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# Recent Advances and Future Prospects for Dye Sensitized Solar Cells: A Review

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***Abstract*:** The Dye Sensitized Solar Cell (DSSCs) has emerged as attractive and promising solar cells in recent years. It offers technically and economically viable option to p-n junction solar cells. However, the efficiencies of DSSCs could not compete with those of silicon solar cells. Numerous researches have been done to enhance the efficiencies of these cells over the past decades. Efficiencies up to 15 % have been achieved by adopting new techniques in the research area. There are good prospects for further improvement in the photo conversion efficiencies and commercial applications of DSSCs through new parameters and methodology. In this review paper, the current state and recent developments in the field of photo electrode, photo sensitizer and electrolyte for dye sensitized solar cells have been reviewed. Also the perspectives for the future development of the technology have been discussed.

***Index Terms*:** Dye Sensitized solar cell; photo electrode; photo sensitizer; cell performance

## I. INTRODUCTION

A dye-sensitized solar cell is a low-cost solar cell belonging to the group of thin film solar cell [1]. It was first employed in early 1970s with the use of oxide semiconductors and dye based sensitizer [2]. It is based on a semiconductor formed between a photo-sensitized anode and an electrolyte, a photo electrochemical system. A later version of a dye solar cell, also known as the Grätzel cell, was invented by Michael Grätzel and Brian O'Regan, showed improved conversion efficiency of 7.12% set a remark in the field of solar cells. Grätzel found that titanium oxide nanoparticles increases the dye absorption area to large scale, by working on Ru-based dyes with a wide range of optical absorption were developed extending from the UV to the near IR region. And an overall efficiency up to 10% had been achieved [3]. Further improvement of the conversion efficiency over a wide range of wavelengths by $TiCl_4$ surface treatment has been reported by Grätzel et al. [4]. Later on numerous efforts have been done on improving the efficiency of the cell. Researches have been done on different areas for developing efficient dssc by modifying electrodes, photo sensitizer and electrolytes. Efforts have been put in developing new materials for photo electrode. Recently perovskite based solar cells have been developed which showed efficiency up to 17%. Various modifications have been done on dyes to reach higher efficiencies. Many new organic photo sensitizers have been synthesized by structure modification which could absorb higher wavelength range. New metallic dyes and natural dyes have also been analyzed. Electrolyte modification has also resulted in the cell durability and increased efficiency of the cell.

## II. DSSC: STRUCTURE AND WORKING

A modern DSSC, the Grätzel cell, contains five components: a conductive mechanical support, a semiconductor film, a sensitizer, an electrolyte, and a counter electrode. A schematic diagram and working of a DSSC is shown in fig 1. It works on the principle of photosynthesis. It is a photo electrochemical cell, which converts light into solar energy. When Sunlight passes through the transparent electrode into the dye layer where it can excite electrons which flow into the titanium dioxide coated FTO electrode. The electrons flow toward the counter electrode where they are collected for powering a load. After flowing through the external circuit, they are re-introduced into the cell on a metal or graphite electrode on the back, flowing into the electrolyte. The electrolyte then transports the electrons back to the dye molecules.

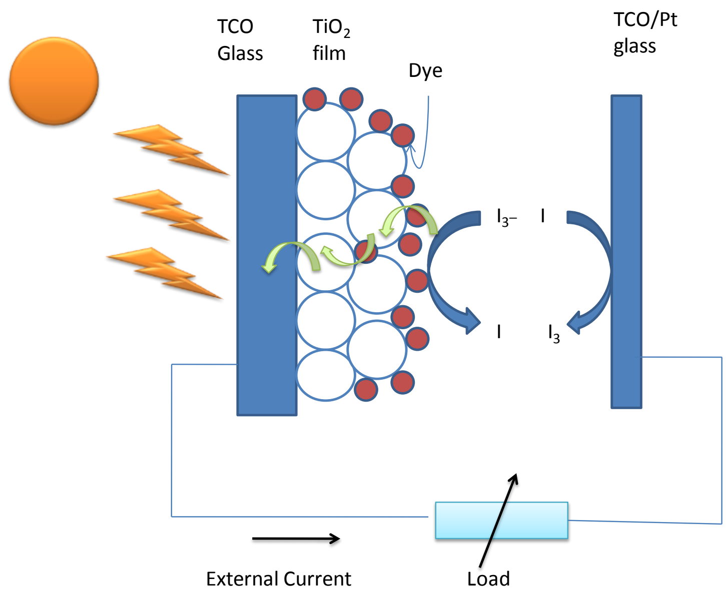



Fig 1: Working of a typical Dye sensitized solar cell

## III. RECENT STATUS OF DSSC AND FUTURE PROSPECTS:

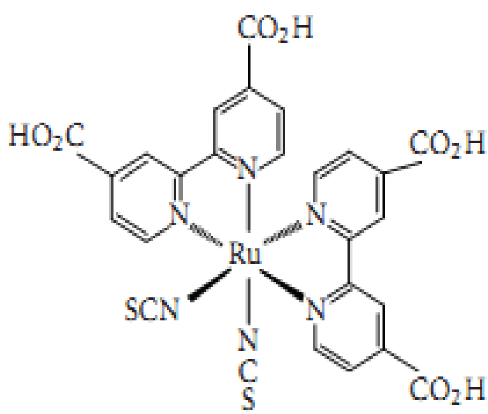
For the first time, dye sensitized solar cell was developed by professor Tsubomura et al. in 1976, using porous zinc oxide as the dye. Later in 1991, Michael Grätzel and Brian O'Regan invented 'dye sensitized solar cell', which had an improved conversion efficiency of 7.12%[5] using black dye. Later he achieved efficiency up to 10 % using Ru-based dye (N749). It led to a boom in the research area. Many innovative research works have been started then to enhance the efficiency of the cell worldwide and a great progress has been achieved also.

Researches have been made to improve the conductivity of $TiO_2$ through various morphological control, such as formation of nanotubes, as well as to coat the surface of $TiO_2$ with different types of oxides e.g. niobium oxide ($Nb_2O_5$) to reduce leakage to the solution. The addition of high conductive $TiO_2$ cemented Ag grids can maintain high performance with enlargement of the cells grids prevent corrosion of the electrolyte, also enhance performance of the cell [6].

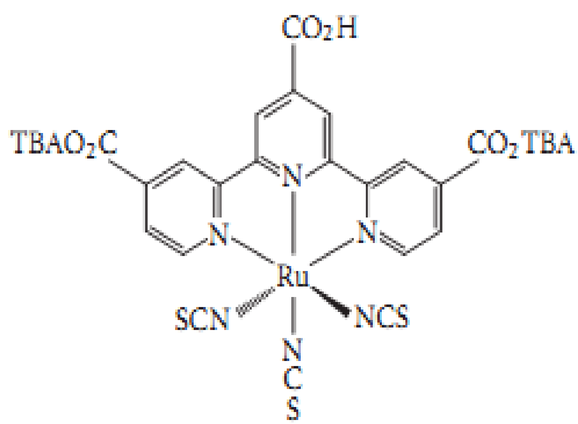
Incorporation of carbon nanotubes and graphene sheets into semiconductor electrodes improved performance of DSSC, with 44% increase in short circuit photocurrent and 18.7% overall energy conversion have been achieved [7.] Carbon material based counter electrode in DSSCs using multiwall carbon nanotubes (MWNTS)/graphene nanotubes (GNS) showed a maximum power conversion efficiency of 4% with 60% MWNTS and 40% GNS[8]. Graphene aerogels as counter electrode worked efficient and showed efficiency close to that of platinum electrode achieved. With the introduction of Titania Aerogels, a class of mesoporous 3D structure, a power conversion efficiency improvement of 16% (7.22vs 8.36%) is achieved as compared with P25%- $TiO_2$ based cells [9.] Recently, researches have been done on 3D electrode fabrication to improve electron collection, hence enhancing cell performance. Moreover electrodes derived from sol-gel synthesized nanoparticles of $TiO_2$ showed higher photoelectric conversion efficiency [10, 11] . A $TiO_2$ double layer composite film on sponge like $TiO_2$ as over layer and commercial grade nanoparticles P25 as under layer showed overall efficiency of 5.48% , which is 51.4% greater than that of P25 nanoparticles film[12.] Mixed nanostructure with different phase composition of $TiO_2$ reported for the improvement of electron transport rate by $TiO_2$ electrode. New chemical techniques for screen printing paste of P25 $TiO_2$ done to form mesoporous $TiO_2$ film showed efficiency of 8.07%. The effect of hydroxyl group attachment on the nanocrystalline $TiO_2$ photo electrodes was investigated and the result showed enhanced performance due to dye absorbed on OH group of the electrode [13.]

Besides $TiO_2$, dye sensitized ZnO solar cells also showed improved performance up to 4.38% after surface treatment through the incorporation of $Zn_2SnO_4$ quantum dots on ZnO nanoparticles [14]. Doping of $TiO_2$ photo anode by 1 mol% ‘Sb’ showed a better photoelectric conversion efficiency of DSSCs and is achieved up to 8.13% which is noticeably higher than that of the undoped DSSCs [15.] Increased performance of photo electrode by 3% N-doping resulted in 23.03% higher than that of pure $TiO_2$.

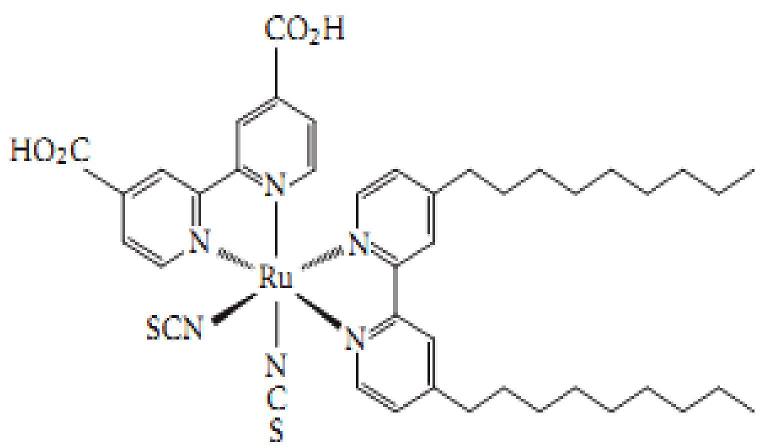
One of the important parts of DSSC is photosensitizer. Selection of efficient dye plays vital role in improving the efficiency of the cell. They can be easily available, modified and studied. The use of sensitizers having a broad absorption band in conjunction with oxide films of nano crystallized morphology permits to harvest large fraction of sunlight. Quantitative conversion of incident photon into electric current is achieved over a large spectral range extending from UV to near IR. Overall solar (Standard AM 1.5) to current conversion efficiency (IPCE) over 10% have been reached. By far the most important sensitizer showing highest conversion efficiency and long term stability are that of Ruthenium and Osmium [16] . Efficiency of the cell is greatly affected by the use of a good photo sensitizer. Many efforts have been put for developing and synthesizing dyes whose absorption can be extended in the near infra red (NIR). Metallic dyes being more stable and efficient are thus frequently researched out. Various modification on metallic dyes have also been worked out in the structure by complexing it with different groups. Metallic dyes are also better in its higher absorption properties. Some of the important molecular structures of three important Ru-dyes are shown in Fig.2




N-3, “red dye”




N-749, “black dye”




Z-907

Fig 2: Molecular structures of Ru- complexes (N-3, N-749, Z-907)

Introduction of thiocynate ligands and additional carboxylate groups acting as anchoring site set a bench mark for all dyes. The structure modification of these dyes has resulted in better results of Ru- based dyes. Also a comparative action spectrum of Ru-complexes is represented in Fig.3 which shows increasing efficiency of the complex with improved Ru- bipyridine carbonyl complexes. Some results of Ru- based dyes have been given in Table 1 which shows the record efficiencies using Ru-sensitizer in DSSC module.

Ta b l e 1: Record efficiencies of DSSC of various device sizes. [17-23]

| Dye* | Surface area ($cm^2$) | H (%) | VOC (V) | ISC (mA /cm2 ) | FF (%) |
|---|---|---|---|---|---|
| N-719 | <1cm2 | 11.2 | 0.84 | 17.73 | 74 |
| N-749 | 0.219 | 11.1 | 0.736 | 20.9 | 72 |
| N-749 | 1.004 | 10.4 | 0.72 | 21.8 | 65 |
| N-719 | 1.31 | 10.1 | 0.82 | 17.0 | 72 |
| N-3 | 2.36 | 8.2 | 0.726 | 15.8 | 71 |
| N-749 | 26.5(sub module) | 6.3 | 6.145 | 1.7 | 60 |

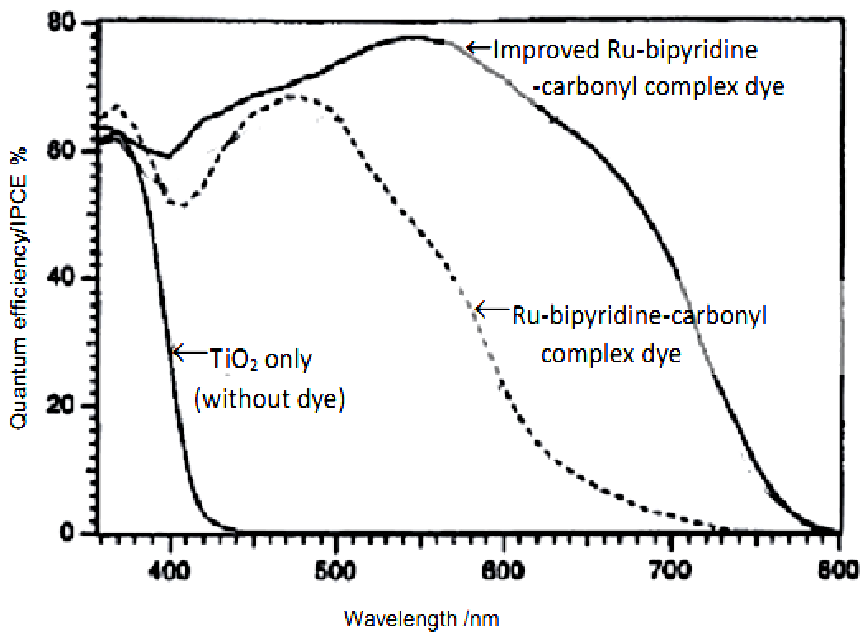



Fig 3: Action Spectrum of Dye-Sensitized Cells with Different Ruthenium (Ru) Dyes [24]

However organic dyes are also extensively used in thin film DSSC these days. The reason being organic dyes are cheaper, have higher molar extinction coefficient and can be easily modified as compared to metallic dyes. The Ruthenium based complexes have fairly broad absorption spectra (delta lambda = 350 nm) but possesses low molar extension coefficients (10,000 – 20,000M$^-$) [25, 26] as compared to number of organic dyes (50,000 – 2, 00,000 M $^-$cm$^-$) [27-30] . Thus organic dyes provide a better alternate to thin film solar cells with higher light harvesting properties.

Many researchers have been devoted in developing efficient organic sensitizers. Some organic dyes like indole derivatives are also showing much progress in the last few years [31]. Derivatives of indole dyes and coumarin dyes have been synthesized which showed better efficiencies. Perylenes [32] and Xanthene based DSSCs have been employed. However the conversion efficiency of these devices is poor. Porphyrin dyes complexed with Zn metal also showed appreciable efficiency 5.6% being highest conversion efficiency for Zn.

A carbazole dye presented by AIST senior research Hara et al. provides an improved cell conversion efficiency and longer life[33.] Efforts have also been done on natural dye based dsscs. Natural dyes extracted from Heena, pomegranate, cherries, bauraini raspberries [34] are also exclusively been researched for DSSCs to produce low cost and environmentally friendly alternative to conventional Ru- complexes. Among natural dyes, anthocyanines has shown best results so far. Further research are also been done on natural Betalain dyes [35].

Presently, research are being going for improvements in designing dyes which can not only give high power conversion efficiency but also greater potential to scale beyond 19GW per year, which is the limit set by the availability of Ruthenium [36.] Work is going on in developing organic sensitizers which can perform well. New efforts are done aimed at structural engineering of donor –pi- acceptor, (D-π-A) 2, dyes to design new more efficient and stable organic dyes. New Di-anchoring dyes were designed with branched $(D\text{-}\pi\text{-}A)_2$ containing rigid alkyl functionized carbazole core as donor part, thiophene units as pi- Bridge and cyano acrylic moiety as acceptor and anchoring part. The highest power conversion efficiency reached 5.01%, 0.70V and photocurrent of 10.52 $mA/cm^2$.

Research have proved that a best dye contain electron rich (donor) and electron poor (acceptor) sections connected through a conjugated pi- bridge. Introduction of two 4-tert-butyl benzene moieties in the donor part of tri phenyl amine group developed an efficient D-π-A organic sensitizer (LI-17) shows conversion efficiency of 5.35% under standard global AM 1.5 solar light [37]. Series of high performance organic dyes with D-π-A structure used in dssc to establish the structure- performance relationship and its influence on the performance of the dye.[38]

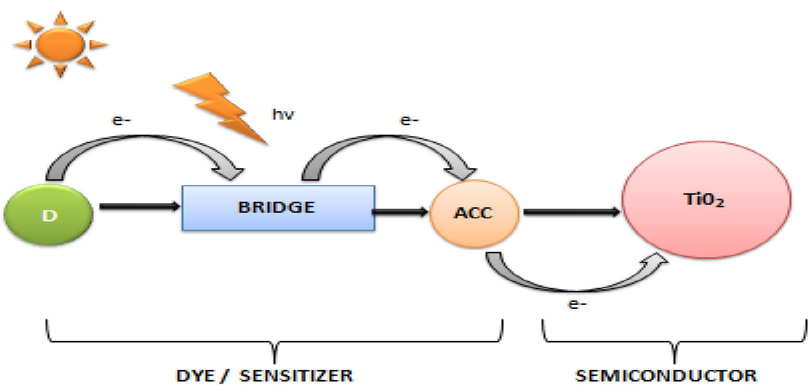



Fig 4: D-π-A (donor –pi- acceptor) dye structure and its function

A D-π-A (donor –pi- acceptor) sensitizer structure has been shown in Fig 3. The figure clearly shows the mechanism supporting the effect of conjugation in the sensitizers. The D-π-A which consist of a donor, acceptor and linker part of the molecule can be independently modified to tune the properties of the molecules[39, 40] . Conjugated linkers can be chain of methene units/ Ar compounds such as thiophene. The commonly used donors are triphenylamine, indoline, perylenes or coumarin units. Besides these electrons donor moieties like carbazole, phenothiazine and diphenylamine were also applied to organic sensitizers containing identical π-spacer and electron acceptor. Examples of acceptors, which include anchoring groups, are cyanoacrylic acid and rhodanine-3-acetic acid. Other anchoring groups are phosphonic acid, silanol and hydroxamate. And an overall efficiency ranged from 1.77% to 2.03% [41] has been reported. Introduction of Thiocynate ligands and additional carboxylate groups acting as anchoring site also set a bench mark for all dyes.

A novel indoline donor based dye Ba-03 has been synthesized which showed the efficiency of 6.38% which was greater than carbazole donor based dye of Ba-01[42]. Researches on innovative dyes have lead to considerable progress in the cell's efficiency. Still a lot of work is going on all around the world for developing efficient and stable metal free organic sensitizer.

Another way of improving conversion efficiency can be done by enhancing open circuit voltage (Voc). An efficient charge injection requires a driving force of about 100-200 meV. However about 650 meV are lost during regeneration of the oxidized dye for $I^{3-}$ – $3I^-$ redox couple. Development of new electrolytes with high oxidation potential seems to increase cell potential, e.g. $Co^{II}/Co^{III}$ [43-45], ferrocene $Fc/Fc^{+}$ [46], copper [I/II 47-49] and all organic [50-52] electrolytes have resulted in more promising power- conversion efficiencies. Earlier $Co^{II}$/ $Co^{III}$ suffered slow recombination rate due to bulky groups on these ligands functioning as insulating spacers[45]. In 2010, Boschloo and co workers demonstrated asignificant improvement in power conversion efficiency of cobalt based systems by adding bulky groups (such as insulating butoxyl chains) to an organic dye[53.]

Other concern for DSSCs in liquid electrolytes is that liquid electrolyte also possesses the problem of sealing thus problems like low stability and lower durability for long term use arises. Solidification of electrolyte has solved this problem up to a limit but still many other factors have to be resolved. A quasi solid electrolyte made by the combination of a non volatile ionic liquid and a gel with a conversion efficiency of above 7% was reported by professor Hayase et al. [54-55]. Fully solid electrolytes are under research using inorganic compounds and polypyrroles etc. Solid state inorganic[56, 57] and organic [58-60] whole conductors have been developed and tested for solid state DSSC. Recently an impressive 6% efficiency were achieved with in situ polymerized poly (3, 4-ethylenedioxythiophene) (PEDOT) as a hole conducting material[61]. Spiro-MeOTAD (2, 2'7, 7'-tetrakis-(N, N-di-p-methoxyphenyl-amine)-9, 9'-spirobifluorene) has been commonly used as a solid state organic hole conductor.

Hole conducting materials like inorganic solids ($Cu^{I}$-salts), organic polymers ($C_{60}$/polythiophene- derivatives) and p- conducting polymers are developed for DSSCs as they are less abrasive than commonly used iodine/ iodide based electrolyte, but still efficiency could not reach as that of the latter. New solid electrolyte films of polypyrolidone (PVP) complexed with KI showed 0.14% efficiency.

## IV. CONCUSION

Dye sensitized solar cell has currently emerged as new dynamic research field for solar cells. It has opened up new dimensions for solar cell technology. Research is going on to develop efficient DSSC to compete the conventional silicon based solar cells. From last few years great progress has been made on various aspects including efficiency, stability and commercialization. These developments can lead the basis for globalization of DSSCs. Also DSSC due to its attractive features like low cost, ease of production, transparency and good performance under typical conditions (temperature and illumination conditions) is proving itself better than Si- based cells, irrespective of its low efficiencies.

Furthermore, performance of DSSC module can be compared with that of Si- based module by the graph in Fig 5. It can be seen that the performance of DSSC module is far better than Si module. Hence, the global energy production of these modules is significantly higher than that of amorphous Si- based module, despite their lower 5% efficiency[62]

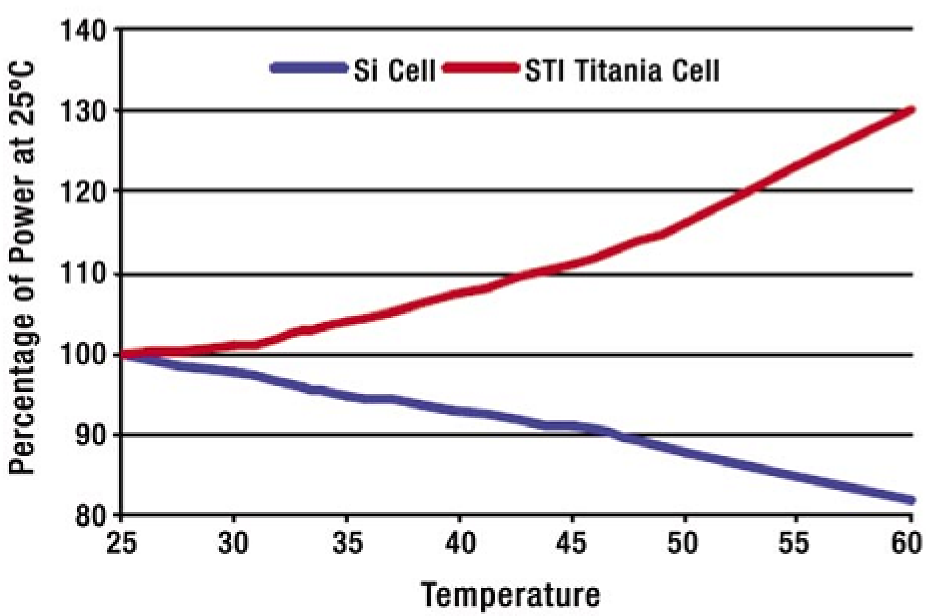



Fig. The performance of dye PV modules increases with temperature, contrary to Si-based modules. (reference[63])

New techniques and ideas have resulted in the better performance of DSSC. Efficiency up to 20% has been achieved, which has opened up a new scope for further research on various aspects of DSSC. Recently a new success has been made in developing dsscs using perovskite based mineral. It has attracted much attraction due to its simple fabrication and greater efficiency up to 17%. Also work is going on for developing solar cells with efficiency up to 50% too.

Inspite of great success of dssc the efficiency could not match with those of the conventional Si-based solar cells. Still it has attracted attention of both researchers and market worldwide from last few years. The ease of fabrication and cost effectiveness of dssc makes it viable and efficient solar cells for the future. It is expected that the low cost for commercially fabricating dsscs along with its good performance will definitely replace conventional solar cells very sooner. Researches are going on for improving the efficiency and viability of the cell. DSSCs are still at the start of their development cycle. Efficiency gains are possible and have recently started more widespread study. These include the use of efficient photo sensitizers for conversion of higher-energy (higher frequency) light into multiple electrons, using solid-state electrolytes for better temperature response, and changing the doping of the $TiO_2$ to better match it with the electrolyte being used. Finally, although there have been a number of initial studies into the development of DSSC modules, a thorough understanding of overall efficiencies, life times and degradation mechanisms of new efficient stable DSSC module. [64]

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