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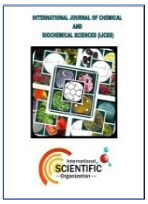

A review on inorganic salts and dye sensitized solar cells (DSSC)

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Abstract

Solar cells convert the direct sunlight into electrical energy. In recent developments, inorganic materials belonging to 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 wide spread attention because it offers an efficient and easily implemented technology for future energy supply. Compared to conventional silicon solar cells (SSC), it provides comparable power conversion efficiency (PCE) at low material and manufacturing costs. Charge separation is initiated at the dye, bound at the interface of an inorganic semi-conductor and a hole, transport material. DSSC materials such as titanium dioxide (TiO_2) 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 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 wok 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

Full length article

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1. Introduction

The standard of human living is significantly affected by the availability of energy resources. The extreme use of traditional techniques was the main contributor to forecast energy and environmental structure. 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" [1]. 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 5 years, reaching upto US$ 48 billion [2].

Photovoltaic technology is the most fascinating field of renewable energy to convert sunlight directly into highly efficient electrical energy. A photonic instrument that transforms different photons having particular wavelengths into electrical energy is characterized as a solar cell. In 1839 a French physicist Alexandre Edmond Becquerel revealed the photovoltaic phenomenon. He was observing the visual aspect 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, cadmium telluride, crystalline silicon and copper indium sulfide. The efficiency of a Si-based cell is highly unstable. The efficiency of the cell mechanically decays at the PV component level. Efficiencies of currently accessible commercialized PV modules fluctuate in between 4% to 8%. They are more suitable for those regions where the sun rises only for a shorter period and can be operated easily at higher temperature conditions [3]. Due to 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 the elementary manufacturing procedure [4].

On the other hand, DSSCs are the most efficient types of solar cells. 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 rate. Currently developed PV technology is mainly established on the electron-hole creation principle. Every cell made up of two separate layers of p-type and p-type semi-conductor substances.

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 produce an electron and a hole pair, and electrical energy is created [5]. 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 PV solar cell production [5]. Currently, DSSCs (Fig.1) come out as a modern class of highly efficient and cheaper energy transformation devices with a straightforward fabrication process. In the Swiss federal institute of technology, a Swiss scientist fabricated the first DSSC solar cell [5]. 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 [6]. The attractiveness of DSSC solar cell is due to the photosensitization of nano-scaled titanium oxide linked with the dyes that are active optically and enhance the efficiencies to a limit more than 10% [7]. Yet, there are a lot of difficulties like dye degradation and also solar cell stability problems [6]. 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 decline cell efficiency [8]. DSSC separation of charges is established by kinetic cooperation same as in the photosynthesis processes directing to 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 kinetic cooperation as produced in the process of photosynthesis [9]. In the photo-electrochemical or DSSC, organic dye substitute with light-absorbing pigments like chlorophylls, while the semi-conductor layer substitute with oxidized NADPH and CO_2 act as electron acceptor. The electrolyte replaces H_2O, and O_2 acts as electron donating species and an oxidation product, respectively [10]. 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 Dye-Sensitized Solar Cells

The DSSC instrument (Fig.2) is made up of four basic constituents: (i) a photo anode contain a mesoporous TiO_2 stick on a lucid conductive substrate made up of glass (ii) a covalently bonded monolayer organic dye sensitizer on the TiO_2 surface to produce electrons by photon emission (iii) an electrolyte to collect electron at counter electrode having I^-/I^{3-} redox couple in an organic solvent. The electrolyte is also effective in the regeneration of dye and (iv) a platinum coated counter electrode.

When the light coming from the sun hits the solar cell, the sensitizer present on the TiO_2 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 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 based on sunlight to electrical power transformation efficiency is given by the formula:

$$\eta=(V_{OC}\,J_{SC}\,FF\times100\%)/Pin$$

Where V_{OC} is the voltage of an open circuit, FF is representing the fill factor, J_{SC} is representing the current density of the short circuit (mA cm^{-2}) and P_{in} is representing the power of the incidental light.

2.1. Transparent Substrate for Both Conducting Electrode and Counter Electrode

Transparent glass surfaces are normally utilized as a substrate due to cheaper in terms of cost, easy accessibility and also greater optical opacity in near-infrared and visible domains. Conductive films in thin crystalline semi-conductive oxide shape are injected on one side of substrate. The film guaranteed a degraded electric resistivity. The nanostructured semi-conductor oxide with a broader band gap is transferred and grownup on the conductive side of the substrate [11]. Ahead of grouping the cell constituents, the counter electrode essentially should be glazed with catalyzing sheet-like graphite to assist the donation of electrons to the electrolyte. One necessarily remembered that transparency levels of CE are not 100% concluded the whole visible as well as near-infrared (NIR) regions. The accumulation of the nanostructured materials cut down the transparency of electrodes [12].

2.2. Nanostructured Photo Electrode

In the past, bulk semi-conductors like GaAs, silicon or CdS were used to fabricate different types of photo-electrodes. Photo-corrosion phenomena occur when light falls on these kinds of photo-electrodes that cause 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 photo-corrosion process. As the surface area of the electrode of bulk semi-conductors with a broad band gap is limited, so the efficiency of converting incident light into the current is low due to deficient adsorption. Light-harvesting efficiency (LHE) is a significant approach to intensify current conversion efficiency by increasing the surface area or roughness factor of the photo-electrode [4].

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 bulk structures [13]. 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 become quite unsubstantial. 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 bandwidth. Gratzel and his co-workers used a nonporous titanium oxide layer instead of bulk TiO_2 semi-conductor as a photo-electrode. They also formulated a new Ru-complex photosensitizer which is very competent in absorbing the broad extent of visible and near-infrared radiations and acquired significant PV cell execution [14].

Nano-porosity of the colloidal solution of titanium oxide is getable by annealing of accumulated titanium oxide coating at around 450°C temperature in a highly vented region for roughly fifteen minutes. Nanostructured photo-electrode is a technique to fabricate nanostructured coating of any semi-conductor substance at 25ºC. The permeable layer is deposited on the conducting surface made up of glass/plastic to utilize in a nano-crystalline DSSC [15].

TiO_2 due to its magnificent chemical as well as economically favorable properties has achieved significant attention in several fields such as gas sensors, photocatalysts, electronic devices and environmental purification [16]. Fabrication techniques of the titanium oxide film are very simple as no vacuum installations are needed. Following methods are well known for the fabrication of titanium oxide layers [17]. Titanium oxide suspension of pH range between 3-4, is prepared by mixing 9 ml solution of HNO_3 to 6 grams of colloidal P_{25} titanium oxide ground powder by grinding in a pestle and mortar. During this mixing process, 8 ml distilled H_2O 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 a surfactant is added in distilled water. HNO_3 solution ratio in the colloidal P_{25} titanium oxide is a hypercritical component to observe the execution of the cell. Increment in the ratio of HNO_3 increases the thickness of the film, while a lower ratio decreases the light absorption efficiency of the cell [18].

Another method named as Doctor Blade method was utilized for the coating of titanium oxide uniformly on highly cleansed ethanol-soaked electrode plates. Then the deposited layer of TiO_2 should be permitted to get dry for 15 minutes and treated at a temperature near about 450°C in a highly ventilated container to form a nano porous TiO_2 layer with the larger surface area. The film must be permitted to cool slowly to 25°C. The drying process is a very essential aspect to withdraw the thermal emphasis and also to avoid the cracking of glass [16].

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 under 20 μm of size to control the diffusion dimensions of photo-electrons. Titanium oxide is one of the best commonly used material because of its excellent electron accepting ability. Different types of semi-conductors having a broad band gap seem 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*., suggested that the nano-rods like arranged electrodes displayed much stable PV possessions and also possessed remarkable energy transformation efficiency [19].

The development of thirst, diluent and denser zinc oxide nanowires is an applicative formulation to intensify the performance of the cell [20]. Further research shows that the zinc oxide nanorods magnitude could be modified easily by dominating the solution modalities like heat, the concentration of the precursor, time of the reaction occurs and also following multi-step development. Nano rod integrated photo-electrodes (Fig.3) offer an outstanding prospective to improve electron transportation. The short circuit density as well as the cell performance was observed to increase significantly as the length of nano-rods increases due to the higher magnitude of adsorbable dye, repentantly rising the conversion efficiency [19].

2.3. Photosensitizer

Dye molecules having appropriate molecular chemical structure are utilized to sensitize broad band gap nanostructured photo-electrode. When the photon is absorbed, the adsorption of the dye molecule to the TiO_2 nanostructured surfaces starts to oxidize and the introduction of an excited electron into nano-structured TiO_2. The compound which has been widely investigated is poly-pyrindyle compounds of Ru(II). It was among the first kind of favorable sensitizers. Most work has centered on the molecular discipline of Ru compounds. Nazeeruddin *et al.*, have described "Black dye" as a favorable sensitizer for charge transformation in DSSC. Natural dye extract sensitization like black rice, shiso leaf pigments, fruits of Calafate, henna, wormwood and rosella. Natural anthocyanins and bamboo leaves have been examined and the PV behavior of the reliable cells shows several possibilities [21]. Using suitable additives to increase open electrical circuit Voc voltage with zero dye humiliation could result in more cell efficiency improvements fashioning the functional implementation of these schemes more worthy for economical feasible solar radiation tools for our social era (Fig.4 and Fig.5) [21].

The magnificent example of charge transfer sensitizer and solar light absorber. One well-known instance is cis-di(thiocyanato)bis(2,2'-bipyridyl)-4,4'-dicarboxylate)ruthenium(II) commonly named as N3/N-719 dye. For dye-sensitized solar cells, hypothetical acquisition of latest ruthenium-based dyes states. The spectra of UV/Visible absorption have been calculated inside the time parasitic density structural hypothesis doctrine. The acquired inflammation forces are in contrast with the empirical consequences [12]. In reality, to be a good sensitizer for dye molecule, it must have many groups of C=O or -OH groups have the ability of extremity to Ti(IV) positions on the titanium oxide surface.

Commercial DSSCs and items manipulate Ru-bi-pyridyl based dyes to get transformation efficiencies exceeding ten percent. Even so, these specific types of dyes are chemically formulated ones though, difficult to set up with an economically not favorable. Given below is the light-harvesting efficiency:

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

In particular λ, A(λ) is the absorbance of the sample. With the concentration of dye extraction, the absorbance and hence the LHE increases. For example with the increase in the concentration of Henna extract, sample absorbance increases and accumulates a wide area of wavelengths. Since none of all the photons dispersed or spread via the nano-crystalline titanium oxide layer is absorbed by single-layered dye molecules, the amalgamation of energy transmits dyes to help in intensifying the light-producing ability. Outstanding improvement in the absorption spectral bandwidth and 26 percent increment energy exchange competence has been established with various sensitizers after energy transmit dyes have been added.

The organic sensitizers without metals like metal independent I_2 fabricated by showed extraordinary efficiency. Total conversion efficiency of indoline dye to convert solar light into current was 6.51%. While on the other hand, the efficiency of N_3 dye with the same conditions was 7.89%. Quantum-dots are a nano-structured type of micro-crystalline semi-conductors, where quantum parturiency effect because of their most effective size consequence in significant optically linear and non-linear activities. The structural formula of Lawsone is shown in Fig.6.

Excitonic sorption of quantum dots is large size dependent for PbS quantum dots expedited in the case of methylbenzene. It is expected that QD is a secondary component instead of dyes to absorb light coming from the sun in DSSC. The light-harvesting process creates excitons/electron-hole pairs in the DSSC. The excitons have a familiar physical change b/w electrons and holes, have in mind as in the case of Exciton Bohr Radius. Normally, the Bohr radius is higher the quantum dot length/diameter directing to the quantum parturiency phenomenon (Distinct energy levels = Unreal molecule). Excitons split up at the quantum dot titanium oxide surface. Later on, the ejected electrons are inserted in the conduction region of titanium oxide, while the other factor known as the hole is injected into an electrolyte. Different dyes that assimilate over comparatively in a constrictive domain, semi-conductor QDs such as lead sulfide absorb powerfully entire photons with higher energy than that of the band gap therefore a greater magnitude of solar light can be modified into useable energy utilizing nanocrystals as compared to the dyes. Dyes are discreditably not too much stable and show the photo bleach phenomena over comparatively fugitive measures of time. QDs processed with a gracility modified external shield are much stable and thus prolonged everlasting solar cells with no debasement in the performance are executable. QD-sensitized cells bring forth greater quantum output than one because of the effective ionization activity.

Remarkable prosperity has been accomplished in the photo transformation efficiency of the solar cells based on Cd and Se light harvesting QD backed with CNT. This is established by the integrated CNT system in nano-structured titanium oxide semi-conductor layer and consequently supporting charge shipping phenomena. Therefore, considerable advancement in the light transition efficiency of a common DSSC is possible. Freshly Fuke *et al.*, reported Cd and Se QD-sensitized light-harvesting cells with approximately 100% intragroup quantum efficiency. Excellent improvement in both of the electron insertion and charge accumulation efficiencies at two different sites was accomplished.

2.4. Redox Electrolyte

Different electrolyte comprising of I/I_3^- redox fragments is significantly utilized in the DSSC to re-create oxidized molecules of the dye and therefore accomplishing the electrical current circuit by immigrating the electrons between both of the nano-structured as well as counter electrodes. NaI, R_4NI and LiI are outstanding examples of iodide mixture normally liquefied in the non-protonic medium like propionitrile, acetonitrile and propylene carbonate to fabricate the electrolyte. The performance of the cell is largely affected by the ionic conduction in the electrolyte, which is instantly modified by the viciousness of the solvent. Hence, the solvent with bunked viscosity is extremely advisable.

Furthermore, the counter iodide ions like sodium$^+$, lithium and R_4N^+ do impact the efficiency of the cell due to their light-harvesting ability of ionic conductivity. It was established that the insertion of tertiary butyl pyridine to redox electrolytes intensifies the cell execution. The Br^-/Br^{3-}redox ions were utilized in the DSSCs and they execute remarkable results. Both V_{OC} and I_{SC} were enhanced for Eosin Y-based dye-sensitized solar cells when Br^-/Br^{3-} was inserted instead of I^-/I^{3-} redox couple. The redox electrolytes necessarily to be selected the diminution of I^{3-} ion by the electron's insertion is blistering and are much efficient.

This subject developed from the concept that the dependency of both hole transportation and accumulation efficiency on the dye cation diminution and I^-/I^{3-} redox couple efficiency at counter electrode to be assumed into the attainment. Also limiting the cell firmness because of the vaporization, liquid electrolytes stamp down the fabrication of multi-cell components, since module fabrication demands the cell be attached electrically even should be isolated chemically. Therefore, an excellent shortcoming of DSSC occupied with liquid regime redox electrolyte is the discharge of the filled electrolyte solution, directing to the cell reduction period and also related scientific difficulties incidental to the instrument protection and prolonged stability.

Different investigation groups analyzed the utilization of the ionic liquids, hole collector electrolytes and polymers to substitute the requirement of organic mediums in different liquid electrolytes. These sympathetic electrolytes despite low efficiency near about 4 to 7.5% are auspicious and can assist the development of commercial dye to sensitize solar cells. Injection of different polymer gels to quasi solidified electrolytes is examined by different investigative groups. It has been established that the insertion of polyviny1idene and poly-fluorene-co-hexafluoropropylene to KI/I_2 electrolyte has reinforced the fill factor as well as light to the current conversion efficiency of cells till 17% in the addition. Gel-based electrolytes are also much fascinating from many of other orientations like efficiency is a cooperation b/w the viscosity of electrolyte and the mobility of ions; gel-based ionic liquids hold an abnormal broad ionic mobility instead of their flooding viscosity and also peculiarly for recognition of massive arrangement of inter-cell protection [22].

Advanced categories of electrolytes like p-type electrolytes, TMA, polymeric electrolytes, PEDOT that transferred electrons from the counter electrode to oxidized molecules of dye inspiriting advance inquires to optimize or organize fresh ones. Freshly latest organized research of charge transportation and also re-combination in the solid DSSC by utilizing coupled polymer hole conveyer has been disclosed by [23]. In his research, he used organic functional indolone dye commonly known as D_{131} as sensitizer and poly-3-hexylthiophene as hole conveyer a pow showing light transformation efficiency of 3.85%. Hence, these kinds of solar cells are anticipated to symbolize to the highest degree of efficiency [23]. Some important chemical structures are shown in Fig.7 to Fig.10.

2.5. Working Principle of Dye Sensitized Solar Cell (DSSCs)

Nano-crystalline like TiO_2 contains a large surface area so it is placed on the conducting surface of the electrode (photo-electrode) and used to adsorb sensitizers or dye molecules. The dye molecules are excited through the adsorption of photons, from HOMO which is the highest occupied orbital to LOMO that is the lower unoccupied molecular orbital state. The electrons inserted into the film of TiO_2 nano-structured then these dye molecules become oxidized. This inserted electron move between the layers of TiO_2 nano-particles and work done as electrical energy. The electrolytes having I^-/I^{3-} redox ions can be used as electron intermediary 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 to internally provided electron and then reduced to I^- ions. The movement of electrons in nano-structured semi-conductor is attended by diffusion of charge-compensating cations in the layer of electrolyte near to nanoparticle surface. Therefore, no transformation is caused by the electric power generation in the DSSC (Fig.11).

The minor energy separation concerning HOMO and LUMO makes certain absorption of photons of short energy in the solar spectrum. Hence, the photocurrent level is dependents 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 energy between LUMO and the bottom of TiO_2, the efficiency of electron insertion into the layer of the TiO_2 conduction band is enhanced. Furthermore, the energy difference between the chemical potential of redox and HOMO is positive, the HOMO level accepts the electrons from the 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 I_0=100mW/cm^2 (Air Mass 1.5) and the conversion efficiency from photon energy to the electricity is demonstrated as:

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

The small circuit current is J_{sc}, V_{oc} shows the 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 whilst the cell is subjected to bright sunlight. The photo-electrode's determined transmittance because of the reflection of light and absorption using conductive photo-electrode and nano-structured TiO_2. Because TiO_2 past is imposed on to the conductive interface, the efficacious zone of the irradiated portion of the cell is extended through the Doctor blade process. Given the difference in composition of the Bahraini Henna extract, the cells developed nearly the voltage of the same open-circuit V_{oc}. On either hand, short circuit 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 sections, the electromagnetic spectrum. The dye concentration was reported to have a significant effect on the severity of the photocurrent received. High Henna extract concentration induces a set of resistance, which eventually restricts the photocurrent produced. In comparison, diluted extracts lessen photocurrent magnitude and cell output [2-4-18-24].

2.7. Charge Insertion, Transportation and Recombination

Several investigators have investigated the electron injection kinetics onto the semi-conductor photo-electrode upon being stimulated from the photosensitizer employing moment-resolved laser spectroscopy. It has been noticed because both the photosensitizer material specification as well as the segregation of energy between convection band stage of the wideband gap semi-conductor are different and thus the photosensitizer's LUMO level adversely affect the transfer rate of electrons to the wideband gap semi-conductor. A diagram description of the DSSC kinetics is shown in Fig.12. The indications displayed suggest perturbation of the dye molecule from the level of HOMO to the level of LUMO, calming of the departure zone, electron insertion from the dye level LUMO to the TiO_2 conductive band, recombine the extracted electron with the dye level HOMO and recombination of the electron in the TiO_2 conductive band with a hole in the electrolyte and restoration of the oxygenated dye by I^- [25].

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 (CB). It has also been reported to a quite quick method 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 image-injected CB electrons through oxidized dye molecules or electrolyte-redox pair oxidized type I (ions) happens in 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, such as Haque *et al.*, examined 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 [26].

The redox triad structure given by Haque and his colleagues, was the first and most effective charge separation in the study. The triad is composed of a ruthenium complex attached with nano-crystalline TiO_2 which is the electron acceptor which then covalently bound to triphenyl-amine that is electron donor polymer chains. Bullets reflect the position of moving electron. 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 show in process 2 from the excited sensitizer state. It will eliminate the direct combination of the predominantly federal charges show in process 3. Specific recombination of predominantly isolated charges shows in process 3 will degrade this energy that is extracted through heat. In the super molecule, this is prevented by that of the related triphenyl-amine electron donor classes' show in process 4 rapidly reducing the ruthenium. The supplementary recombination phase show in phase 5 here between inserted electron as well as the oxidized amine radical is progressively sluggish even though the positive charge on their surface will hop through 1 triphenyl-amine feature to the adjacent that along the chain shown in the process 6, as well as the hole turns not here from the TiO_2 surface. It consists of a synchronous electron stream from those at the beginning of the polymer chains to the oxide (right) [27].

The electrons migrate to the electrode in TiO_2 nanoparticle DSSCs, jumping amongst particles 10^3-10^6 times [28]. Here is a significant propensity of recombining the photo-excited electron employing the electrolyte for each step, because both the diffusion and recombination levels have been on the range of milliseconds. 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 expresses as a highway to the anode, resulting in a higher rate of diffusion thereby slowing the rate of recombination lowering cell efficiency [29].

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-} which is the hole carrier in the electrolyte solution. This is, therefore, a down-reaction which must be removed or reduced. Decreases of dark current increases cell's open-circuit voltage which is inferred from the following specific solar cell equation comparing the voltage of open-circuit VOC together with the I_{inj} penetration current as well as the Dark dark current.

$$\mathbf{VOC=lnkaT\ (I_{nj}+1)/q}$$

Dark (12) in which kB is a Boltzmann constant, the complete cell temperature is shown as T, and the electron charge amplitude denoted by q. Besides, the 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_2 is a good way to suppress dark current [30].

2.8. Efficiency of DSSC

The characterization of solar cells is defined by many important steps. It's 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 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 here between the TiO_2 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 0.7 V. DSSCs give a much higher voltage than silicon. There are only minor variations so that variations in the real world are influenced by current output, J_{sc}.

DSSCs are highly effective in terms of Quantum Efficiency. There is a high probability in which a photon can be absorbed because of its "width" in the nanostructure, and the dyes are very efficient in converting them into electrons. Much of the minor losses that occur in DSSC's are due to conductive failures in the TiO_2 and transparent electrode, or front-electrode optical losses. Depending on their size, the quantum performance of typical designs varies but is almost the same as the DSSC [31].

While the dye is extremely effective in transforming absorbed photons or electrons in the TiO_2, in the end only photons absorbed through dye and generate current. The rate of the absorption of photons depends on the absorption spectrum of the sensitized TiO_2 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, meaning that a smaller number 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^2 [32].

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 (coloring). DSSCs also operate in a wide variety of lighting environments. Therefore, they are very common in rainy weather, whereas conventional cells become a failure. The DSSC cutoff is so small they were 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 cells that range from 5% to 13%. DSSCs perform at low indoor temperatures [33].

Production of DSSCs involves heavy electricity consumption, high performance and slide-to-roll fabrication technique. DSSCs use affordable nanomaterials that are environmentally sustainable. Indoor DSSC modules are extremely versatile, lightweight yet 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 DSSCs is highly controllable and testable. Screen printing methods can be used to get mass output in DSSCs.

The physical design of the dye-sensitized solar cells and materials used are eco-friendly with environment, low-cost and the manufacturing and understanding of specific colors (such as the sensitizing dye used) is quite easy. The Australian company Sustainable Technologies International manufactured large-scale electric-power glass sheets for 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 mobile devices implementations. Solar cells sensitized to the dye can be crafted as vibrant indoors.

The flexible dye-sensitized solar modules provide possibilities for their integration with several wearable devices, luggage, gears and outfits. The dye-sensitized panels with an output of 10 percent are an attractive option for replacing 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 can be attained.

4. Drawbacks of Dye Sensitized Solar Cells (DSSCs)

For a large scale, the DSSCs are not considered a decent choice because greater-cost and sophisticated-efficiency cells are more viable for use. 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 cell architecture uses the liquid electrolyte is not stable for high temperatures, which freezes the electrolyte at lower temperatures. As the fluid extends at higher temperatures it is a very difficult process to seal the doors. Electrolyte solution DSSCs include volatile organic solvents that are muted.

5. Commercialization of Dye Sensitized Solar Cells (DSSCs)

On almost all continents, marketing of dye-sensitized solar cells and modules takes place. Throughout Asia, throughout Japan in particular: IMRA-Aisin Seiki/Toyota, Sony, Toshiba, Dai Nippon, Peccell Technologies; About Australia: Dye sol. Konark in the USA. G24i in Great Britain and Solaronix in Switzerland are commonly used brands. In 2007, G24i announced a 25MW capacity DSC module development in Cardiff, Wales (UK), with expansion plans up to 200MW by the end of 2008.

6. Recent Developments in DSSC Components

6.1. Recent Developments in Photo-Anodes

The photo-anode works as dual functions like it acts as a support for loading of sensitizer, used as a transporter from sensitizer to external circuit of photo-excited electrons and nanostructured semi-conductors are the background of DSSC photo-anode. The large surface area is required for great dye loading and the efficiency of electrons collection increases by increasing the rate of charge transport. The ideal photo-anode is defined by these two important properties [34-35]. While the nanoparticles that containing large surface area which allows a high capacity of dye loading, the disorderly network with various grain borders weakens the mobility of electrons and shows slow transport and then recombination of the photo-excited electrons. This critically constrains the total competence of this device [22-36-37]. The inborn problems related to the construction of standard photo-anode force a search to construct more active nano-structured photo-anode tools and morphologies [38].

6.1.1. Doping with Different Ions

Ion doping is extensively used to regulate the position of both, the 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 increases their efficiency by doping [39].

6.1.2. Decoration with Noble Metals

The optical path length extended by surface plasmon resonance effect (SPR) of noble metal like Au, Ag nanoparticles can be found to localize incident light [40]. 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 the decoration with Au nanoparticles and it depends on different size ranges [22]. The Ag, TiO_2, and SiO_2 nanostructures can be prepared. In this method, the SiO_2 covering prevents the decomposition of Ag type nanoparticles using I/I_3 electrolyte and increases surface plasmon and light scattering effect. This directed to enhancement in light absorption property [41]. Therefore, the influence of noble metal nanoparticles in DSSCs is still contentious and methodical research due to their specific role is essential in the future.

6.1.3. Coating with Up/Down Conversion Materials

Conventional sensitizers such as organic dyes and ruthenium are characteristically used in DSSCs which absorb sunlight only in the visible region. Consequently, an unconventional scheme for light-harvesting to the near-infrared region can be improved by fabricating up-conversion of the nanoparticles in which absorption of sensitizers converts near-infrared light into visible light [42]. 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 central constituent of DSSCs is a sensitizer. It is used to gather sunlight at the semi-conductor region to produce photo-excited electron. Some requirements are necessary for batter performance of sensitizers such as the dye regeneration from the electrolyte and proper LUMO level and HOMO levels for current charge addition into the semi-conductor, high stability, and good photo-stability, the load of the semiconducting materials by the chemically adsorbed groups, for light-harvesting the coefficient of high molar extinction into the visible region and near-infrared region, and in some different cases, for example, the use of some cobalt-based electrolytes to hamper the recombination by creating the spacing between photo-anode and electrolyte. Previously, the incredible effort has been dedicated to developing a diversity of sensitizers that can be distributed into different five forms.

6.2.1. Ruthenium Polypyridyl Dyes

Ru(II) polypyridyl dyes is the best widespread sensitizer of DSSCs because they show excellent performance due to their high molecular stability, wide light absorption ranges from the ultraviolet region to near-infrared light region (Dl 350 nm) and appropriate energy levels concerning I/I^3 electrolyte and TiO_2 photo-anodes. Therefore, as primary in the mid-1990s the Ru (II) dye established DSSCs and its efficiency had 10.0%, with successive efficiencies of 11.2% in 2005, and in 2010 showed 11.7% efficiency.

Some strategies such as exchanging the ligands of thiocyanate with some chelating anions, phosphate groups in Ru(II) dye can be studied, hydroxamate as an alternative of carboxylate and including functionalized ancillary ligands like triazolylpyridine and butyloxy-substituted benzene ring. Though, over the past ten years, the competence of Ru(II) dye based DSSCs has lingered quietly. The new type of sensitizers with a low cost like ruthenium and coefficients such as Ru(II) polypyridyl (e=10,000–20,000 $M^{-1}cm^{1}$) with low molar extinction have been investigated [43].

6.2.2. Metal Free Organic Dyes

Metal-free organic dyes have some important properties such as high flexibility in molecular structure, high molar extinction and cost-effective. Due to these properties, the metal-free organic dyes gained high research interest as favorable for sensitizers in DSSCs [23]. A large number of organic dyes can be designed with a donor–P spacer–acceptor (D– P–A) structure and used widely for DSSCs [44]. These organic dyes usually contain electron-rich moieties like indulines triarylamines and carbazoles used as donor parts, P-conjugated groups such as benzothiadiazole, polyenes, thiophenes and units as electron-withdrawing for example pyridines, cyanoacrylic acid and rhodamines used as acceptor parts. 10% is the transformation efficiency of DSSCs with D–P–A type of organic dyes. Conversely, some properties such as the adverse dye aggregation, narrow absorption bands and variability, characterize a major blockage for additional improvements in metal-free organic dye sensitizers [45-46].

6.2.3. Dyes of Porphyrin

In current years, the porphyrin dyes have been investigated and predominantly the push-pull type dipolar Zn(II) porphyrins are used as DSSCs because of their extreme absorption in the region of 400–500 nm and 500–700 nm, appropriate energy levels with versatile structure and excellent molecular stability [47]. 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 [45]. Earlier studies have been shown that it becomes a challenge to harvest the sunlight from ultraviolet to near-infrared region by using single porphyrin dye sensitizer as it bears effective injection of the photo-excited electrons into photo-anodes [48]. The light-harvesting range and DSSC's proficiency, increases by co-sensitized methods. The $YD^{2-}OC_8$ co-sensitized with organic dye in 2011 and obtained 12.3% efficiency in DSSCs [49].

6.3. Recent Developments in DSSC Electrolytes

In the previous few years, the electrolytes of iodide–tri-iodide (I_3/I) are best worldwide redox shuttle because of their adequate kinetic properties, like at the photo-anode/electrolyte fast oxidation, effective regeneration of dye and at the electrolyte/counter electrode reduction of $I_{3,}$ excellent infiltration, low cost, high carrier collection and easy preparation [36]. Although this, numerous shortcomings are present for I_3/I electrolyte. But some disadvantages are present such as the corrosion of the counter electrode like Pt and Au of noble metal, at 430 nm the absorption of visible light, and using electrolyte system further development of DSSCs. Accordingly, some alternative electrolytes have been investigated, with thiolate/disulfide mediator, ferrocenium/ferrocene couple, Cu (I/II) complex, and Co (II/III) polypyridyl complex [47].

6.3.1. Quasi-Solid Electrolyte

Quasi-solid-state electrolytes undergo leakage of solvent therefore it requires suspicious treatment of sealing when it is used in very high environmental temperatures. Subsequently in the future, solid-state electrolytes become the main focus for the research of DSSC electrolytes and industrial development. The liquid electrolytes are replaced by the 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 materials [50]. CuI/CuSCN has high hole mobility. However, the SS-DSSCs show a 3.8% PCE value because fast crystallization rates result in poor filling into photo-anode films. $CsSnI_3$ 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 up to 10.2% PCE yield for SSDSSC [25].

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 transport into the solid-state electrolyte. The main requirements for the counter electrode (CE) are (i) tremendous stability (ii) increasing conductivity for charge transport and (iii) good electro-catalytic activity [47]. Noble metals, like Ag, Pt and Au are the greatest rare CE materials due to their large electro-catalytic activity (e.g. Pt) for their reduction or 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 [51-52].

6.4.1. Carbon Materials

The carbon-based materials like carbon nanotubes, graphene and porous carbon have used as CEs material in DSSCs because of their important properties like low cost, high electrical conductivity, corrosion resistance, good electro-catalytic activity and thermal stability [53]. The electrochemical activity of CEs materials can be amplified by combining the different forms of carbons such as carbon nanotube/graphene nano-ribbons and porous carbon/carbon nanotubes [54]. The different forms of CE materials and the combination of diverse carbon materials become a popular area for advanced research [55].

6.4.2. Inorganic Compounds

Sulfides, nitrides, carbides, phosphides, metal oxides and tellurides have been used as effective CE materials due to their vital applications in low-cost and large-scale production of DSSCs. Though the stability and performance of inorganic complexes for DSSCs still a necessity to be more developed [51].

6.4.3. Conductive Polymers

Some polymers such as 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 their transparency. The PEDOT is the utmost usually used CE material and used in DSSCs to increase their electrical conductivity and solubility, different doping materials such as TsO, polyoxometalate (POM), ClO and poly (styrene sulfonate) to increase their properties. More development of conductive polymer like CE-based DSSCs is required [56].

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:

1. Non-optimized dark current
2. Low working of dyes in the region of NIR
3. Between the electrodes poor contact
4. High viscosity and low volatility of the electrolytes
5. The properties of electrolyte degraded by UV absorption of light

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

1. To reduce the dark current, improve the morphology of semi-conductors

2. Improvement in the structure of dye to absorb the radiation in the NIR region

3. Improve the rate of charge transfer, develop the less viscous and low volatile electrolytes

4. High viscosity and low volatility of electrolytes

5. Use of additives for dyes and electrolytes to increase their properties

The efficiency and stability of DSSCs cannot depend on a single factor. There must depend on different factors to increase the performance of DSSCs [57].

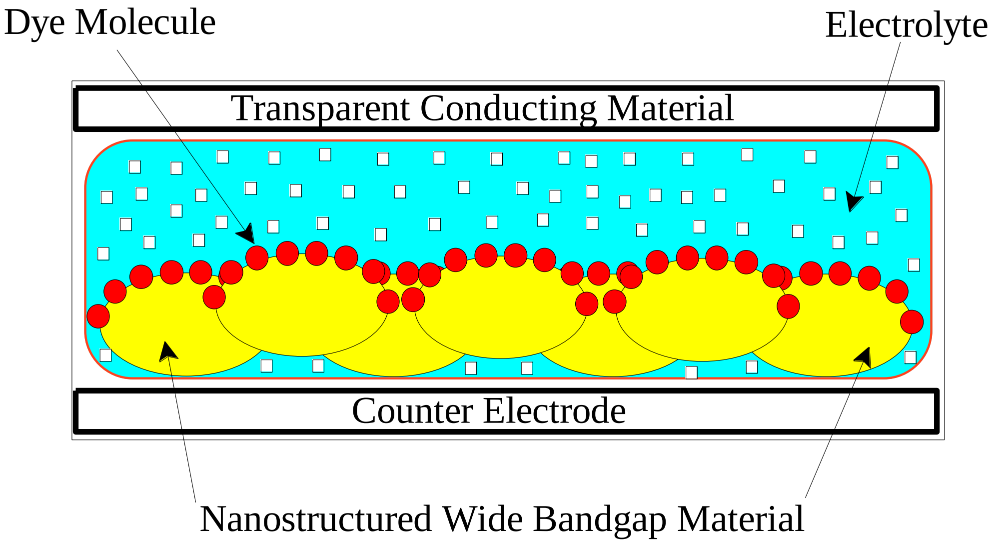

Fig.1 Schematic representation of DSSC

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

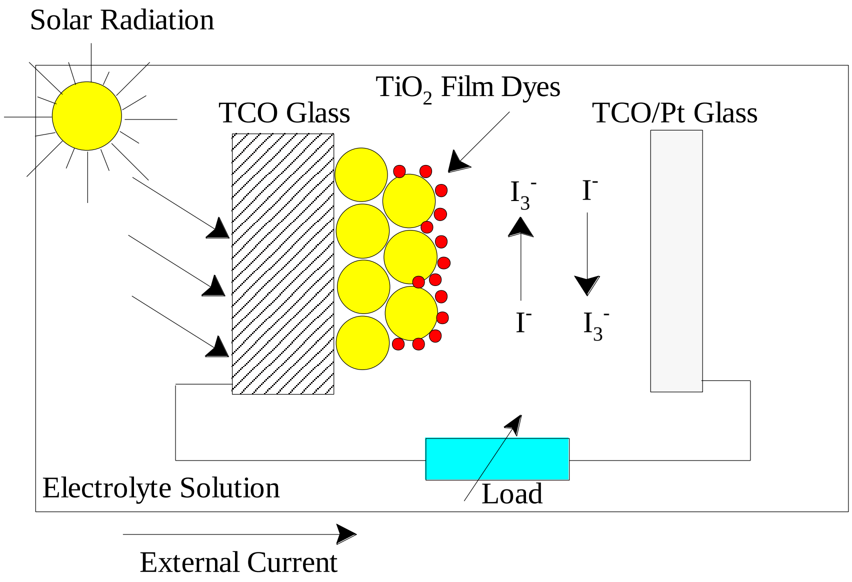

Fig.2 Schematic diagram of a dye-sensitized solar cell [11]

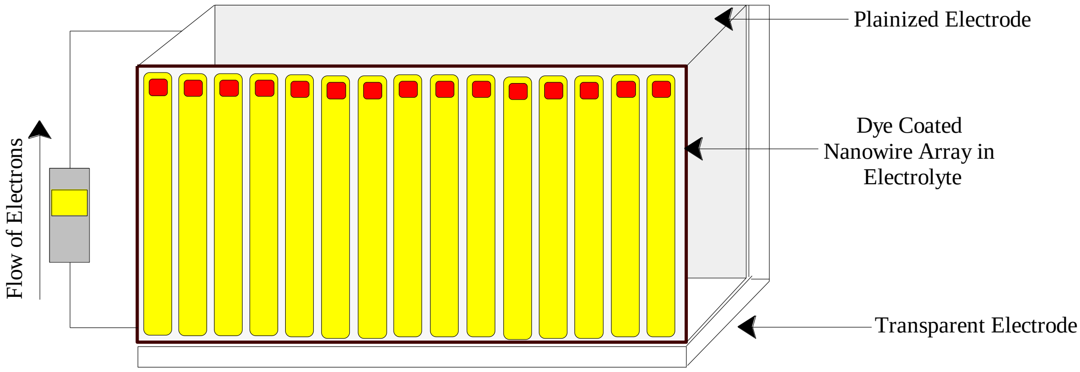

Fig.3 Schematic demonstration of ZnO nanowire DSSC, light is incident through the bottom electrode [58]

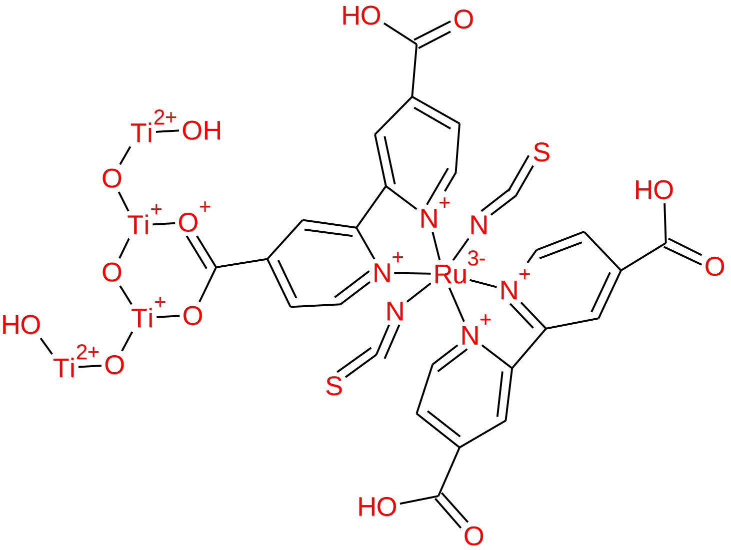

Fig.4 On the surface of titanium dioxide, the adsorption of dye Ruthenium based red or "N_3" [59]

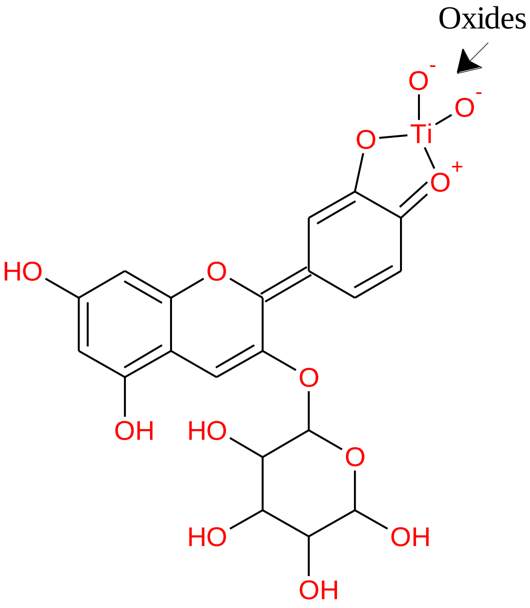

Fig.5 On the titanium dioxide surface the cyanin coloring material adsorbed to the centers of titanium metal [59]

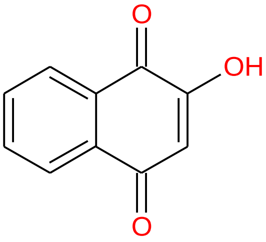

Fig.6 Structural formula of Lawsone molecule

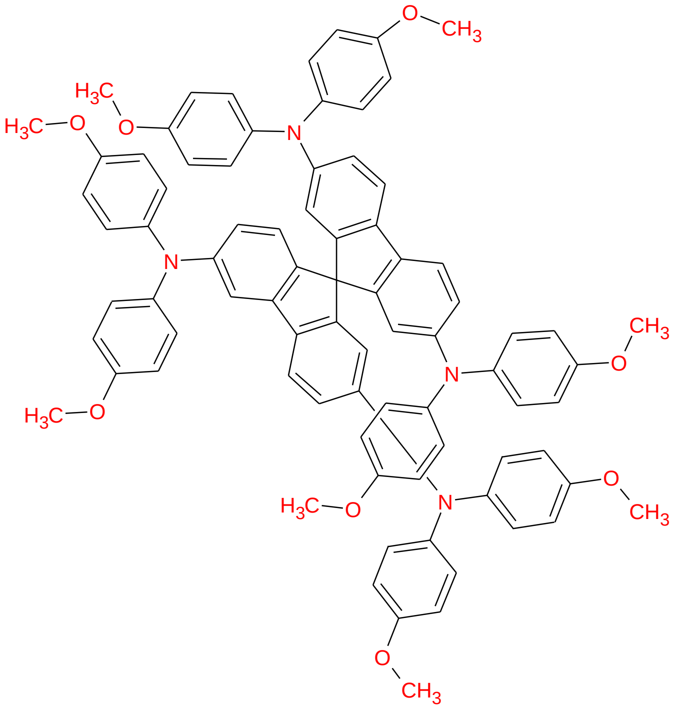

Fig.7 Chemical structure of the hole-conductor spiro-OMeTAD resulted in cells energy conversion efficiency η=4%

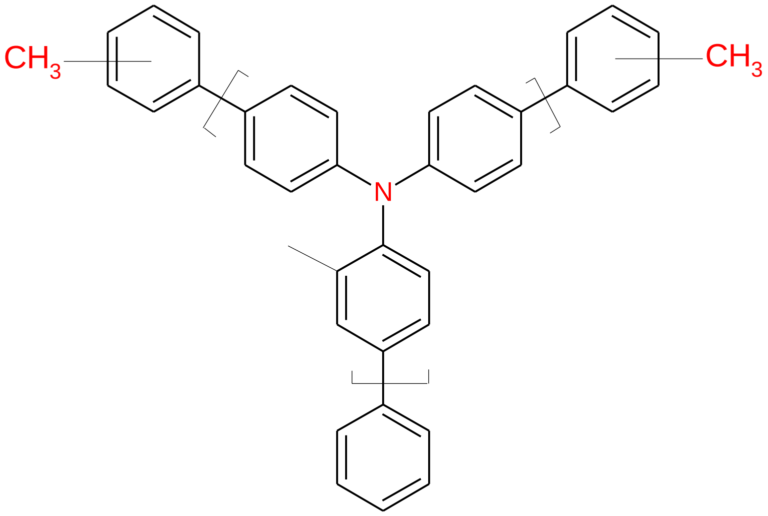

Fig.8 Chemical structure of AV-DM resulted in cells with η=0.9%

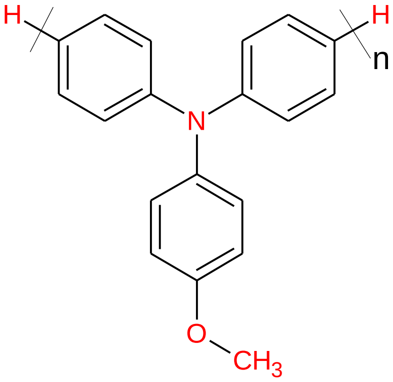

Fig.9 Structure of AV-OM. resulted in cells with η=2%

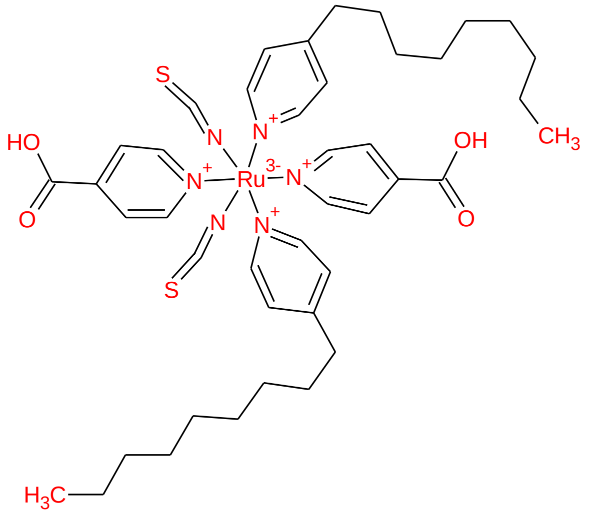

Fig.10 Structure of the Z907 dye used for all solar cells as a sensitizer of the nanostructured TiO_2 film

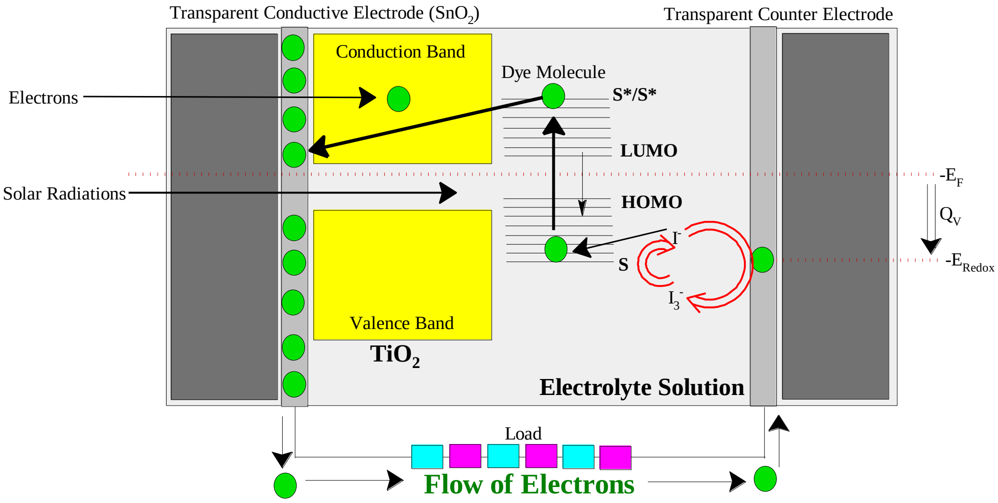

Fig.11 The diagram shows the working principle of the DSSCs

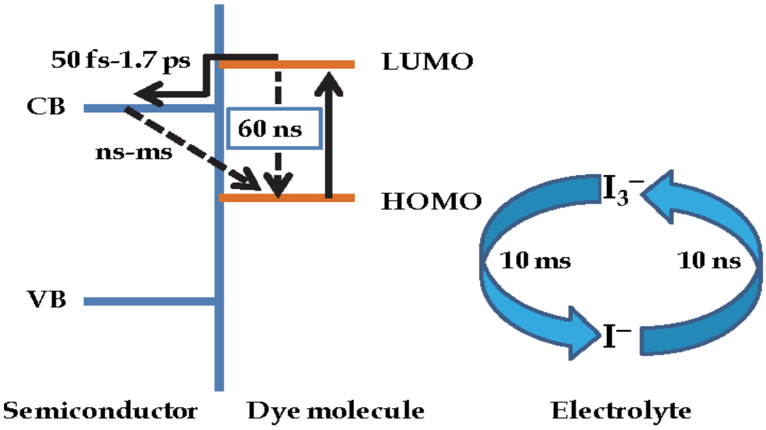

Fig.12 Schematic image of kinetics in the DSSC [53]

Conclusion

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, environmentally 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 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 dye sensitized solar cell in low power applications, flexible DSSCs have been intensively investigated. 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 low cost and ease of production, their performance increases with temperature, possessing bifacial configuration-advantage for diffuse light, have transparency for power windows, color can be varied by selection of the dye, invisible PV-cells based on near-IR sensitizers are feasible, and they are outperforms amorphous Si. It is believed that nano-crystalline solar devices are becoming viable contender for large scale future solar energy converters.

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