Dye Sensitized Solar Cells as Futuristic Green Energy Harvesting   Technology

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ABSTRACT

The human life is highly affected by availability of energy. Renewable energy resource such as solar energy is considered as the easily available and a wide source for our requirements in terms of energy needs. Among the various techniques for harnessing of solar energy the sensitized solar cells are very promising. In present review an attempt is made to focus on the construction, mechanism and future possibilities of DSSC.

Key words: Dye Sensitized Solar Cells, Energy Resources, DSSC, DFT.

1. INTRODUCTION

To fulfill the goal of a balance, between the demand and supply of energy requirements of the present day human needs, several groups of workers are in continuous practice to achieve sustainable energy resource   harvesting technologies. Use of fossil fuels are neither sufficient nor environment friendly for our energy related requirements. The main sources for renewable energy include hydro power, wind power, wave power solar energy and geothermal energy. Among all these, the solar energy is best for our needs in efficient and sustainable way. The solar technology is the answer

of all the challenges for the harvesting and storage of the solar energy in most applicable method.

The innovation of honorable Alexander Edmond Becquerel, who introduced us first time photo electro chemical effect, is the mile stone of photo voltaic cells. There are a large number of inventions in this track have been introduced for harnessing of solar energy in the human uses. Photovoltaic cell is a device which permits the direct conversion of solar light in electricity through the photo electric effect. There are many types of photovoltaic cells are available.

A dye sensitized solar cell (DSSC) is a low cost photovoltaic cell belonging to the group of thin film solar cells. It is based on a semiconductor formed between a photo sensitized anode and an electrolyte. The structure and performance of photovoltaic cells have been covered a long route of journey from "Gratzel cell" to advanced nano structured DSSC.

The main parts of DSSC[1] composed of four elements namely, the transparent conductive glass, semiconductor, sensitizer, electrolyte and counter electrode.

2. MATERIALS AND METHODS

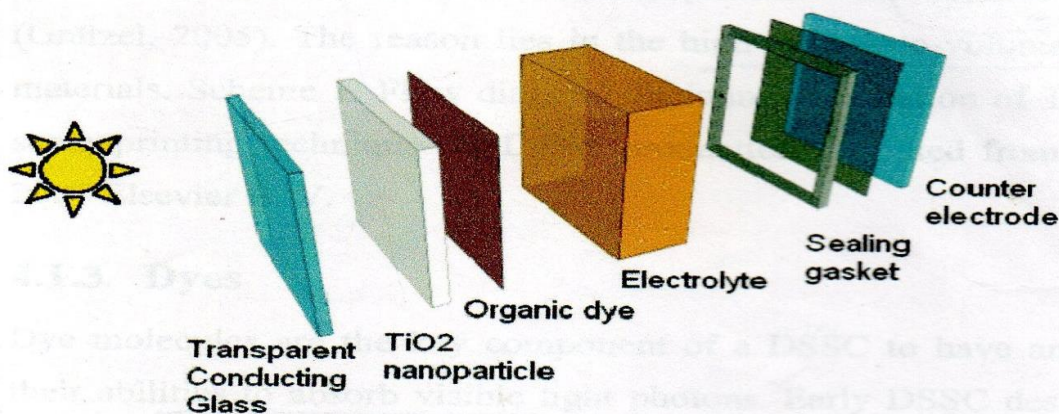Construction of DSSC involves stacking of a series of components in a sealed gasket (Fig.-1).

Fig. 1 Typical Configuration of a DSSC

Transparent Conducting Glass: The first component is a glass substrate, on the top layer of which covers a thin layer of transparent conducting layer. This layer is crucial since it allows sun light penetrating into the cell while conducting electron carries to outer circuit. F-doped or In-doped tin oxide (FTO or ITO) and aluminium doped zinc oxide (AZO) are in use. Among these AZO is more favourable due to non-toxic and inexpensive nature.

Nano Structured Photo electrode: In the old generation photovoltaic cells the photo electrodes were made from bulky semiconductor materials like Si, Ga or CdS. They have been replaced due to photo corrosion problem by sensitized wide band gap semiconductors like TiO_2 or ZnO_2. After achieving the chemical stability there is another problem related with bulky single or polycrystalline wide band gap material. The area occupied by one dye molecule is much larger than its optical cross section for light capture. Gratzel et al[2] replaced bulky layer of TiO_2 with TiO_2 nano particles layer. In further attempt to improving the efficiency of DSSC, the introduction of TiO_2 nano tube in place of TiO_2 nano particle reveal new aspects in DSSC research. W-Y. Rho[3] reported the various aspects of application of TiO_2 nano tubes in anode of DSSC. Delay in charge transfer occurred due to trapping of energy by combined band of energy states of different particles. This problem has been overcome in TiO_2 nano-tubes by omitting the boundary effect of grain. The idea of scattering process in light harvesting and depression of electron recombination process has been introduced. Part et.[4] reported the method of preparation of TiO_2 nano tube array on FTO glass, after that Chen and Xu[5] introduced annealing method and prepared crystalline TiO_2 nano tubes. The fabrication of DSSC with open ended TiO_2 nano tube interconnected to the FTO glass and an iodine based electrolyte for front illumination, have also been reported. Li et al.[6] published dry etching method BCl_2/Cl_2 in plasma reactor for the preparation of 'bottom open ended nano tube. The thickness of barrier layer between the FTO and TiO_2 nano tube array can be controlled by varying the time for ion-milling step[7]. Nbelagmis and co workers[8] reported the use of plasmonic nano particles (NPs) in DSSC. In an effort to improve the power conversion efficiency , they have prepared DSSCs using Ag@TiO_2 NPs-doped TiO_2 photo anodes. The work of Staurt and Hall[9] they report use of silker nano particle to enhance the photocurrent up to 18 times for light sensitive device with 165 nm thick silicon-on-insulator photo detector at wavelength 800 nm. Schadt et al [10] reported gold nano particle based doped Si wafer solar cells. Rho et al[11] prepared front illuminated DSSC, using TiO_2 nano tube array constructed by electrochemical anodization on the TCO glass. Ag nano particle with diameter smaller than the light wavelength is helpful in the absorption of light very much, because of surface 'plasma resonance effect'.

TiO_2 nano tube filled with TiO_2 nano particles are used for the fabrication of some new concepts and this is followed by treatment with $TiCl_4$ after filling with nano particles. The 40% increase in efficiency was reported due to enhancement to total absorption surface area for dye and better transfer of electrons to the electrode.

3. Photosensitizer:

The prime requirement of chromophore or dye or photo sensitizer is that it can absorb the light in the required range and it must be properly absorbed on the semiconductor surface. There are different categories of chromophores have been reported i.e. inorganic, organic and natural dyes.

Ruthenium based chromophores : Ruthenium polypyridal complexes[12-23] are most commonly used in early stages of DSSC research. Chromophores N3, N719, Black dye, K3, K19, K945, Z907, Z91, K51, N945, K73, HRS1, K77 and Z955 have been reported (Fig. 2)
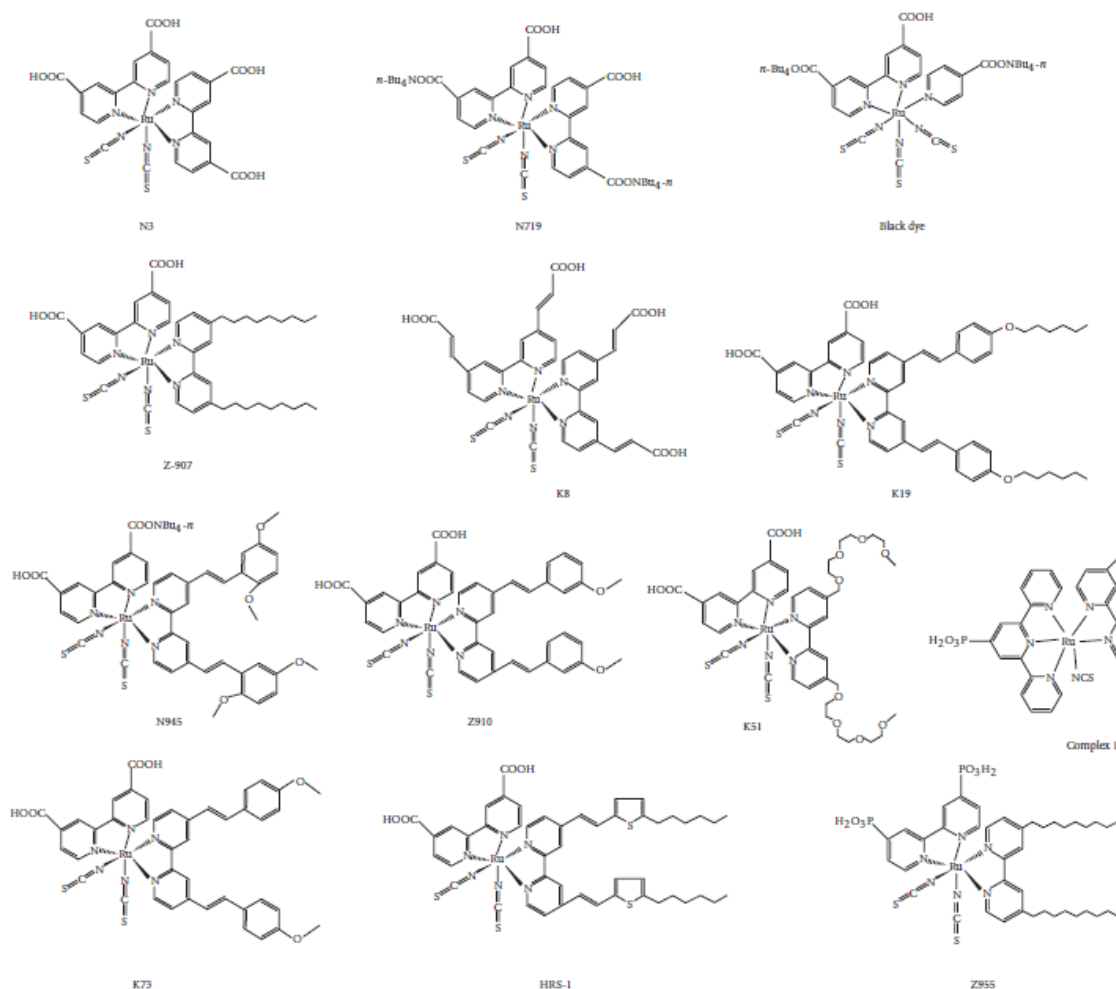

Fig. 2 Ruthenium based chromophores

Porphyrin based Chromophores: Officer et al [24] published his work on a series of zinc porphyrin based chromophores. Panda and co-workers[25] reported multi chromohporic DSSCs based on supramolecular zinc prophyrin--- perylene imide dyads . In 2014 Zhao et al[26] reported five di-chromophoric zinc porphyrin dye with the same porphyrin core, a carbazole unit attached in the meso-position through a phenylene linkage. The performance of new dyes has been increased by as much as 30% compared to single chromophore Zn porphyrin dye. The draw back of porphyrin dye is complicated synthesis and difficult purification.

Transition metal complexes as chromophores: Among metal based chromophores, reports are available on Os (II) , Cu(II) , Fe(II) and Pt(II) other than the most popular metal ruthenium[27-29]. Different sulfur and nitrogen containing ligands based complexes have been reported[30] (Fig. 3).A theoretical study by density functional theory and time dependent density functional theory   have been published[31].
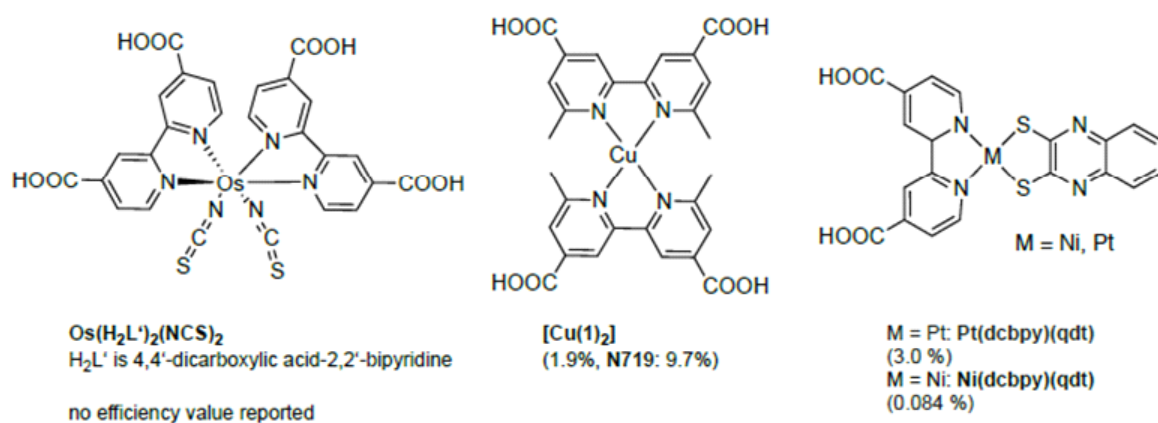

Fig. 3 Transition metal based chromophores

Organic Chromophores: Organic-π-systems represent an important materials for electronics and opto electronics as well as in photovoltaics. Donor-acceptor interaction in donor-π-acceptor molecules have been widely studied for their charge transfer chromophoric nature. Push-pull tuning[32] through the donor (with + M effect functional groups (N, N-dimethyl amino, alkoxy groups, heterocyclic compounds etc.); through the π-system and   through the acceptors have been reported. Several papers have been available based on coumarins , tri phenyl amines (Fig. 4) , indolines , di keto pyrrole based dyes and various others organic dyes. Organic dyes have some advantages over conventional metal based chromophores as photo sensitizers. They exhibit high molar extinction coefficients and are suitable for the thin TiO_2 films required in solid state device. Plenty of work has been reported for DSSCs based on phthalocyanin [33] dyes.
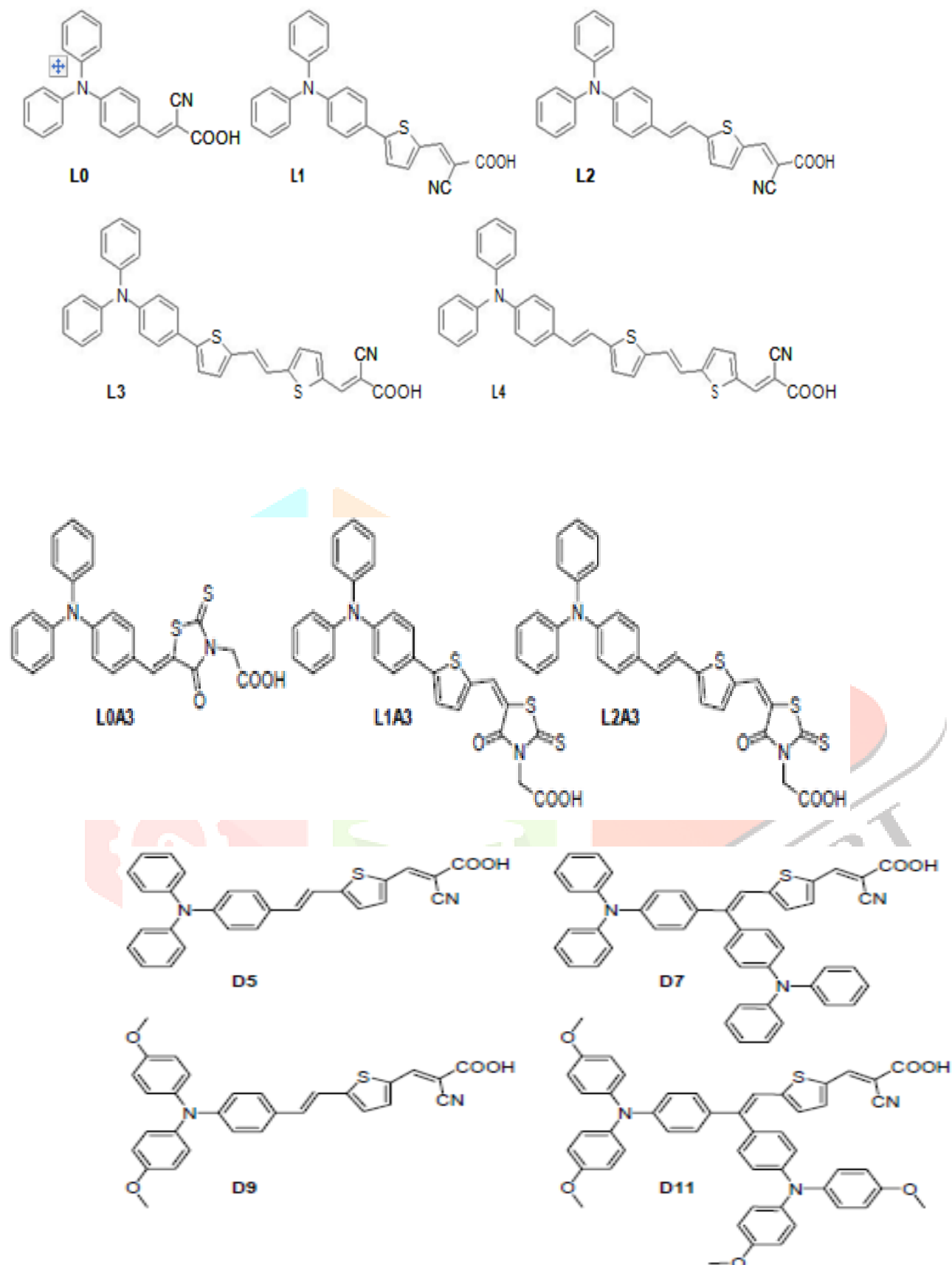
Fig. 4 Some tri phenyl amine based dyes

Merocyanine dye MC[18, 1], $\eta = 4.5\%$

IDS $\eta = 4.8\%$

BTS $\eta = 5.1\%$

Hemicyanine dye

coumarin, $h = 5.6\%$

NKX-2677, $\eta = 7.7\%$, $\eta = 7.4\%$

NKX-2883, $\eta = 7.6\%$

D-SS, $\eta = 6.23\%$

Indoline dye D149, $\eta = 8\%$, 9.03%

$R = C_2H_5$, $h = 6.6\%$
$R = CH_3$, $h = 6.8\%$

Phenyle-conjugated
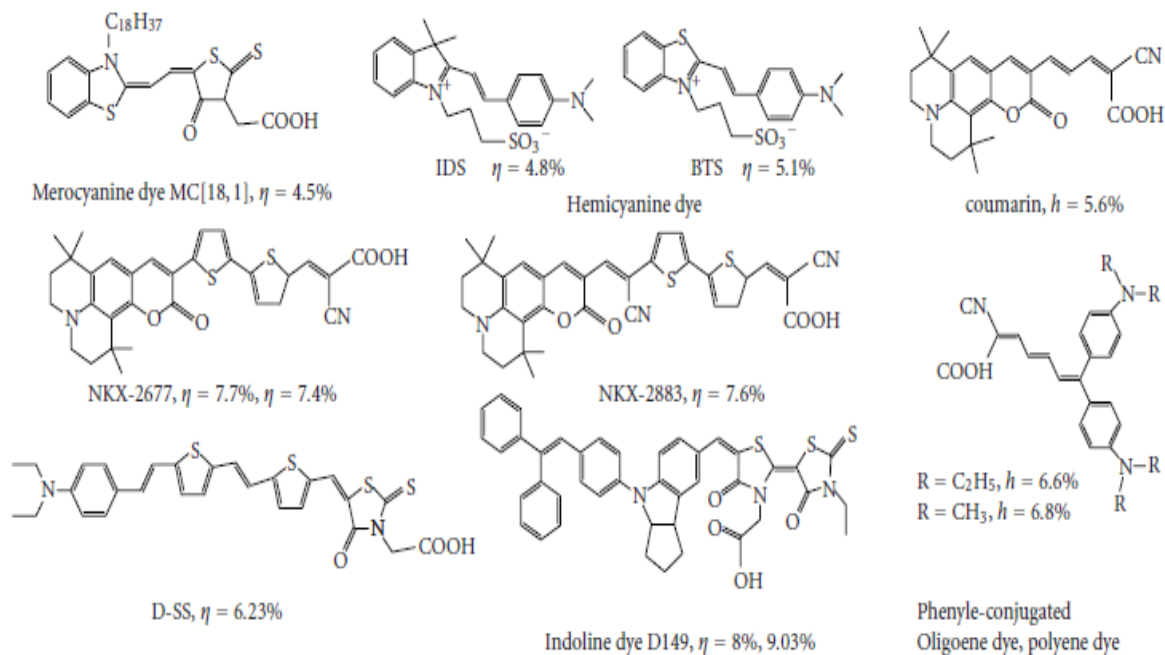Oligoene dye, polyene dye

Fig. 5   Natural chromophores

Natural Chromophore: Sensitization of natural dye (Fig. 5) extract such as natural anthocyanins, Fruit of calafate , Rosella, Henna , Jasmin, Worm Wood Bamboo leaves (Lin et al, 2006) have been reported[34]. They are eco friendly and have long term stability as well as cost effective.

4. Electrolyte

Currently, three different kinds of electrolyte have been used in real DSSCs.

Liquid Electrolyte: The most commonly used electrolyte is I^-/I_3^-. Redox ions I^-/I_3^- are used to regenerate the oxidized dye molecules and hence completing the electric circuit by involving the electron transfer process between the nano structured electrode and counter electrode NaI, LiI and R_4NI are most commonly used iodide mixture dissolved in non-protonic solvents such as acetonitrite, ethylene carbonate, propylene carbonate and 3-methoxy propionitrile to make electrolyte. The absorption of counter cations, for example Na^+, Li^+ and R_4N^+ also affect the cell performance. Similarly, the viscosity of which affect the ion conductivity in electrolyte also affect very much to the performance of DSSC. The hole transport and collection efficiency on the dye cation are important. The V_{OC} and I_{SC} increased for Eosin – Y--based DSSC when redox couple is changed from I^-/I_3^- to Br^-/Br_3^- [35].

Limitation of Liquid Electrolyte:

1. Long term stability is limited due to volatilization of liquid electrolyte.

2. Leakage of electrolyte is another short coming of liquid electrolyte .

The use of ionic liquid electrolytes are good for chemical and thermal stability and have negligible vapour pressure, non-inflamability, high solubility and high ionic conductivity. Alkyl imidazolium based ionic liquid with the counter ions I^-, $N(CN)_2^-$, $B(CN)_4^-$, $(CF_3COO)_2N^-$, BF_4^-, PF_6^-, NCS^-. High viscosity of the ionic liquid causes hindering effect for mobility of I_3^- ions. Redox couple of $SCN^-/(SCN)_2$ and $SeCN^-/(SeSN)_2$ couple were also reported by Nang and Bergeron group of scientisst[36-37] .Substituted bipyridyl cobalt(III/II) couple as redox couple were reported [38] as efficient electron-transfer mediators in DSSC.

Use of additives: Use of additives has been reported in the electrolytes containing 4-tert-butylpyridine (TBP) and N-methylbenzimidazole (NMBI). The addition of these additives could suppress the dark current and improves the photoelectric conversion efficiency. TBP could reduce the recombination of electrons in the conduction band of the semiconductor and the electron acceptor in the electrolyte through the co-ordination between N atom and Ti ion in incomplete co-ordination state on the surface of TiO_2 film.

Quasi-solid-electrolyte: Kubo and co-workers[39] reported quasi-solid state DSSC using room temperature molten salts and a low molecular weight gelator. After that M. Gratzel et al [40] introduced an efficient organogelator for ionic liquids to prepare stable quasi-solid-state dye-sensitized solar cells. Several polymer like PVDF-HFP (poly vinylidene flouride Co-hexaflouro-propylene)[41] and low molecular weight gelators, aragose and silica nano particles[42-43] have been used in DSSC to overcome the problem of leakage in ionic electrolytes.

Solid state dye sensitized solar cell:

An alternative to the iodide/tri-iodide system is an amorphous organic hole conductor such as spiro- OMe-TAD (Fig.6) have been introduced.
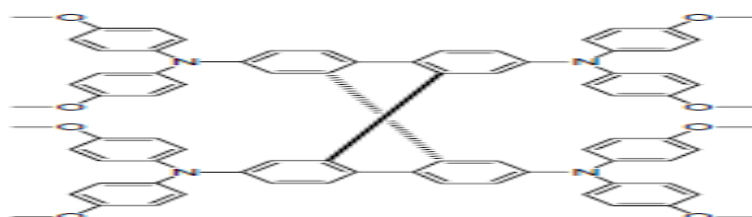

Fig. 6 Structure of spiro -OMe TAD

The replacement of the liquid electrolyte with a solid state charge carrier is advantageous when we come to the long term stability problems of the volatile liquid electrolyte.
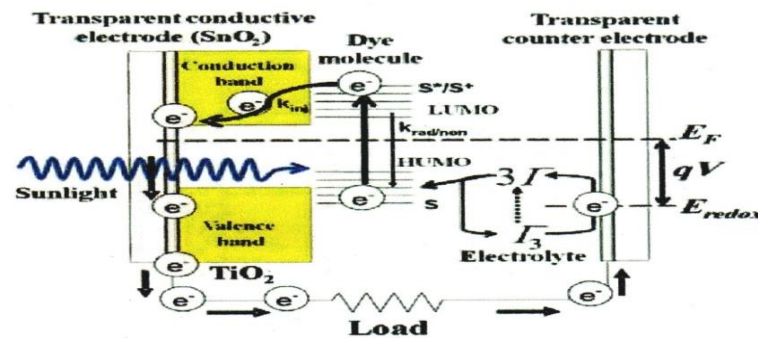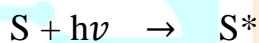
MECHANISM

Fig. 7 Schematic illustration of operation principle of dye sensitized solar cell.

The mechanism involve following steps on interfaces (Fig. 7)

The first and very important event is adsorption of sensitizer to the semiconductor.

1. After adsorption the next important event is photon excitation

$$S + h\nu \quad \rightarrow \quad S*$$

The energy of photon is used to excite the sensitizer, where an electron gets excited from ground state to the high energy state.

2. This important step involves injection of electron from sensitizer to the conduction band of semiconductor. This process must be very rapid.

3. The result of the above process is formation of a mobile electron which is further used for the energy generation and simultaneously a dye cation is formed. The semiconductor is utilized as transport medium and it transport the injected electron to the back conductive contact.

4. Reduction of oxidized dye is important and it can be done by the electrolyte which works as a hole transport material.

$$S^+ + e^- \rightarrow \quad S$$
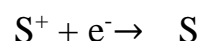
The oxidized redox mediator I^{3-}, diffuses towards the counter electrode and then it is reduced to I^- ions.

$$I_3^- \quad + \quad 2e^- \quad \rightarrow \quad 3I^-$$
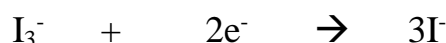
The efficiency of the DSSC depends upon how efficiently the above mentioned process takes place. The Following processes (Fig. 8) are responsible for energy loss in DSSC.
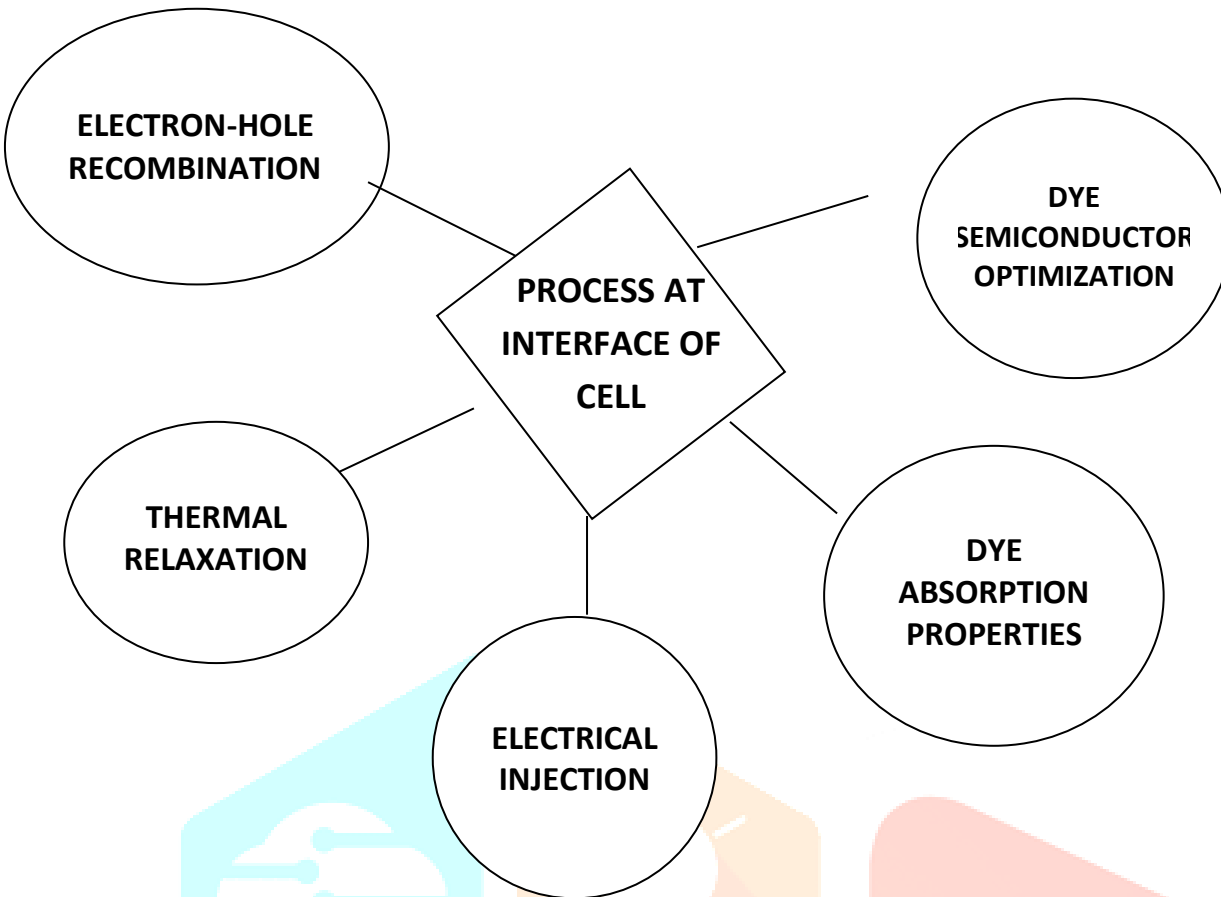
Fig. 8 Different processes at dye -semiconductor interface responsible for energy loss.

i.   Thermal relaxation:

Electrons in the excited state of the chromospheres either easily jump back to ground state if not quickly inject to TiO_2, conduction band or injected electrons in semiconductor conduction band undergo to the thermally relaxed state of the conduction band edge rapidly.

ii.   Radiative recombination:

Electron in TiO_2 conduction band will recombine with hole in electrolyte and dye if not efficiently transfer to the conducting band, causing power loss by emitting photon.

iii.   Spectrum losses:

Only the radiation of the photons which have energy greater than the HOMO-LUMO band gap can be absorbed by the dye in DSSC. Therefore it is clear that only UV- visible range of the spectrum are responsible for energy generation and infrared or micro wave part of the radiation does not involve at all.

iv.   Black body radiation

The surrounding environment has approximately 7% of electromagnetic radiation around the solar cell for making thermal equilibrium.

Optical absorption capability of dye:

According to Shockley and Queisser[44] calculation to get better efficiency in solar cell, the ideal absorption thresh hold energy must be ranges between 1.3-1.4eV (roughly 940-890nm) which is readily met by bulk semi-conductors that have a direct allowed optical transition at the appropriate band gap energy. However, molecular absorber always has absorption on set much higher than the calculated value.

PERFORMANCE OF DSSC

The performance of a solar cell can be determined by incident photon to current conversion efficiency (IPCE), short circuit photo voltage (Voc) and overall efficiency of the photovoltaic cell (η_{Cell}).

$$IPCE = LHE \cdot \Phi_{inj.} \eta_{Cell}$$

LHE = Light harvesting efficiency, $\Phi_{inj.}$ = Quantum yield of charge injection

η_{Cell} = Charge collection efficiency of the back contact

LHE depends upon the active surface area of semiconductor and light absorption of the molecular sensitizer depends on the kinetic parameters.

$$IPCE(\%) = \frac{1240 \times J_{Ph} \times 100}{\lambda . \Phi}$$

J_{Ph} = Short circuit photocurrent density for radiation (mA/cm^2) ,

λ = excitation wave length (nm)   , Φ = intensity (mWcm^{-2})

Overall efficiency, $\eta = \frac{J_{SC} . V_{OC} . ff}{\Phi}$

J_{SC} = Short circuit photo current density , V_{OC} = Open circuit voltage.

Φ = Intensity of incident light ,   ff = fill factor

DFT CALCULATIONS AND SOLAR CELL PROGRESS

DFT and TD-DFT are very useful tool for the study of various aspects in solar cells as follow :

1. The investigation of influence of structural twisting on dye/TiO_2 interface and election hole recombination by determining the recombination dynamics.

2. The computational study [45] of electronic and opto electronic properties of chromophoric compounds helps in understanding of ground state geometry. The predicted theoretical results of molecular geometries from DFT method when compared with the experimental X-ray diffraction data reveal the useful information about the structural details; like molecular planarity, terminal angle. etc. This helps finest systematic engineering of dye.

3. Value of bond length and terminal angle in ground state and excited state can be compared.

The electronic spatial distribution of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in the ground state give information about the structure and performance of photo voltaic cell.

$$V_{oc} = E_{LUMO} - c_{CB}$$

$$J_{sc} = \int_{\lambda} LHE\,(\lambda)\emptyset_{in}\eta_{coll}.\,d\lambda$$

By the use of DFT/B3LYP method one can investing theoretical analysis of geometries with electronic properties.

4. Prediction of injection rate cab be done .

5. Many election density self consistently propagating real time excited state trajectories at each steps and forces can be determined.

Conclusion:

The dye sensitized solar cells are low cost energy conversion device with simple manufacturing procedure. With the help of nano-structured semiconductor, molecular level engineering of dye, solid state electrolyte and assistance of DFT-TDDFT computational analysis make DSSC much advanced in performance. A comparison of solar cells is presented in Fig. 9 . As compare to silicon solar cells DSSC are more practicable, and economic but have low efficiencies comparatively. While, perovskite sensitized solar cells have more efficiency than DSSC.
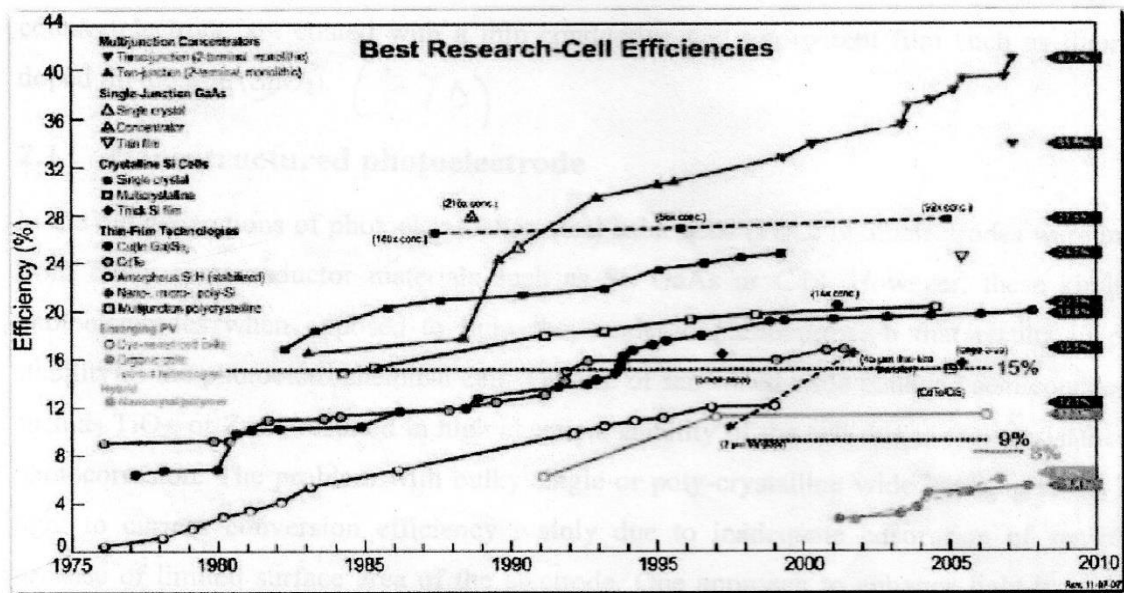
Fig. 9 Comparison of different types of solar cells

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