurs when the wavelength is decreased, which is associated with an increase in frequency of electromagnetic waves. The color is changed in visible light, moving from the red to the blue ends of the spectrum.

13.5 Dye Preparation

As will be further discussed in the case study at the end of this chapter, the steps for dye preparation are as follows: The Ru-complex sensitizers are dissolved in a 1:1 mixture of ethanol or tert-butanol and acetonitrile at a concentration of 0.2–0.3 mM. After the electrodes have been preheat-treated and coated with TiO_2 , they are submerged in the dye for more than 12 h at 25 $^\circ\text{C}$ to enable the dye to adsorb to the TiO_2 surface. Because of the strong electrical interaction between the ligand and the TiO_2 conduction band, electrons may be effectively injected from the Ru-complex into the TiO_2 upon attachment of the carboxyl groups of the Ru-complex to the TiO_2 surface. Analysis of FT-IR absorbed energy show that the Ru-complex is adsorbed on the TiO_2 surface through carboxylate bidentate coordination or ester bonding. Because of the TiO_2 surface area and the dye quantity, the N3 dye covers approximately 100% of the TiO_2 surface.

13.6 Redox Electrolyte

Electrolytes utilized in DSSCs include I^-/I_3^- redox ions, which enable the transfer of electrons between the sensitizers and the counter-electrode. Lithium iodide, sodium iodide, potassium iodide, tetraalkylammonium iodide (R4 NI), and imidazolium-derived iodides in nonprotonic organic solvents at concentrations of 0.1–0.5 M (M: molar concentration) and 0.05–0.1 M I₂ are all examples of iodide mixtures. DSSC often makes use of nitrile solvents, which are organic solvents with a relatively low viscosity. Some examples of these solvents are acetonitrile, propionitrile, methoxyacetonitrile, and 3-methoxypropionitrile. Solvent viscosity is very important as it impacts the electrolyte ionic

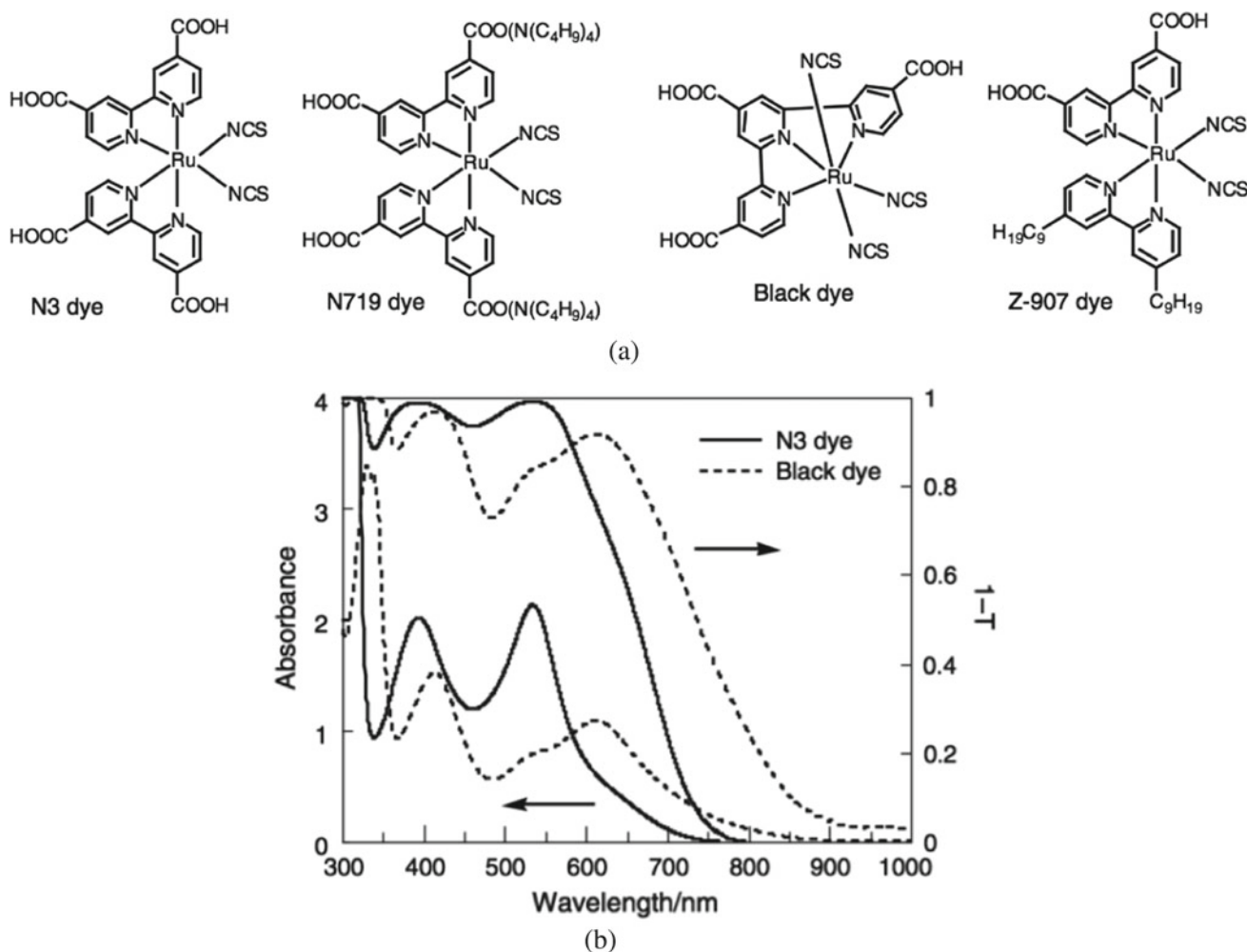


Fig. 9 a Chemical structure of ruthenium-based synthetic sensitizers and b absorbance in the UV–Vis region for the N3 and black dyes (nm) (Nazeeruddin et al. 2004). (With permission 5,364,120,164,714)

conductivity and hence, the solar cell's performance. Low viscosity is desired to enhance the J_{sc} of the solar cell, but the problem is that it is going to evaporate, and whose long-term seal is similarly difficult to achieve. On the contrary, high viscosity results in harder ionic motion and thus low current. The diffusion coefficient of I^{-3} in methoxyacetonitrile = $5.4 - 6.2 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$, which is the best range.

13.7 Counter-Electrode

At the counter-electrode, the triiodide ions I_3^- , which are produced when dye cations are reduced with I^- ion, are oxidized back to I^- ions. The electrocatalytic process involving the reduction of triiodide ions requires a counter-electrode with a high level of electrocatalytic activity. The counter-electrode functions as a collector of the positive charges (holes), and this is where the reduction of

the electrolyte takes place. A good conductive material which has a good catalytic activity should be utilized. The material used as a counter-electrode could be 100% platinum, but its main issue is the high cost. The counter-electrode consists of sputtered Pt coated on a TCO substrate ($5-10 \mu\text{g}\cdot\text{cm}^{-2}$ or around 200 nm thickness). Pt colloids are formed on the surface of a TCO substrate with a sputtered layer of Pt on top of it, by dropping a controlled quantity of an alcoholic solution of H_2PtCl_6 over the surface, drying it, and then heating it at 385°C for 10 min. Resistance of the counter-electrode and electrolyte interface have an impact on the solar cell's fill factor. Polymers and carbon-based materials (i.e., PEDOT) are the other alternatives for the counter-electrode instead of Pt. The electrocatalytic activity required for the reduction of triiodide ions corresponds to an exchange current density of $0.01-0.2 \text{ A cm}^{-2}$. Pt is not the only material suitable for use as a counter-electrode; carbon and polymers like PEDOT are other viable options.

14 Performance of Highly Efficient DSSCs

Incident photon-to-current conversion efficiency (IPCE) is calculated from:

$$\text{IPCE}(\%) = \frac{1240(eV \cdot \text{nm}) \times J_{\text{ph}}}{\lambda \times \phi} \times 100 \quad (6)$$

where the constant 1240 has the energy unit of electronvolt (eV) multiplied by the wavelength unit of nanometer (nm), J_{ph} (mA cm^{-2}) designates the short-circuit photocurrent density when exposed to monochromatic irradiation, λ (nm) and ϕ (mW cm^{-2}) are the wavelength and intensity of the external monochromatic light, respectively. The highest IPCE is typically lower than 90%:

$$\text{IPCE} = \text{LHE} \times \phi_{\text{inj}} \times \eta_c \quad (7)$$

where LHE is the light harvesting efficiency, ϕ_{inj} is the electron injection efficiency, and η_c is the collection probability of charge carriers (charge collection efficiency).

14.1 Performance of Ru Sensitizer-Based DSSCs

Ru sensitizer are standard and give the best FF and η . The high η values, more than 11% were obtained with DSSC, e.g., with N719 dye ($J_{\text{sc}} = 17.7 \text{ mA cm}^{-2}$, $V_{\text{oc}} = 0.846 \text{ V}$, FF = 0.75), and with black dye ($J_{\text{sc}} = 20.9 \text{ mA cm}^{-2}$, $V_{\text{oc}} = 0.736 \text{ V}$, FF = 0.72).

14.2 Mechanism of Dye to Metal Oxide Electron Injection

Being an electrochemical device, it is important to analyze not only the electronic motion in wires and contacts, but also their physical diffusion behavior across all different layers of the cell. An intramolecular MLCT transition takes place as a consequence of the photoexcitation of a Ru-complex sensitizer. In this transition, the HOMO and LUMO are generated from the d-orbital of the Ru metal and the π^* orbital of the bipyridyl ligand, respectively. Negatively moving the HOMO level (which results in the red shift of the complex's absorbance) is accomplished by the NCS ligands, which are powerful electron donors. In addition, these ligands take electrons donated by iodide ions. Following photoexcitation, excited electrons from the bipyridyl ligands are effectively injected into the TiO_2 electrode's conduction band via the carboxyl groups bonded to the TiO_2 surface.

The oxidation potential of the excited state of the sensitizer is greater, or more negative, than the voltage of the conduction band, E_{CB} , and the difference needed is determined to be larger than 0.2 V as was shown in Fig. 6. Since TiO_2 is nanoporous, it is reasonable to assume that the energy heterogeneity of the nanoporous metal oxide electrode surface is sufficient to produce the necessary ΔE_1 . Ru-based dyes provide quick intersystem crossover from singlet to triplet excited states, followed by injection from the triplet excited state to the conduction band, and thus allows for the detection of injection from the excited state of the dye using a TiO_2 electrode. Hence, electrons will transport mainly by diffusion. The charge diffusion equation is governed by:

$$Q = -D \frac{dc}{dx} \quad (8)$$

where D refers to the electrons coefficient of diffusion and c refers to their concentration. The current response to a slight variation in incident light has been used to calculate the nanoporous TiO_2 material's diffusion coefficient D . As measured by the current response, the diffusion coefficients improved from 10^{-8} to $10^{-4} \text{ cm}^2/\text{s}$ as the light intensity increased, while the value in crystal TiO_2 is on the order of $100 \text{ cm}^2/\text{s}$ (Supriyanto et al. 2019).

Since there exist various charged species with opposite electrical charges, the diffusion coefficient is usually affected by the resulting electric field. The electron current is coupled by a cation current, and the slower current dictates the measured (observable) current. In electrolyte solutions with low cation concentrations, the electron diffusion is additionally constrained by the cation diffusion current rather than only the trapping and de-trapping events. This is known as ambipolar diffusion, the coefficient of which is written as:

$$D_{\text{amb}} = \frac{(n+p)}{(n/D_p) + (p/D_n)} \quad (9)$$

Annealing, which is heat treatment of the nanoporous electrodes, is done to enhance the diffusion and ionic motion of TiO_2 anatase that needs high temperature, unlike TiO_2 Rutile. This process also allows the electron lifetime to be increased with increasing temperature. This is related to the formation of traps at the boundary. Figure 10 shows the electron transfer process through a typical DSSC, along with the mechanism and the time scale at which the transfer can occur. The sensitizer in this case is an N3 one (see <https://www.solaronix.com/materials/products/ruthenizer/>). Figure 10 is a schematic depicting the injection process.

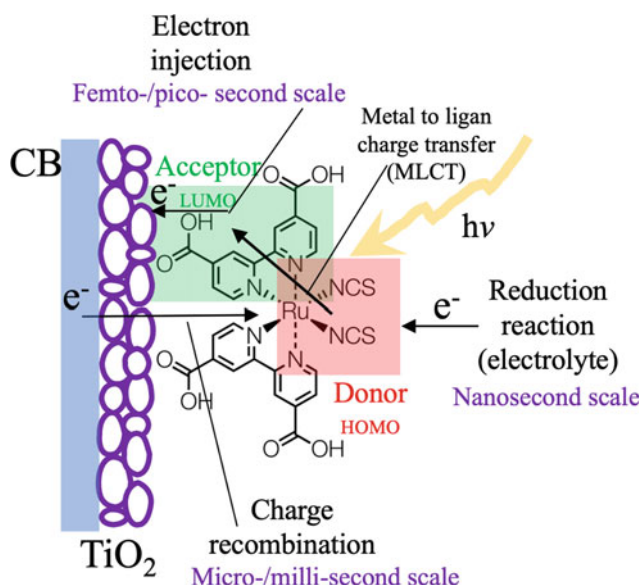


Fig. 10 Electron transfer process in DSSC

14.3 Commercialization

Many aspects have to be perfected in the development of DSSC technologies before they can be commercialized. The high sheet resistance of the TCO electrode on scale-up of the DSSC, which causes a loss of efficiency, is one of the obstacles that has to be solved, along with the primary issues of fill factor, stability, and lifespan in severe environmental conditions. There is also the decision on what size should the DSSC cell be within a module. In Si-based technologies, the wafer size was determined according to restriction of production processes or material properties (surface tension).

Among the many advantages of DSSC production technologies is the ability to deposit the layers on almost any substrate. For example, flexible DSSC deposited on flexible TCO-covered PET substrate is a stark advantage over silicon solar cells. Also, since cell size is not bound except by the substrate size, fabricating large area DSSCs can be done by two ways: either by making small solar cells and connecting them together or by producing large size cells. All the components should have high quality TCO with low resistance. When the DSSC is scaled up, the TCO substrate's sheet resistance rises, which reduces the device's efficiency, specifically its fill factor. In comparison, the efficiency of a cell measuring 3 cm² was 7.6%, while the efficiency of a cell measuring 1 cm² was 8%. A module made up of 12 connected cells with a total size of 112 cm² was able to attain a rate of 7% efficiency. The optimization of cell connectivity remains a topic for future research for third-generation photovoltaics.

14.4 Connectivity Options

There are two main types of module connectivity are the Z-type and the W-type, as shown in Fig. 11. Each TCO substrate has a three-step deposition process consisting of a Z-type connection, a TiO₂ electrode, and a counter-electrode. Because the TCO substrate and separator have been scribed to provide electrical isolation between the cells, it is essential that the cells be connected to one another. For each TCO substrate, a TiO₂-based photoanode and a corresponding counter-electrode are printed, in a W-type connection, eliminating the need for interconnecting them. Because light is illuminated via the counter-electrode in this type, the counter-electrode should be transparent.

15 Do-It-Yourself (DIY) Project and Case Study

The process of constructing a DSSC is simple. This section highlights the most important steps to do so for educational and testing purpose. The project is best executed in a lab setting under a fume hood as it entails using solvents and sintering using heating plates (at 550 °C). The required equipment is detailed below, but said equipment are not difficult to acquire. The authors have also recorded the steps in a video on YouTube (<https://youtu.be/jjpoMzrWrPk>), and simplified procedural steps are given next. A list of materials is presented in Table 1.

- Anionic liquid detergent/deionized (DI) water is used to clean the conductive glass (FTO) substrate before being placed in an ultrasonic bath for 20 min. Following this, the samples are cleaned and immersed in DI water once more before being returned to the ultrasonic bath for another 15 min. The samples are dried in an oven at 70 °C after being rinsed with ethanol, such as shown in Fig. 12.
- Place the electrodes in UV-Ozone treatment for 20 min.
- Prepare TiO₂ paste by mixing TiO₂ powder and polyethylene glycol (1:1 mass ratio), and a drop of surfactant in a mortar.
- Take a swab of TiO₂ paste and blade (spread) it on the FTO electrode.
- Coated photo-electrode to be heated (ramp heating) on a hot plate for 30 min to reach 500 °C and let it cool to 70 °C, the process is shown in Fig. 13.
- Soak TiO₂-coated samples in ruthenium dye solution (ruthenium dissolved in ethanol) for a day (in a dark environment) and then take them out and dry them using a clean tissue; steps are shown in Fig. 14.

Fig. 11 DSSC module connectivity, Z-type (above) and W-type (below)

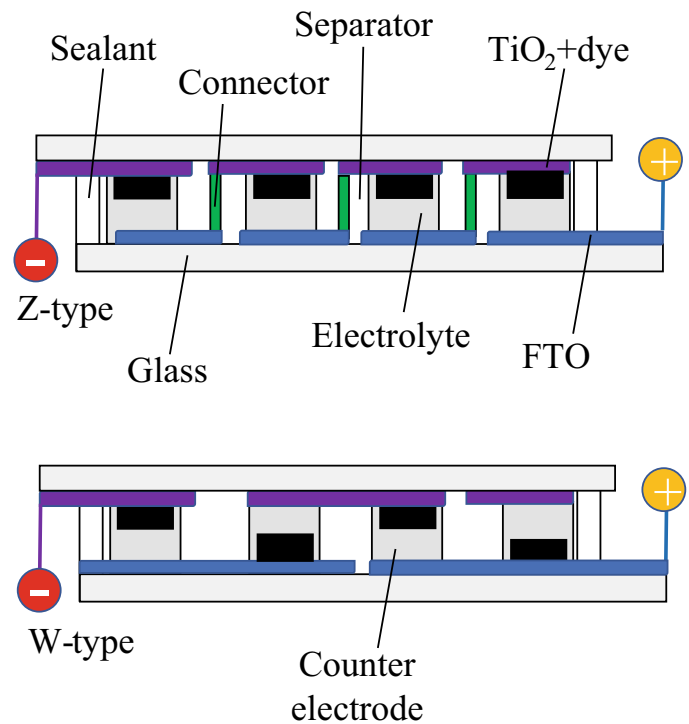


Table 1 DSSC DIY materials and usages

Material	Usage
<i>Electrode</i>	
FTO-coated glass	Substrate
Di water	Cleaning
Anionic liquid detergent	Cleaning
Ultrasonic bath	Cleaning
Ethanol	Cleaning
Oven	Drying
<i>Photoanode</i>	
TiO ₂ powder	TiO ₂ paste preparation
Polyethylene glycol	TiO ₂ paste preparation
Mortar	TiO ₂ paste preparation
Doctor blading	TiO ₂ paste Deposition
Hot plate	TiO ₂ layer processing
Ruthenium	Dye preparation
Ethanol	Dye preparation
<i>Cell assembly</i>	
Iodide/Triiodide	Electrolyte
Syringe	Electrolyte injection
Pt-coated glass	Counter-electrode
Paper clips	Sandwiching cell parts
<i>Cell testing</i>	
Solar simulator	Light source
Potentiostat	Data acquisition

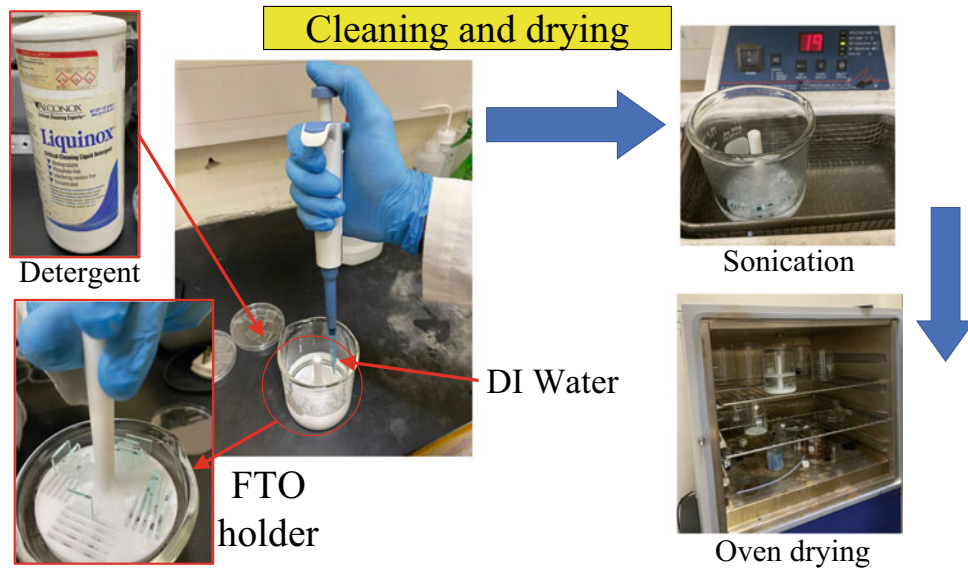


Fig. 12 Cleaning process for TCO substrates

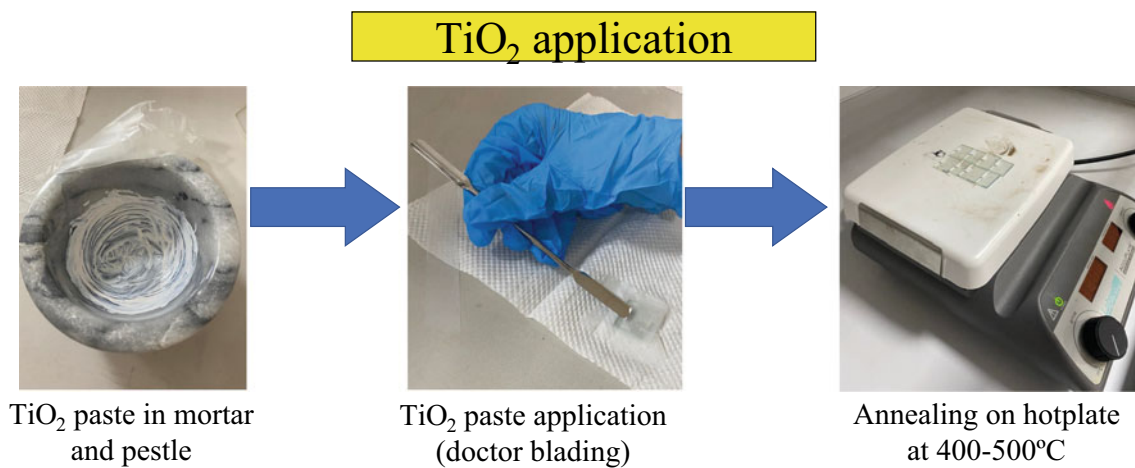


Fig. 13 TiO₂ paste preparation, deposition, post-treatment (annealing)

- Tape the area that is not covered with the TiO₂ while leaving a small region that has the exposed FTO, so that there is no short-circuiting between the sample and the counter-electrode.
- Take out a drilled counter-electrode and place it on the top with Pt surface facing the photo-electrode.
- Use a syringe to inject electrolyte between the two electrodes.
- Clean excess solution and flip it upside-down, and steps are shown in Fig. 15.
- Cell is done!
- Make sure you have a light source and a reference cell, use a potentiostat, and connect a terminal to each side of the cell, and you are ready to do the measurements (J-V test); steps are shown in Fig. 16.

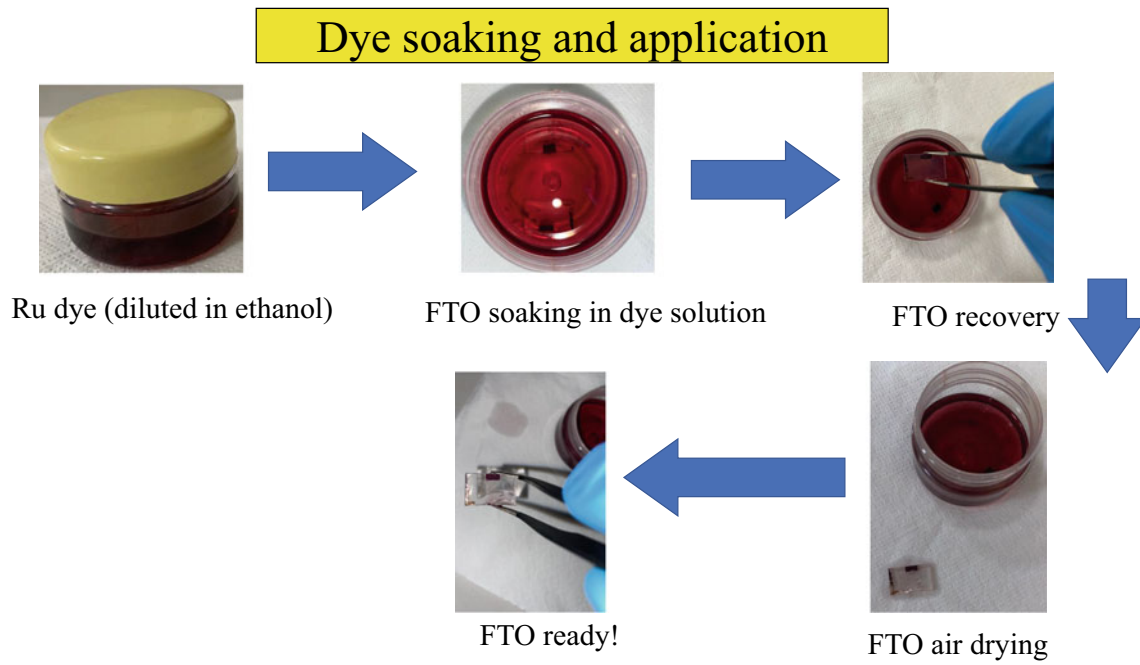


Fig. 14 Dye deposition on TiO_2 substrates

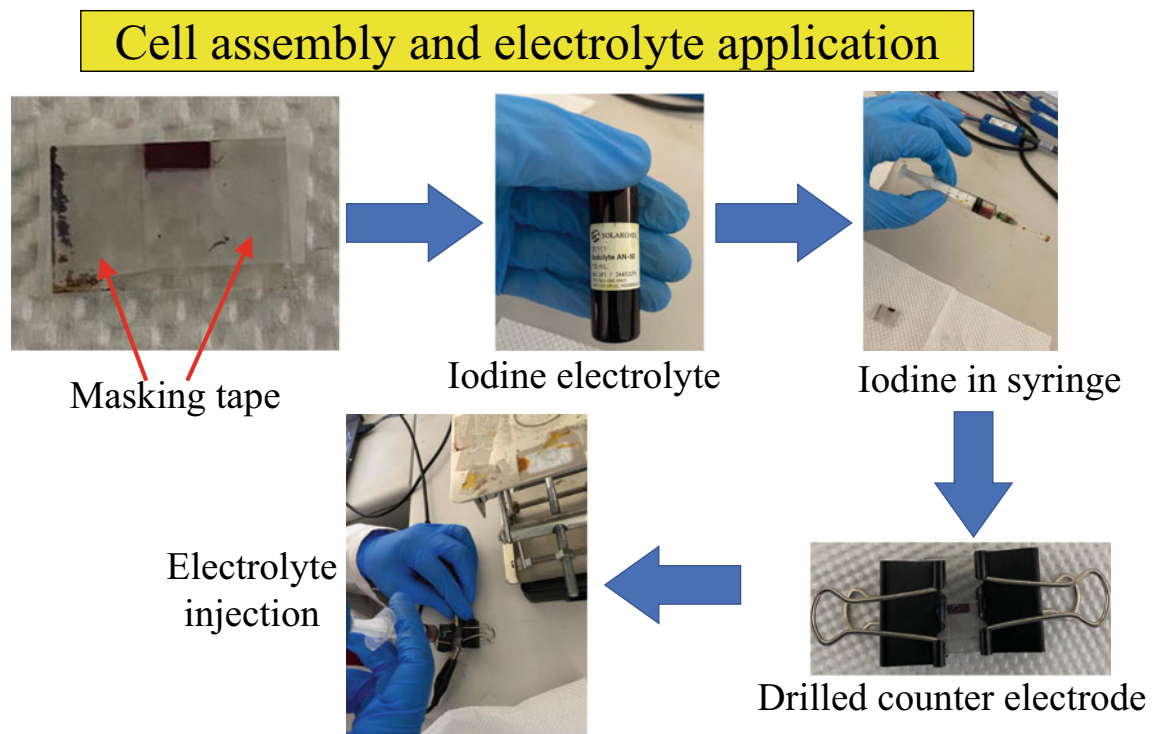


Fig. 15 Cell finalization and electrolyte injection

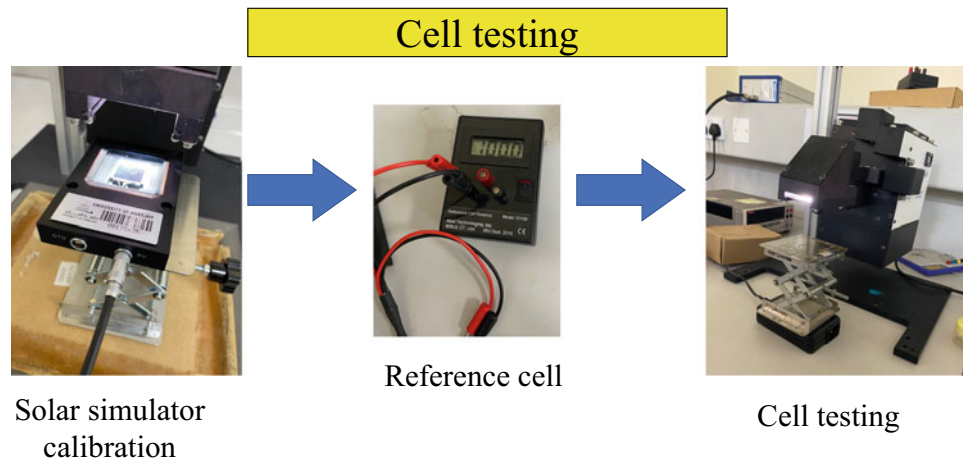


Fig. 16 Dye-sensitized solar cell testing setup

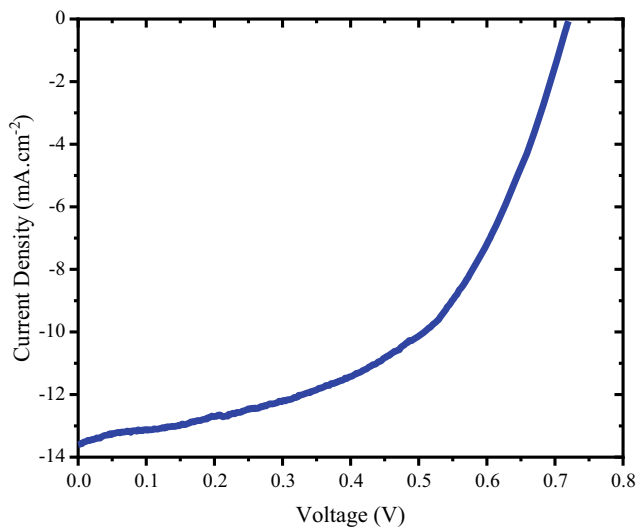


Fig. 17 Dye-sensitized solar cell J-V curve

- Figure 17 shows the J-V curve for a dye-sensitized solar cell with an efficiency of 5.11%.

References

- CleanEnergyWIKI. <http://cleanenergywiki.org/index.php?title=Special:ListFiles&offset=20110615223058%7CRamanmic.swf> (Accessed 07 Aug 2022)
- Conibeer G (2007) Third-generation photovoltaics. *Mater Today* 10 (11):42–50. [https://doi.org/10.1016/S1369-7021\(07\)70278-X](https://doi.org/10.1016/S1369-7021(07)70278-X)
- Nazeeruddin MK et al (2004) Stepwise assembly of amphiphilic ruthenium sensitizers and their applications in dye-sensitized solar cell. *Coord Chem Rev* 248(13–14):1317–1328. <https://doi.org/10.1016/j.ccr.2004.03.012>
- Supriyanto E, Alviati N, Kartikasari HA, Rohman L, Triyana K (2019) Simulation of electron diffusion coefficient interpretation on the optimum thickness of TiO₂ photoanode in dye-sensitized solar cell (DSSC). In: *IOP conference series: materials science and engineering*. 515(1). <https://doi.org/10.1088/1757-899X/515/1/012058>