

## A review on inorganic salts and dye sensitized solar cells (DSSC)

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### Abstract

Solar cells convert the direct sunlight into electrical energy. In recent developments, inorganic materials belonging to the first and second generations are replaced by organic materials or natural dyes. Now-a-days, dye sensitized solar cells (DSSC) belonging to third generation has attained the widespread attention because it offers an efficient and easily implemented technology for future energy supply. Compared to conventional silicon solar cells (SSC), DSSC provides comparable power conversion efficiency (PCE) at low material and manufacturing costs. DSSC materials such as titanium dioxide (TiO<sub>2</sub>) are inexpensive, abundant, and harmless to the environment. Since DSSC materials are less prone to contamination and processable at ambient temperature, a roll-to-roll process could be utilized to print the DSSCs on the mass production line. DSSCs perform better under lower light intensities, which make them an excellent choice for indoor applications. Up till now, such benefits have attracted considerable research interests and efforts. However, still much work has to be done to reach the optimal device efficiencies. Therefore, this review highlights the recent developments in DSSCs structure, components, working principle, advantages, disadvantages, and the key challenges. It also emphasizes the role of the sensitizers to improve the performances of the dye sensitized solar cells as well as some recent developments in this field.

**Key words:** Titanium dioxide, dye sensitized solar cells, power conversion efficiency

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### 1. Introduction

The standard of living is significantly affected by the availability of energy resources. The excessive use of traditional techniques was the main contributor to forecast energy and environmental structure [1]. Renewable energy sources like solar power are considered a viable option since "Earth produces much energy from sunlight in 1 hour than that of all the energy produced by humans in the entire year" [2]. A new study by InterTech Pira reported that after experiencing a slow period, the international photovoltaic (PV) industry is supposed to be doubled in the incoming five years, reaching up to the 48 billion US dollars [3].

Photovoltaic technology is the most fascinating field of renewable energy to efficiently convert sunlight directly into the electrical energy [4]. A photonic instrument that transforms the different photons having particular wavelengths into electrical energy is characterized as a solar cell. In the year 1839, a French physicist Alexandre Edmond Becquerel revealed the photovoltaic phenomenon. He was observing the visual aspects of light on the metal electrodes dipped in the solution of an electrolyte. Photovoltaic cells of first and second generations are primarily build-up from different semi-conductors including compounds of group III

to group V such as cadmium telluride, crystalline silicon, and copper indium sulfide. The efficiency of a Si-based cell is highly unstable [5]. The efficiency of cell mechanically decays at the PV component level. Efficiencies of currently accessible commercialized PV modules fluctuate in between 4 to 8 percent [6]. They are even suitable for those regions where the sun rises only for a shorter period of time and can be operated easily at higher temperature [7]. Due to the low efficiency and higher production cost, Si supported solar cells are confined to the PV industry. DSSCs are more efficient and cheaper than that of the common Si-based solar cells because of elementary manufacturing procedure [8].

On the other hand, DSSCs are the most efficient types of solar cells [9-13]. A DSSC consists of a semi-conductor titanium dioxide which is an ordinarily used dye and a dye sensitizer extracted from different useful natural sources with a negligible expenditure of energy. Currently, developed PV technology is mainly established on the electron-hole creation principle. Every cell is made up of two separate layers of p-type and n-type semi-conductors.

When a photon of an adequate energy is projected on the surface of p-type and n-type junction, an electron is emitted by absorbing a certain amount of energy from a

targeted photon and penetrates from upper layer to inner one. These phenomena generates an electron and a hole pair resulting in the production of electricity [14]. Different varieties of semiconducting materials are used for the fabrication of PV solar cells including single crystalline, poly-crystalline and amorphous silicon. Copper-indium-gallium-sulfide, cadmium-telluride, and copper-indium-gallium-selenide are also suitable semi-conductors for the production of PV solar cells [14]. Currently, DSSCs (Figure 1) come out as a modern class of highly efficient and cheaper energy transformation devices with straightforward fabrication process. In the Swiss federal institute of technology, a Swiss scientist fabricated the first DSSC solar cell [14]. DSSCs supported solar cells specifically utilize the dye material between different electrodes. There are four main constituents of a DSSC solar cell, a semi-conductor electrode, dye sensitizer, a redox inter-mediator and a counter electrode made up of carbon or platinum.

The DSSCs is very fascinating because of simple fabrication techniques like printing method that are extremely flexible, cheaper and more transparent [15]. The attractiveness of DSSC solar cell is due to photosensitization of nano-scaled titanium oxide linked with the dyes that are optically active and enhance the efficiencies to a limit more than 10% [16]. Yet, there are a lot of difficulties like dye degradation and problems in the stability of solar cells [15]. These difficulties are due to the low optical activity of dye sensitizers that badly affects the transformation efficiency. When UV or IR radiation falls on the dye substances, it reduces the lifetime of dye molecules and also affects the stability of solar cells. A coating which is also used to enhance the fabrication ability is costly and decreases cell efficiency [17]. DSSC separation of charges is established by the kinetic cooperation same as in the photosynthesis processes directing to the PV activity. The comparison b/w different semi-conductor supported solar cells and DSSCs is given in Table 1.

In a real sense, in a semi-conductor supported solar cell, the separation of charges is established by the electric field induced by the junction itself. On the other hand, in the case of DSSC, separation of charges is established by the kinetic cooperation as produced in process of photosynthesis [18]. In the photo-electrochemical or DSSC, organic dye substitute with light-absorbing pigments like chlorophylls, while the semi-conductor layers substitute with oxidized NADPH and CO<sub>2</sub> act as electron acceptor. The electrolyte replaces H<sub>2</sub>O, and O<sub>2</sub> acts as electron donating species and an oxidation product, respectively [19]. As a whole, the collective efficiency of DSSC is directly proportional to the insertion efficiency of nano integrated semi-conductors with a broad band gap.

## 2. Structure and working principle of DSSCs

The DSSC instrument (Figure 2) is made up of four basic constituents: (i) a photo anode having a mesoporous TiO<sub>2</sub> stick on a lucid conductive substrate made up of glass (ii) a covalently bonded monolayer organic dye sensitizer on the TiO<sub>2</sub> surface to produce electrons by photon emission (iii) an electrolyte to collect electron at counter electrode having I<sup>-</sup>/I<sup>3+</sup> redox couple in organic solvent. The electrolyte is also effective in production of dye molecule and (iv) a platinum coated counter electrode.

When the light coming from the sun, hits the solar cell, the sensitizer present on the TiO<sub>2</sub> surface causes the electron emission and these electrons are transferred to the titanium oxide conduction band. These inserted electrons went to the anode through mesoporous film and employed to carry out the useful activities. Eventually, to accomplish the whole cycle, these emitted electrons are accumulated by the counter electrode of electrolytes for the regeneration of dye. The total efficiency of a DSSC is based on the sunlight to electrical power transformation efficiency that is given by the following formula (1):

$$\eta = \frac{(V_{oc}J_{sc}FF \times 100\%)}{P_{in}} \dots \dots (1)$$

Where, V<sub>OC</sub> is the voltage of an open circuit, FF is representing the fill factor, J<sub>SC</sub> is representing the current density of the short circuit (mA cm<sup>-2</sup>) and P<sub>in</sub> is representing the power of the incidental light.

### 2.1. Transparent substrate for both conducting electrode and counter electrode

Transparent glass surfaces are normally used as a substrate due to low cost, easy access, and greater optical opacity in near-IR and visible region of electro-magnetic spectrum. In case of thin crystalline semi-conductive oxide, conductive films are injected on one side of substrate. The film guaranteed a degraded electric resistivity. The nano-structured semi-conductor oxide with a broader band gap is transferred and grown up on the conductive side of substrate [20]. Moving towards the grouping of cellular constituents, the counter electrode should be glazed with catalyzing sheet like graphite; to assist the donation of electrons towards the electrolyte. The accumulation of nanostructured materials cut down the transparency of electrodes [21].

### 2.2. Nanostructured photo electrode

In the past, bulk semi-conductors like GaAs, silicon or CdS were used to fabricate the different types of photo-electrodes. Photo-corrosion phenomena occur when light falls on these kinds of photo-electrodes causing a diminution in the stability of the cell. On the other hand, materials like titanium oxide or zinc oxide with a broad band gap; are highly stable and they also show remarkable resistance to the process of photo-corrosion. Light-harvesting efficiency (LHE) is a significant approach to intensify the current

conversion efficiency by increasing the surface area and roughness factor of the photo-electrode [8].

In the modern era, nanostructured materials have gained considerable attention because of their significant modifications in magnetic, chemical, optical, mechanical and electrical properties as compared to the bulk structures [22]. Furthermore, as the area engaged by a dye molecule is greater than the area of the cross-section to capture the light, absorption by the dye molecule become quite unsubstantial. Photovoltaic (PV) effect can only be acquired by using a nano-structured layer of higher surface area as compared to a common semi-conductor with a wide band width. Gratzel and his co-workers (2005) used a nonporous titanium oxide layer instead of the bulk TiO<sub>2</sub> semi-conductor as a photo-electrode. They also formulated a new Ru-complex as a photosensitizer which is very competent in absorbing the broad range of visible and near-infrared radiations resulting in the better execution of PV cells [23].

Nano-porosity of the colloidal solution of titanium oxide can easily be achieved by annealing of accumulated titanium oxide coating at around 450°C in a highly vented region for fifteen minutes only. Nanostructured photo-electrode is a technique to fabricate nanostructured coating of any semi-conductor substance at 25°C. The permeable layer is deposited on the conducting surface made up of glass/plastic to utilize in a nano-crystalline DSSC [24].

Due to the excellent chemical properties and high economic feasibility, TiO<sub>2</sub> has gained significant attention in several fields such as gas sensors, photocatalysts, electronic devices and advanced environmental purification systems [25]. Fabrication techniques for the films of titanium oxide are very simple as no vacuum installations are required. Following methods are well-known for the fabrication of titanium oxide layers [26]. Titanium oxide suspension of pH ranging from 3 to 4 can be prepared by mixing 9 ml solution of HNO<sub>3</sub> to 6 grams of colloidal P<sub>25</sub> titanium oxide ground powder by grinding in a pestle and mortar. During this mixing process, 8 ml distilled H<sub>2</sub>O is added to achieve a pure white freely flowing glue type paste. Eventually, to ensure the uniformity of coating as well as adhesion on TCG electrode, minute quantity of surfactant is added in distilled water. HNO<sub>3</sub> solution ratio in the colloidal P<sub>25</sub> titanium oxide is a hypercritical component to observe performance of the cell. Increment in the ratio of HNO<sub>3</sub> increases the thickness of the film, while a lower ratio decreases the light absorption efficiency of the cell [27].

Another method named as "Doctor Blade method" was utilized for the coating of titanium oxide uniformly on the highly cleaned ethanol-soaked electrode plates. Then the deposited layer of TiO<sub>2</sub> is allowed to dry for 15 minutes and treated at temperature of about 450°C in a highly ventilated container to form a nano porous TiO<sub>2</sub> layer with the larger surface area. The film must be permitted to cool slowly upto 25°C. The drying process is a very critical process during

the manufacturing of glass as the rapid cooling leads to the formation of cracks and cervices [25].

The dimension of the nano-structured titanium oxide layer is a crucial factor that alters the efficiency of the cell. The thickness of the titanium oxide layer should be less than 20µm in order to control the diffusion dimensions of photoelectrons. Titanium oxide is one of the best and commonly used materials because of its excellent electron accepting ability. Different types of semi-conductors having a broad band gap seems to be common like zinc oxide which features a band gap of exactly 3.37 electron volts and also exhibits a huge amount of binding energy near about 60 meV. Kim *et al.*, (2006) suggested that the nano-rods like arranged electrodes displayed much stable PV possessions and also possessed remarkable energy transformation efficiencies [28-29].

The development of dried, diluent and denser zinc oxide nanowires is an important application to increase the performance of cell [30]. Further researches on this topic showed that the magnitude of zinc oxide nanorods could be further enhanced by optimizing the reaction conditions like heat, concentration of precursor, time of reaction and multi-step developments. Nanorods integrated photo-electrodes (as shown in Figure 3) offers huge potential to improve the transportation of electrons. The short circuit density and cell performance was found to be significantly increased as the length of nano-rods increased due to higher magnitude of absorbable dye resulting in enhanced conversion efficiency [28].

### 2.3. Photosensitizer

The dye molecules having appropriate chemical structures are used to sensitize the nanostructured photo-electrodes having broad band gap. When the photons are absorbed, the adsorption efficiency of the dye molecules is enhanced and the surface of nanostructured TiO<sub>2</sub> starts to oxidize. As a result of this oxidation, excited electrons are introduced into nanostructured TiO<sub>2</sub>. Sensitizer compounds such as the poly-pyrindyle compounds of Ru(II); are one of the most studied compounds in this technology. It was among the first kind of favorable sensitizers. Most work has done on chemical characterization and molecular orientation of Ru based compounds.

Some recent researchers have described the "Black Dye" as most favorable sensitizer for charge transformation in DSSC. Few other natural dyes and dye extracts, used for sensitization in DSSC are: (i) black rice (ii) shiso leaf (iii) fruits of Calafate (iv) henna (v) wormwood and (vi) rosella. Natural anthocyanins and bamboo leaves have also been checked to be used as a natural sensitizers and the photo-voltaic behavior of reliable cells shows several possibilities [31]. Use of suitable additives to increase the Voc (voltage of an open circuit), results in the improved cell efficiency (Figures 4-5) [31].

The *cis*-di-(thio-cyanato)-bis-(2,2'-bi-pyridyl)-4,4'-di-carboxylate) ruthenium(II) (also named as N3/N-719) dye is also used as an excellent sensitizer molecule. For DSSCs, use of advanced ruthenium-based dyes is attractive option for the future researches. However, still extensive research is required to use the UV visible regions of electro-magnetic spectrum in photo-voltaic cells [21]. In reality, for a dye to be a good sensitizer, it must have large number of carbonyl and hydroxal groups having ability to maintain the position of Ti(IV) on the surface of titanium oxide.

Commercial scale DSSCs and other related items manipulate Ru-bi-pyridyl based dyes to get transformation efficiencies exceeding ten percent. These dye molecules are known to have specific molecular formula and unique chemical structure to be an efficient sensitizer for DSSCs. Therefore, it is very difficult to select the specific low cost dye molecule having economic feasibility. Given below is the light-harvesting efficiency:

$$\text{LHE}(\lambda) = (1 - 10^{-A(\lambda)}) \times 100$$

In particular,  $A(\lambda)$  is the absorbance of the sample. With the increase in concentration of dye extract, the absorbance and "light harvesting efficiency" (LHE) of PV cells increases. For example, with the increase in the concentration of henna extract, sample absorbance increases and accumulates a wide range of wavelengths. All the photons emitted from the nano-crystalline layers of titanium oxide are not absorbed by the single layer of dye therefore, accumulation of emitted photons helps to intensify the light production potential. By the addition of different types of dye sensitizers, absorption efficiency of the DSSCs can be increased upto twenty six percent with improved spectral absorptions.

The organic sensitizers like fabricated  $I_2$  are known to have better efficiencies as compared to the metal based DSSCs. Total conversion efficiency of the indoline dye, to convert solar light into current, was found to be 6.51%. While on the other hand, the efficiency of  $N_3$  dye with the same conditions was 7.89%. Quantum-dots are the nano-structured microcrystalline semiconductors with pronounced quantum effects due to suitable size and appropriate linear and non-linear optical activities. The structural formula of Lawsone is shown in Figure 6.

The "excitonic sorption of quantum dots" is a size dependent phenomenon significantly affecting the quantum dots of lead sulphide and this process is more pronounced in case of methyl benzene. It is expected that quantum dots is a secondary component instead of dyes to absorb light coming from the sun in DSSCs. The light-harvesting process creates excitons/electron-hole pairs in the DSSC. The excitons result in a similar kind of physical change between electrons and holes as in case of Exciton Bohr Radius. Normally, the Bohr radius is higher than the diameter of quantum dots. Excitons split up at the surface of quantum dot titanium oxide. Later on, the ejected electrons are inserted in the

conduction region of titanium oxide and holes are injected into the solution of electrolyte.

After accumulation of dye molecule on conduction band, semi-conductor quantum dots like lead sulfide absorbs the huge amount of photons with energies higher than that of the band gap in between conduction band and valence band. Therefore, the huge amounts of solar radiations are converted into useable forms of energies using nanocrystals as compared to the dye molecules. Unfortunately, dyes are not very stable compounds and undergo the photo bleach phenomena with the passage of time. On the other hand, quantum dots have external shield, thus are more stable and produce highly durable solar cells having better efficiency and long term sustainability. Quantum dot-sensitized cells are known to show better quantum output and effective ionization potential as compared to the simple DSSCs.

According to an estimate, higher efficiencies have been achieved by the photo transformation of the solar cells based on cadmium and selenium quantum dots supported by carbon nano-tubes. This is established by integrated system of carbon nano-tubes in nano-structured titanium oxide semi-conductor layer, consequently supporting the charge shipping phenomena. Therefore, considerable advancements in the light transition efficiency of a common DSSC is possible. Some recent researchers reported that cadmium and selenium quantum-dots-sensitized-light-harvesting-cells are known to have hundred percent intragroup quantum efficiencies. Excellent improvement in both of the electron insertion and charge accumulation efficiencies at two different sites was accomplished in past few decades.

#### 2.4. Redox electrolyte

Different electrolytes comprising of  $I/I_3^-$  redox fragments is significantly utilized in the DSSC to re-create oxidized molecules of the dye thereby completing the electrical circuit through movements of electrons in between nano-structured counter electrodes. The NaI,  $R_4NI$  and LiI are some of the examples of iodide mixture normally liquefied in the non-protonic medium such as propionitrile; acetonitrile and propylene carbonate to fabricate electrolyte. The performance of the cell is largely affected by the ionic conduction in the electrolyte, which mainly depends on the viscosity of solvent. Hence, the solvent with optimum viscosity is ultimately required.

Furthermore, the counter iodide ions like sodium<sup>+</sup>, lithium<sup>+</sup> and  $R_4N^+$  do have significant impacts on the overall efficiency of the cell due to light-harvesting ability and ionic conductivity. According to an estimate, insertion of tertiary butyl pyridine to redox electrolytes improves the cell performance. The  $Br^-/Br^{3-}$  redox ions were used in DSSCs and exhibit the excellent results. Both  $V_{OC}$  and  $I_{SC}$  were enhanced for Eosin Y-based dye-sensitized solar cells by inserting the  $Br^-/Br^{3-}$  instead of  $I^-/I_3^-$  redox couple. The

selection of redox electrolytes is very important to decrease the concentration of  $I^{3-}$  ion by the addition of electrons.

Three major things that must be considered while selecting the appropriate device are: (a) dependency of the transportation of hole (b) the rate of accumulation of dye molecule and (c) redox couple efficiency of  $I^-/I^{3-}$  at counter electrode. Evaporation of liquid electrolyte not only limits the stability of cells but also inhibits the manufacturing of multi-cell components, since module fabrication demands the cell to be attached electrically and isolated chemically. Therefore, the major disadvantage of DSSC having liquid redox electrolyte is the uncontrolled discharge of electrolyte solution resulting in decrease of life cycle of cell. However, there are also large number of technical issues, instrumental problems and several questions to the long term stability of DSSCs.

Different research groups analyzed the utilization of ionic liquids, hole collector electrolytes and polymers to substitute the requirement of organic medium in different liquid electrolytes. Despite the low efficiency (nearly about 4 to 7.5%), these types of electrolytes are very promising; and can assist in the development of commercial scale dye to sensitize the solar cells. Injection of different polymer gels to quasi solidified electrolytes is examined by different research groups. It has been established that the insertion of polyvinylidene and poly-fluorene-co-hexafluoropropylene to  $KI/I_2$  electrolyte has improved the fill factor and light-to-current conversion efficiency of the cells upto 17%. Gel-based electrolytes are also very fascinating due to following reasons such as: (i) high efficiency and better compromise in between the viscosity of electrolyte and the mobility of ions (ii) gel-based ionic liquids have high ionic mobility due to low viscosity and (iii) high degree of cellular arrangements in between the inter-cell-sealing [32].

Advanced categories of electrolytes include p-type electrolytes, tetra-methyl-ammonium (TMA) electrolyte, polymeric electrolytes and poly-(3,4-ethylene-di-oxy-thiophene) poly-styrene sulfonate (PEDOT) electrolyte. These types of electrolytes are mainly involved in the transference of electrons from counter electrode to oxidized molecules of dyes in order to optimize the reaction conditions and to design the new types of cells. Some recent researches have been successfully implemented to ensure the targeted charge transportation and also to recombine the conjugated polymer hole transporter with solid state DSSC [33]. In a recent research investigation, scientists and researchers try to use the indolone dye having organic functional group commonly known as  $D_{131}$  as sensitizer and poly-3-hexylthiophene as hole transporter and achieved the transformation efficiency upto 3.85%. Hence, these kinds of solar cells are known to have the highest degree of efficiency [33]. Some important chemical structures are shown in Figures 7-10.

## 2.5. Working principle of dye sensitized solar cell (DSSCs)

*Khalid et al., 2019*

Nano-crystalline structures such as  $TiO_2$ , contains a large surface area and thus used as a conducting surface of electrode (photo-electrode) to adsorb the sensitizers or dye molecules. Dye molecules are excited through adsorption of photons starting from HOMO (highest occupied molecular orbital) to LUMO (lowest unoccupied molecular orbital) state. The electrons inserted into the film of nano-structured  $TiO_2$  then oxidize the dye molecules. This inserted electron moves between the layers of  $TiO_2$  nano-particles and work is done as electrical energy. The electrolytes having  $I^-/I^{3-}$  redox ions can be used as electron intermediate between the counter electrodes coated with carbon and  $TiO_2$  photo-electrode. The  $I^-$  ion redox arbitrator are oxidized to another form like tri-iodide ions ( $I^{3-}$ ) and then regenerate the photo-sensitizer or oxidized dye molecules. The  $I^{3-}$  substitutes the internal electron and then reduced to  $I^-$  ions. The movement of electrons in nano-structured semi-conductor is attributed by the diffusion of charge-compensating cations in the layer of electrolyte near the surface of nanoparticles. Therefore, no transformation is caused by the electric power generation in the DSSC (Fig.11).

Similarly, a small charge separation in between HOMO and LUMO makes sure the absorption of photons of short energy from solar spectrum. Hence, the photocurrent level is dependent on the separation level between HOMO-LUMO which is similar to the energy band gap of inorganic semi-conductors. Actually, by increasing the separation of charge between LUMO and bottom of  $TiO_2$ , the efficiency of electron insertion into the layer of  $TiO_2$  conduction band is enhanced. Furthermore, the energy difference between the chemical potential of redox and HOMO is positive and the HOMO level accepts the electrons from redox moderator.

## 2.6. Photovoltaic performance

The nature and concentration of the dye show a significant effect on the magnitude of photocurrent. The irradiation of solar spectrum with photon flux equal to  $I_0=100mW/cm^2$  (Air Mass 1.5) and conversion efficiency from photon energy to the electricity is shown as:

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{I_0}$$

The  $J_{sc}$  is "small circuit current",  $V_{oc}$  is "voltage of the open circuit" and FF shows the "fill factor of solar cell" and it can be calculated by this equation.

Photocurrent as well as voltage drop, were reported automatically on an adjustable charge when the solar cell is subjected to sunlight. The transmittance of photo-electrode can be determined by absorption and reflection of sunlight using conductive photo-electrode and nano-structured  $TiO_2$ . The layer of  $TiO_2$  is pasted on to the conductive surface of electrode by using "Doctor Blade Process" and this result in increased "effective surface area" of the irradiated part of the cell. Based on the difference in composition of Bahraini Henna extract, the cells are developed on the voltage nearly

equal to the "open circuit voltage"  $V_{oc}$ . On the other hand, "short circuit current"  $I_{sc}$ , fluctuates with the concentration of henna extraction. Concentrated derivatives from Bahraini Henna resulted in non-ideal I-V features as it maintains 100% of light-harvesting ability in the UV visible region of electromagnetic spectrum. Dye concentration was reported to have a significant effect on the concentration of photo current received. High Henna extract concentration results in high electrical resistance, which eventually restricts the photo current produced. In comparison with concentrated extracts, diluted extracts lower the photo current magnitude and cell output [3-8-27-34].

## 2.7. Charge insertion, transportation and recombination

Several investigators have investigated the electron injection kinetics onto the surface of semi-conductor photo-electrode after being stimulated from the photo-sensitizer by using the "time-resolved-laser-spectroscopy". It has been noticed that the material specification for photosensitizers and separation of charges in between convection band stage of the wideband gap semi-conductor are different. Thus, the photosensitizer's LUMO level adversely affects the transfer rate of electrons to the wideband gap semi-conductor. A diagram presenting the kinetics of DSSC is shown in Fig.12. The arrow heads shown in diagram suggests the excitation of the dye molecule from the level of HOMO to the level of LUMO. With the passage of time, excited electrons are relaxed and electron insertion from the dye level LUMO to the  $TiO_2$  conductive band results in the recombination of emitted electron with the dye level HOMO. After this, recombination of electrons take place in the  $TiO_2$  conductive band with a hole in the electrolyte and restoration of the oxygenated dye by  $I^-$  [35].

Electron insertion from the excited state of the dye containing  $N_3$  dye or  $RuL_2(NCS)_2$  form a complex into the  $TiO_2$  valence band (VB). This process has reported to be a very quick one that takes place in femtosecond level. The oxidized ion reduces by  $I^-$  ions of the redox electrolyte take place in a time of  $10^{-8}$  seconds or so. Recombination of the image-injected "conductance-band-electrons" through the oxidized dye molecules or electrolyte-redox pair oxidized type  $I^-$  (ions) happens in just micro-seconds. The velocity constants for charge insertion would be within the picosecond range to ensure reasonable quantum yield. To conclude, quick sensitizer recovery is critical for long-term sustainability. Long-lasting separation of the charges is also a very critical factor in solar cell efficiency. As a result, researchers have documented new products for broader conjugated dye-sensitizer molecules as recent researchers examined the hybrid super molecules which effectively delay the recombination of the load-separated state and it ensures improved energy proficiency by enhancing the lifetime of light-induced load-separated substances [36].

The redox triad structure given by Haque and his colleagues was the first and most effective charge separation method at that time. The triad is composed of a ruthenium complex attached with nano-crystalline  $TiO_2$  (it is electron acceptor) which then covalently bound to triphenyl-amine (it is an electron donor) polymer chains. Bullets reflect the position of moving electrons. Its first stage of moving electron acts as the light-induced chromophore excitation. Regarding this, an electron is promptly introduced into the  $TiO_2$  semi-conductor conductive band as show in process 2 from the excited sensitizer state. It will then eliminate the chances of direct combination of charges show in process 3. Specific recombination of predominantly isolated charges shown in process 3 will degrade this energy that is extracted from heat. In the super molecule, this is prevented by the related triphenyl-amine electron donor classes as show in process 4 rapidly reducing ruthenium. The supplementary recombination stage shown in phase 5 here between inserted electron and oxidized amine radical is progressively slow even though the positive charge on their surface will hop through 1 triphenyl-amine. The chain and hole shown in the process 6 do not move back from the surface of  $TiO_2$ . It consists of a synchronous electron stream from those at the beginning of the polymer chains to the oxide (right) [37].

The electrons migrate towards the electrode in  $TiO_2$  nanoparticle DSSCs, jumping amongst the particles with the speed of  $10^3$ - $10^6$  times [38]. At this stage, there are high chances of recombination of photo-excited electrons and electrolyte for each step, because both the diffusion and recombination levels have been on the range of milli-seconds. It then requires recombination to restrict the productivity of the cells. Alternatively, the nanowires or photo-electrode as tube-structured (e.g.,  $ZnO_2$ ) gives a good realistic path that acts as a highway to the anode, resulting in a higher rate of diffusion thereby reducing the rate of recombination and lowering the cell efficiency [39].

Poor DSSC current is primarily due to the loss of inserted electron from nano-structured broad electron mobility semi-conductor which gives  $TiO_2$  to  $I^{3-}$  (it is the hole carrier in the electrolyte solution). Therefore, a down-reaction must be removed or reduced. Decrease of dark current increases the cell's open-circuit voltage ( $V_{oc}$ ) which is inferred from the following specific solar cell equation comparing the voltage of open-circuit  $V_{oc}$  together with the  $I_{nj}$  penetration current and the dark current dark.

$$V_{oc} = \frac{kaT \ln(I_{nj} + 1)}{q \times I_{dark}}$$

In this equation, "kB" is a Boltzmann constant, the complete cell temperature is shown as "T", and the electron charge amplitude is denoted by "q". Besides, dark current appears primarily at the interface of  $TiO_2$ /electrolyte in where no photosensitizer has been solubilized. The use of one of the pyridine derivatives e.g. test-butyl pyridine TBP as

adsorbates on the surface of the nanostructured TiO<sub>2</sub> is a good way to suppress dark current [40].

### 2.8. Efficiency of DSSC

The characterization of solar cells is defined by many important steps. Its most apparent is the quantity of electrical power generated to shine on the cell for a given amount of solar power. Measured in terms, this is called the "output of the solar conversion". The electrical power is the "combination of current and voltage" hence the maximum values are also essential for these quantities,  $J_{sc}$  and  $V_{oc}$ , accordingly. The average voltage that the cell produces is probably the difference between TiO<sub>2</sub> Fermi level as well as the electrolyte's redox potential in solar illumination ( $V_{oc}$ ) circumstances. Therefore, if an activated DSSC were attached to a voltmeter in an "open circuit", it will interpret around 0.7V. DSSCs give much higher voltage than silicon. There are only minor variations so that variations in the real world are influenced by the current output ( $J_{sc}$ ).

DSSCs are highly effective in terms of the quantum efficiency. There is a high probability of photon absorption because of its "width" in the nano-structure, and the dyes are very efficient in converting them into electrons. Much of the minor losses that occur in DSSC's are due to the conductive failures in the layer of TiO<sub>2</sub> and transparent electrode, or front-electrode optical losses. Depending on their size, quantum performance of typical designs varies but is almost the same as the DSSC [41].

The dyes are found to be effective in transforming the absorbed photons or electrons in the layer of TiO<sub>2</sub>. At the end of reaction, only photons absorbed through dye are used to generate current. The rate of absorption of photons depends on the absorption spectrum of the sensitized TiO<sub>2</sub> and the frequency of solar fluxes. The difference between these both spectra will decide the maximum photocurrent feasibly. Generally used dye molecules typically in the red part of the spectrum have lower absorption in the red part as opposed to silicon. It means that small numbers of photons are available for the generation of current from sunlight. Such considerations inhibit the current provided by a DSSC; and a conventional chemical-based solar cell provides about 35 mA/cm<sup>2</sup> [42].

### 3. Drawbacks of dye sensitized solar cells (DSSCs)

In a DSSC, the semi-conductor is mainly used to carry charges, and the photoelectrons are generated by a separate renewable source. DSSCs also operate in a wide variety of lighting environments. Therefore, they are very common in rainy weather where conventional cells become a failure. The DSSC cutoff is so small that they are supposed to be ideal for both interior and exterior use. Dye-sensitized solar cells are the solar technology of the third generation and are used as solar panels on the rooftop. The performance of DSSCs is about 11% as compare to thin-film

technology that range from 5% to 13%. DSSCs perform at low indoor temperatures [43].

Production of DSSCs involves heavy electricity consumption, high performance and slide-to-roll fabrication technique. DSSCs use affordable nanomaterials that are also environmentally sustainable. Indoor DSSC modules are extremely versatile, lightweight and long-lasting. Because it is built on a thin film, flexible, durable, plastic substratum, DSSC may also be extended to metal and glass substrates. The surface area of advanced DSSCs is highly controllable and testable. Screen printing methods can be used to get mass output in the DSSCs.

The physical structure of dye-sensitized solar cells and materials used; are eco-friendly and low-cost and ensure the use of multiple dyes quite easily. Australian company Sustainable Technologies International manufactured large-scale electric-power glass sheets for the testing and practical implementation. The production of inconsequential versatile dye-sensitized cells or components is desirable for a room or outside light-driven computers, devices and large number of mobile equipments. Solar cells sensitized to the dyes can be crafted as vibrant indoors.

The flexible dye-sensitized solar modules provide possibilities for their integration with the several wearable devices, luggage, gears and outfits. Dye-sensitized panels with an output of 10 percent are an attractive option for replacing the traditional crystalline Si-based modules in power generation. In 2010, Sony claimed the manufacture of components with approximately 10 percent output and thus the ability to sell DSSC components on a large scale.

### 4. Drawbacks of dye sensitized solar cells (DSSCs)

For the large scale implementations, the DSSCs are not considered to be a decent choice because higher cost and poor efficiency of the cells are major hurdles in this regard. The high cost of solar panels of silicon to other forms of solar technology taking a back seat, such as "Solar Thin" and "Thermal Film Technology". Dye-sensitized solar cells uses liquid electrolyte that is not stable at high temperatures and even freezes at lower temperatures. As the fluid expands at higher temperatures, it is a very difficult to seal the doors of entire apparatus. Electrolyte solution of DSSCs mainly includes the volatile organic solvents.

### 5. Commercialization of dye sensitized solar cells (DSSCs)

In almost all continents of the world, marketing of dye-sensitized solar cells and related modules are taking place at rapid pace. Throughout the Asia and Japan, more specifically in: (i) IMRA-Aisin Seiki/Toyota (ii) Sony (iii) Toshiba (iv) Dai Nippon (v) Peccell (vi) Dye sol. Konark in the USA (vii) G24i in the Great Britain and (viii) Solaronix in Switzerland are the most commonly used brands. In 2007, G24i announced a 25 megawatts capacity DSC module

development in Cardiff, Wales (UK), with expansion plans upto 200 megawatts by the end of 2008.

## 6. Recent developments in DSSC components

### 6.1. Recent developments in photo-anodes

The photo-anode has a dual function like it acts as a support for loading of sensitizer (used as transporter from sensitizer to external circuit of photo-excited electrons) and nanostructured semi-conductors (that are the background of DSSC photo-anode). The large surface area is required for better dye loading capacity and the efficiency of collection of electrons increases by increasing the rate of transportation of charge. The ideal photo-anode is defined by these two important properties [44-45]. The nanoparticles that contain large surface area allows a high capacity of dye loading and disordered network with various grain boundaries weakens the mobility of electrons and shows slow transportation and recombination of the photo-excited electrons [32-46-47]. The problems related to the construction of standard photo-anode forces the scientists and manufacturers to construct more active nano-structured photo-anode tools having better morphological features [48].

#### 6.1.1. Doping with different ions

Ion doping is extensively used to regulate the position of both, valence band (VB) and conduction band (CB) of semi-conductor constituents for the applications of photo-catalysis. The reduction of the lifetime of an electron in photo-anode and reduction in recombination resistance is attained by doping of ion, for example, Mg, F, I, Cu and Nb in DSSCs and doping also increases the overall efficiency of the cell [49].

#### 6.1.2. Decoration with noble metals

The optical path length extended by the "surface plasmon resonance" (SPR) effect of noble metal like Au and Ag nanoparticles; can be found to localize the incident light radiations [50]. The light-harvesting efficiency of DSSCs increases by the incorporation of this property in photo-anodes. The electron transfer efficiency in conjunction with "scattering" and "plasmonic" effects increases by coating with Au nanoparticles and it depends on the different size ranges [32]. The Ag, TiO<sub>2</sub> and SiO<sub>2</sub> nanostructures can be prepared by using different methods. In this method, the layer of SiO<sub>2</sub> prevents the decomposition of Ag type nanoparticles using I/I<sub>3</sub> electrolyte and increases surface plasmon and light scattering effect. These types of effects enhance the light absorption capacity [51]. Therefore, the influence of noble metal nanoparticles in DSSCs is still continued and future researches are required to develop the better methods.

#### 6.1.3. Coating with up/down conversion materials

Conventional sensitizers such as organic dyes and ruthenium based compounds are characteristically used in DSSCs which absorb sunlight only in the visible region of electromagnetic spectrum. Consequently, an unconventional scheme for light-harvesting to the near-infrared region can be improved by fabricating the nanoparticles in which absorption of sensitizers converts near-infrared light into visible light [52]. The up/down capabilities are used to increase the proficiency of the light-harvesting region of DSSCs using different hetero-structured photo-anodes of semi-conductor type materials.

### 6.2. Modern developments in DSSC sensitizer

The major constituent of DSSCs is a sensitizer. It is used to gather the sunlight at the semi-conductor region to produce photo-excited electrons. Some requirements are necessary for better performance of sensitizers such as (i) dye regeneration from electrolyte (ii) proper LUMO level and HOMO levels for current charge addition into the semi-conductor, high stability and good photo-stability (iii) load of the semiconducting materials by the chemically adsorbed groups (iv) for light harvesting the coefficient of high molar extinction into the visible region and near-infrared region, and (v) use of cobalt-based electrolytes by creating space in between photo-anode and electrolyte. Since the past few decades, incredible efforts have been made to develop the different types of sensitizers and according to the simplest division, there are five major forms of dye sensitizers.

#### 6.2.1. Ruthenium polypyridyl dyes

Ru(II) polypyridyl dyes is the widespread sensitizer of DSSCs because it show excellent performance due to (i) high molecular stability (ii) wide light absorption ranges from the ultraviolet region to near-infrared light region (DI 350 nm) and (iii) appropriate energy levels concerning I/I<sub>3</sub> electrolyte and TiO<sub>2</sub> photo-anodes. Therefore, in the middle of 1990s, Ru (II) dye established DSSCs and its efficiency was 10.0%, with successive efficiencies of 11.2% in 2005, and 11.7% in 2010.

Some strategies such as exchanging the ligands of thiocyanate with some chelating anions, phosphate groups in Ru(II) dye can be studied. Similarly, hydroxamate as an alternative of carboxylate anion and ancillary ligands like tri-azolyl-pyridine and butyloxy-substituted benzene can also be studied. Over the past ten years, the competence of Ru(II) dye based DSSCs is still maintained. The new type of sensitizers with a low cost like ruthenium and coefficients such as Ru(II) polypyridyl ( $\epsilon=10,000\text{--}20,000\text{ M}^{-1}\text{cm}^{-1}$ ) with low molar extinction have been investigated [53].

#### 6.2.2. Metal free organic dyes

Metal-free organic dyes have some important properties like high flexibility in molecular structure, high molar extinction coefficient and cost-effectiveness. Because



of these properties, the metal-free organic dyes gained high research interest as favorable for sensitizers in DSSCs [33]. A large number of organic dyes can be designed with a donor–P spacer–acceptor (D–P–A) structure and used widely for DSSCs [54]. These organic dyes usually contain electron-rich moieties like indolines triaryl amines and carbazoles used as donor parts, P-conjugated groups such as benzothiadiazole, polyenes, thiophenes and other related units as electron-withdrawing groups for example pyridines, cyanoacrylic acid and rhodamines used as acceptor parts. Almost 10% is the transformation efficiency of DSSCs with D–P–A type of organic dyes. Conversely, some properties such as adverse dye aggregation, narrow absorption bands and variability, characterize a major blockage for additional improvements in metal-free organic dye sensitizers [55-56].

### 6.2.3. Dyes of porphyrin

In recent few years, the porphyrin dyes have been investigated and dipolar Zn(II) porphyrins are used as the DSSCs because of their extreme absorption in the region of 400–500 nm and 500–700 nm [57]. Porphyrin-prepared DSSCs with the YD-2 dye achieved an 11% PCE in 2010 and more increased to 11.9% using an additional porphyrin dye in 2011 [55]. Earlier studies have been shown that it becomes a challenge to harvest the sunlight from ultraviolet to near-infrared region by using the single porphyrin dye sensitizer as it bears effective injection of the photo-excited electrons into photo-anodes [58]. The light-harvesting range and DSSC's proficiency, increases by co-sensitized methods. The YD<sup>2</sup>-OC<sub>8</sub> co-sensitized with organic dye in 2011 and obtained 12.3% efficiency in DSSCs [59].

### 6.3. Recent developments in DSSC electrolytes

In past few years, the electrolytes of iodide–triiodide (I<sub>3</sub>/I) are the best worldwide redox shuttle because of following reasons: (i) adequate kinetic properties (ii) photo-anode/electrolyte fast oxidation (iii) effective regeneration of dyes (iv) electrolyte/counter electrode reduction of I<sub>3</sub> (v) excellent infiltration (vi) low cost and high carrier collection and (vii) easy preparation [46]. In spite of all these facts, numerous shortcomings are present for I<sub>3</sub>/I electrolyte. But some disadvantages are also present such as (a) corrosion of counter electrode including Pt and Au of noble metal (b) absorption of visible light at around 430 nm and (c) further development of DSSCs by using combination of electrolyte. Accordingly, some alternative electrolytes have also been investigated with the thiolate or disulfide mediator, ferrocenium or ferrocene couple, Cu (I/II) complex and Co (II/III) polypyridyl complex [57].

#### 6.3.1. Quasi-solid electrolyte

Quasi-solid-state electrolytes undergo the leakage of solvent and require proper sealing when it is used in high environmental temperatures. With the passage of time, these

solid-state electrolytes become the main focus of research for DSSC electrolytes in order to commercialize the product. The liquid electrolytes are replaced by conductor of solid-state hole transport, various electrolytes and transporting materials for example various organic and inorganic p-type materials are successfully used in solid-state DSSCs [60]. CuI/CuSCN is known to have high hole mobility. However, the SS-DSSCs show a 3.8% PCE value because of fast crystallization rates resulting in poor filling into photo-anode films. The CsSnI<sub>3</sub> having high hole mobility, rich raw materials and low-cost processing is another capable p-type semi-conductor HTM. This type of electrolyte-based device has upto 10.2% PCE yield for SSDSSC [35].

### 6.4. Modern developments in counter electrodes

The counter electrode (CE) in various DSSCs plays an important role in the assembly of electrons from the outer circuit and then transports it into the solid-state electrolyte. The main requirements for the counter electrode (CE) are: (i) high stability (ii) increased conductance for the charge transport and (iii) good electro-catalytic activity [57]. Noble metals like Ag, Pt and Au are the rare and expensive CE materials due to their (a) large electro-catalytic activity (e.g. Pt) (b) high reduction potential and (c) active hole transfer in solid-state electrolytes like Au and Ar. Conversely, noble metals are more costly, so alternative materials are used to replace the noble metals as CEs [61-62].

#### 6.4.1. Carbon materials

The carbon-based materials like carbon nanotubes, graphene and porous carbon have also been used as a CEs material in DSSCs because of their important properties like (i) low cost (ii) high electrical conductivity (iii) corrosion resistance (iv) good electro-catalytic activity and (v) thermal stability [63]. The electrochemical activity of CEs materials can be amplified by combining different forms of carbons such as carbon nanotube/graphene nano-ribbons and porous carbon/carbon nanotubes [64]. The different forms of CE materials and combination of diverse carbon materials become a popular area for advanced research [65].

#### 6.4.2. Inorganic compounds

Sulfides, nitrides, carbides, phosphides, metal oxides and tellurides have been used as an effective CE material due to their vital applications in low-cost and large-scale production of DSSCs. Though, the performance and stability of inorganic complexes for DSSCs is still necessary to be developed further [61].

#### 6.4.3. Conductive polymers

Some polymers such as the polypyrrole (PPy) and polyaniline (PANI) can be used as CE materials for flexible DSSCs and simple DSSCs due to their high stability, high conductivity and excellent transparency. The PEDOT is the

commonly used CE material, found to be useful in DSSCs. In order to increase the electrical conductivity and solubility, different doping materials such as TsO, poly-oxo-metalate (POM), ClO and poly (styrene sulfonate) are also used to increase their properties. More development of conductive polymers like CE-based DSSCs is further required [66].

**7. Key challenges and recommendations**

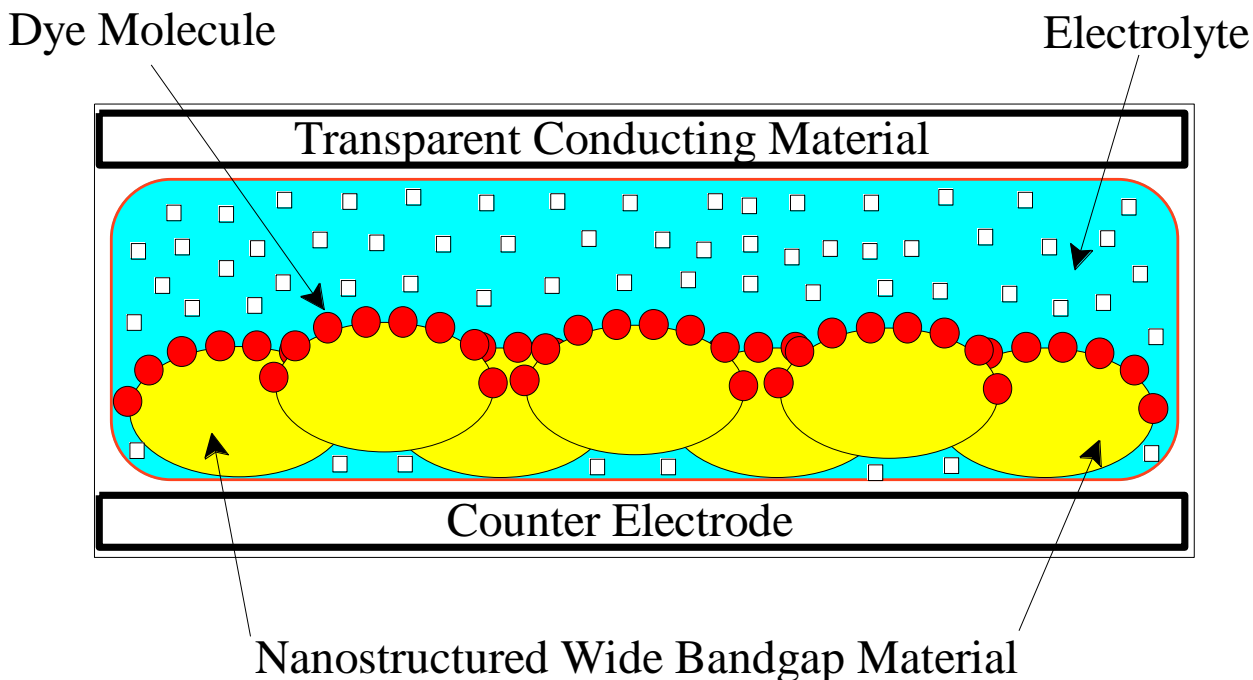
Low efficiency is the main task for the commercial distribution of DSSCs. Following factors are responsible for the low stability of DSSCs:

- Non-optimized dark current
- Low working of dyes in the region of NIR
- Poor contact between the electrodes
- High viscosity and low volatility of the electrolytes

- The properties of electrolyte degraded by the UV absorption of light

Following steps are required to improve the efficiency and the stability of DSSCs:

- Reduce the dark current
- Improve the morphology of semi-conductors
- Improvement in the structure of dye to absorb the radiation in the NIR region
- Improve the rate of charge transfer, develop the less viscous and low volatile electrolytes
- Use high viscosity and low volatile of electrolytes
- Use additives for dyes and electrolytes to increase their properties [67].



**Figure 1:** Schematic representation of DSSC

**Table 1:** Comparison between common semi-conductors supported solar cells and DSSC

Processes	Semi-conductor Solar Cells	DSSC
Transparency	Opaque	Transparent
Pro-Environment (Material and Process)	Normal	Great
Power Generation Cost	High	Low
Power Generation Efficiency	High	Normal
Color	Limited	Various

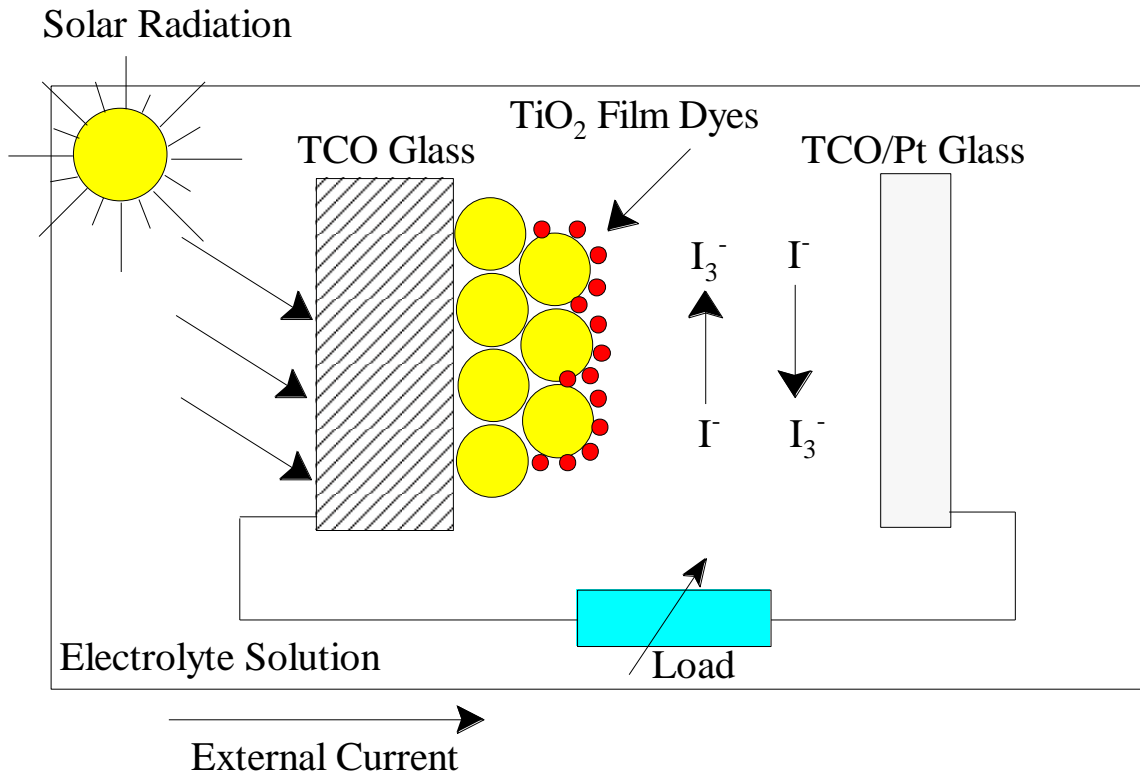


Figure 2: Schematic diagram of a dye-sensitized solar cell [20]

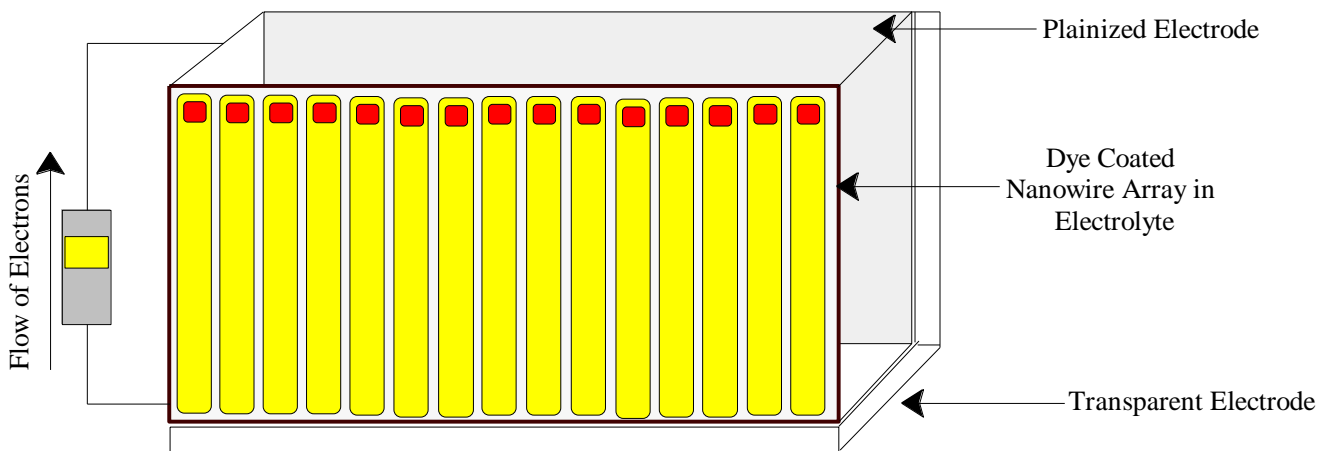
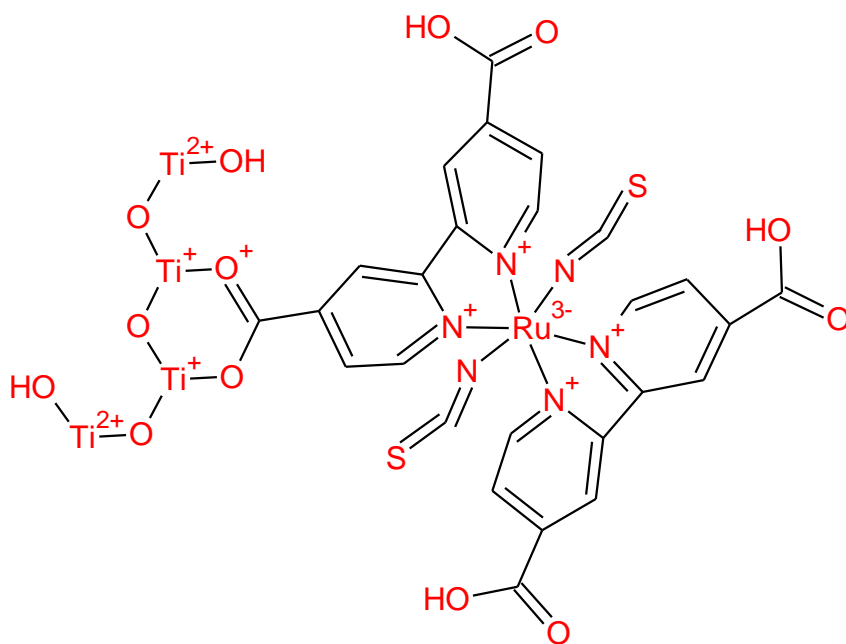
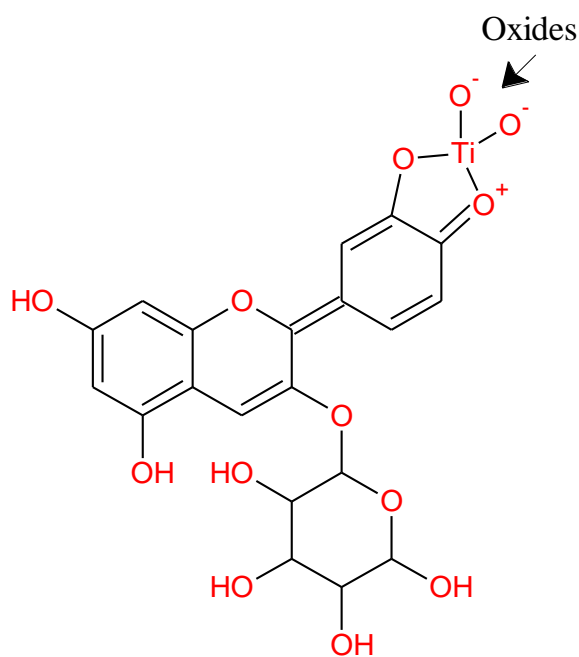


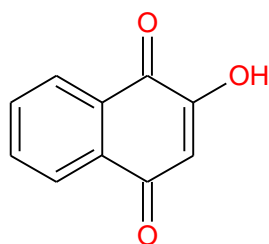
Figure 3: Schematic demonstration of ZnO nanowire DSSC, light is incident through the bottom electrode [68]



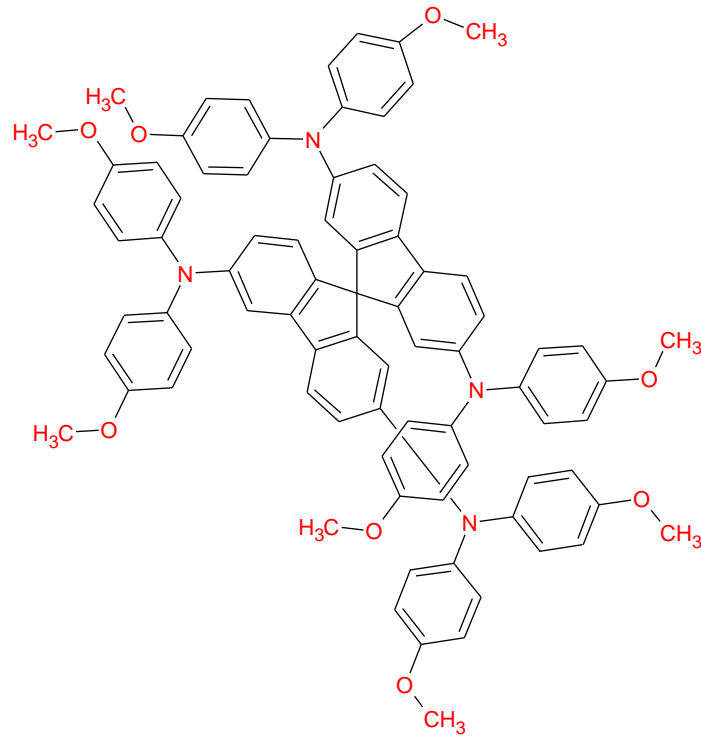
**Figure 4:** On the surface of titanium dioxide, the adsorption of dye Ruthenium based red or "N<sub>3</sub>" [69]



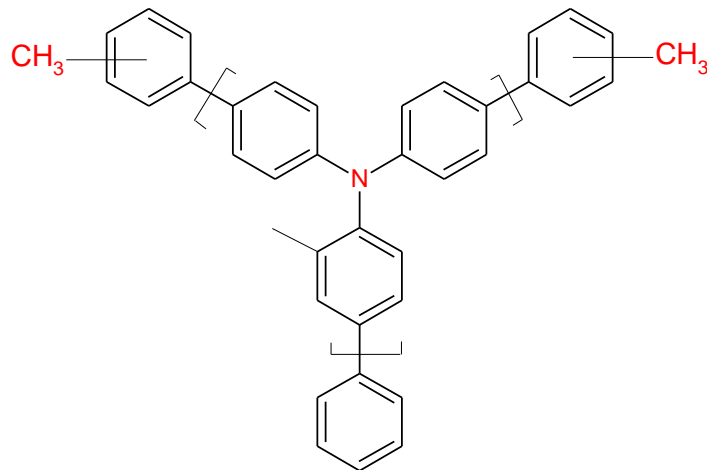
**Figure 5:** On the titanium dioxide surface the cyanin coloring material adsorbed to the centers of titanium metal [69]



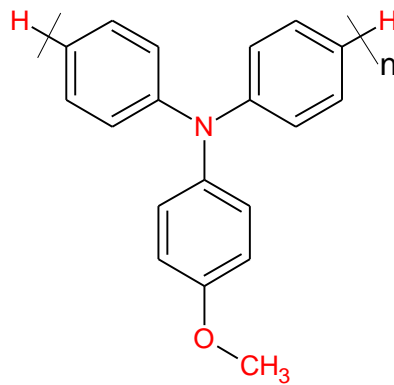
**Figure 6:** Structural formula of Lawsone molecule



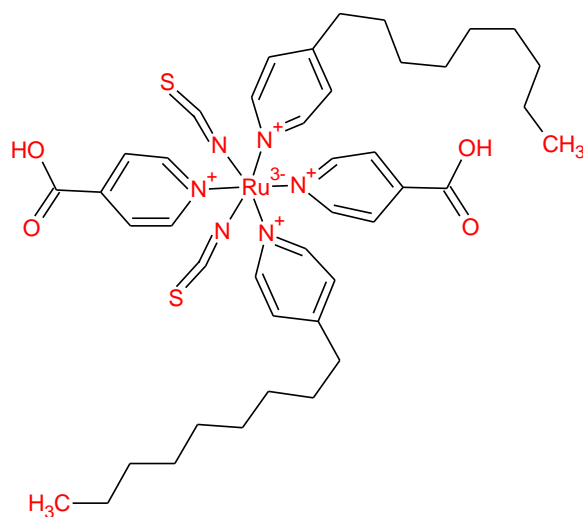
**Figure 7:** Chemical structure of the hole-conductor spiro-OMeTAD resulted in cells energy conversion efficiency  $\eta=4\%$



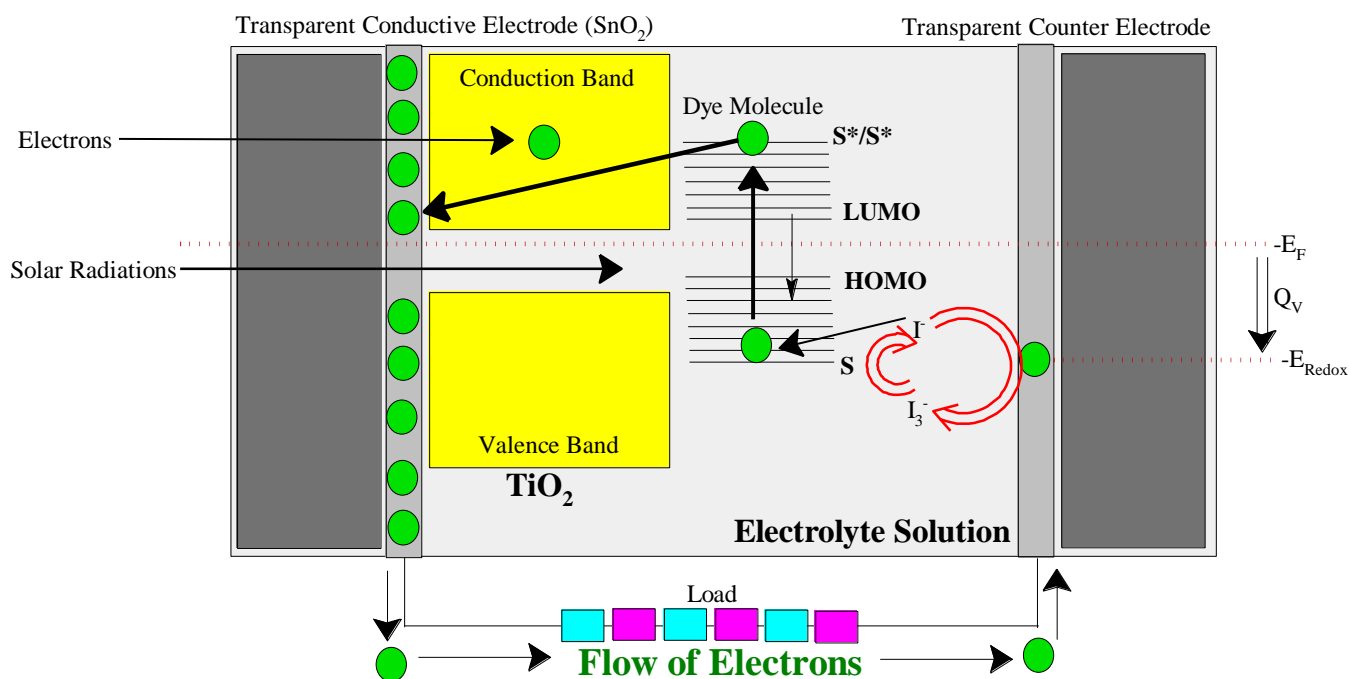
**Figure 8:** Chemical structure of AV-DM resulted in cells with  $\eta=0.9\%$



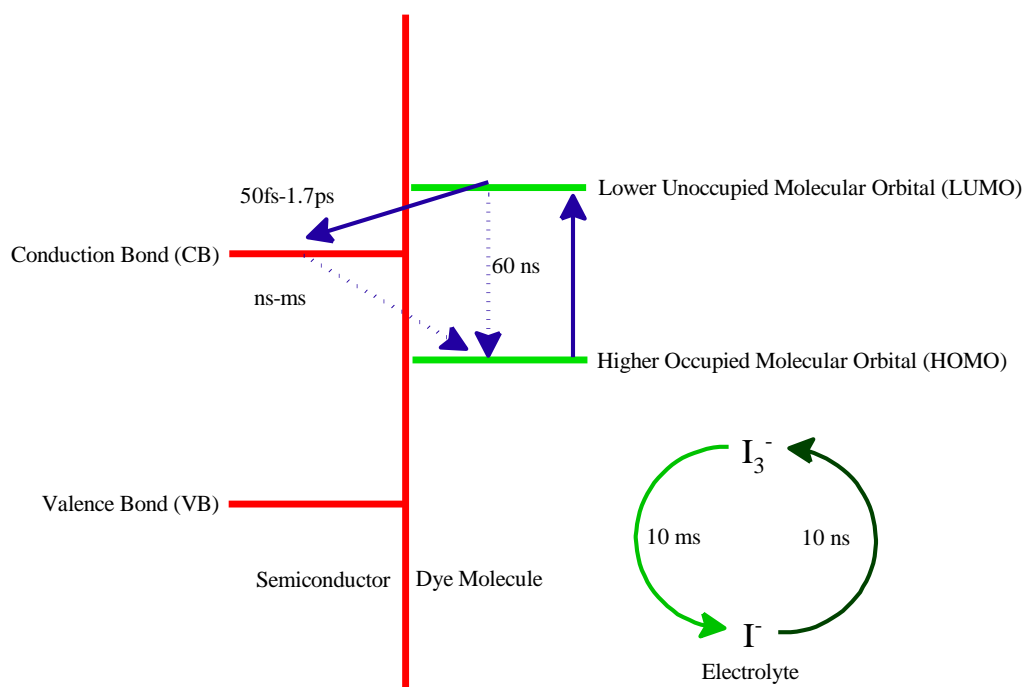
**Figure 9:** Structure of AV-OM. resulted in cells with  $\eta=2\%$



**Figure 10:** Structure of the Z907 dye used for all solar cells as a sensitizer of the nanostructured TiO<sub>2</sub> film



**Figure 11:** The diagram shows the working principle of the DSSCs



**Figure 12:** Schematic image of kinetics in the DSSC [63]

## Conclusions

The third-generation solar cells, called "photo-electrochemical cell" and now called as "dye sensitized solar cells" (DSSC) or "Gratzel cell". Dye sensitized solar cell (DSSC) is classified as a low cost, environmental friendly, and capable of being highly efficient cell mainly due to materials, charge carrier's generation and transport within the cell structure. The dye sensitized solar cell (DSSC) is going to provide economically credible alternative to present day p-n junction photovoltaics. In dye sensitized solar cell, electricity is generated as a result of electron transfer due to photo-excitation of dye molecules adsorbed to the nano-structured wide bandage material photo electrode. In dye sensitized solar cells, light absorption is separated from carrier transport. Since dye sensitized solar cell, DSSC is mimicking photosynthesis in plants, it provides the basic principles of biological extraction, chemistry, physics, environmental science and electron transfer.

In order to commercialize the dye sensitized solar cell in low power applications, flexible DSSCs have been much studied. Nanowires and quantum dots QDSSCs may be a promising solar cell design. We found that the nano-crystalline material based solar cell system exhibits an excellent optical absorption parameter for visible and near infrared portion of the electromagnetic spectrum. The performance of natural dye extracts sensitized nano-crystalline solar cells can be appreciably enhanced by optimizing preparation technique, using different types of electrolytes. In short, compared to Si based solar cells, dye sensitized solar cells are of (i) low cost and offer ease of

production (ii) their performance increases with increase in temperature (iii) possessing bifacial configuration-advantage for diffuse light (iv) have transparency for power windows (v) color can be varied by selection of the dye (vi) invisible PV-cells based on near-IR sensitizers are feasible and (vii) they are outperforms amorphous Si. It is believed that nano-crystalline solar devices are becoming a viable contender for large scale future solar energy converters.

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