

## Review Article

# Recent Advances in Dye Sensitized Solar Cells

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Solar energy is an abundant and accessible source of renewable energy available on earth, and many types of photovoltaic (PV) devices like organic, inorganic, and hybrid cells have been developed to harness the energy. PV cells directly convert solar radiation into electricity without affecting the environment. Although silicon based solar cells (inorganic cells) are widely used because of their high efficiency, they are rigid and manufacturing costs are high. Researchers have focused on organic solar cells to overcome these disadvantages. DSSCs comprise a sensitized semiconductor (photoelectrode) and a catalytic electrode (counter electrode) with an electrolyte sandwiched between them and their efficiency depends on many factors. The maximum electrical conversion efficiency of DSSCs attained so far is 11.1%, which is still low for commercial applications. This review examines the working principle, factors affecting the efficiency, and key challenges facing DSSCs.

## 1. Introduction

The world energy demand is continuously increasing and the world power consumption, which is 13 terawatts (TW) currently, is expected to reach about 23 TW in 2050 [1]. Fossil fuels, which are depleting rapidly, meet 80% of the energy requirement of the whole world [2]. Moreover, the burning of fossil fuels raises the amount of carbon dioxide in the atmosphere. Owing to growing energy demand, exhaustion of oil resources, and global warming issues, there is a need for clean and renewable energy technologies. Photovoltaic technology employing solar energy is regarded as the most efficient technology among all the sustainable energy technologies such as tidal power, solar thermal, hydropower, and biomass [3].

The solar radiation from the sun is approximately  $3 \times 10^{24}$  J per year, which is ten times the current energy demands [4]. The first practical photovoltaic cell was designed in 1954 at the Bell Laboratories [5] using diffused silicon p-n junction technology with an efficiency of 6% [6]. Although the light to

electricity conversion efficiency of silicon based solar cells has reached 15% to 20% [7], the need for highly purified silicon, use of toxic chemicals in their manufacture, and the high cost has restricted their worldwide use. These constraints encouraged the search for environmentally friendly and low cost solar cells. In 1991, O'Regan and Grätzel developed a new photovoltaic cell working on the principle of plant photosynthesis. The efficiency of this PV cell, which became known as dye sensitized solar cell (DSSC), was reported as 7.1% to 7.9% [8]. DSSCs comprise of a photoelectrode and a catalytic-electrode with an electrolyte between them. The measuring parameters of DSSCs such as electrical conversion efficiency ( $\eta$ ), open circuit voltage ( $V_{oc}$ ), close circuit current density ( $J_{sc}$ ), fill factor (FF), interface charge resistance, and an incident photon to current efficiency (IPCE) depend on the morphological properties of semiconductors, spectroscopic properties of dyes, and the electrical properties of electrolytes. DSSCs are an important type of thin film photovoltaic technology because of their low cost of manufacturing, ease

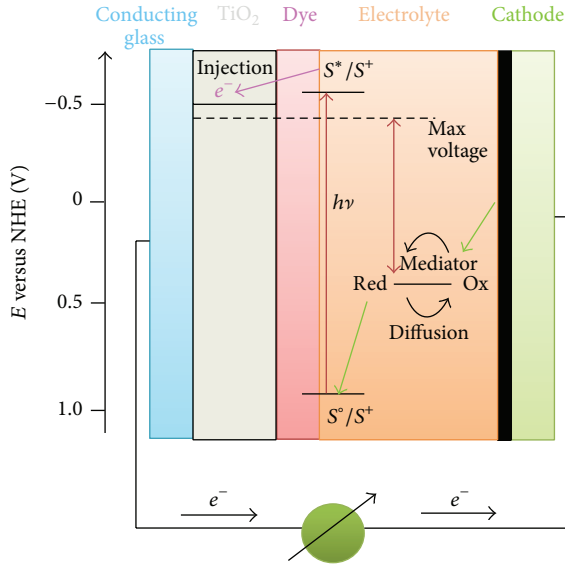


FIGURE 1: Structure and working principle of DSSC, with  $S^0/S^+/S^*$  representing sensitizer in the ground state, oxidized state, and excited state, respectively. Red/Ox = redox mediator [11].

of fabrication, and light weight product [9]. In the near future, the venture of DSSCs as a competitive technology will thus be revealed. The latest efficiency of DSSC is more than 11% [10].

*Structure and Mechanism of DSSC.* The structure and working principle of DSSC is shown in Figure 1. A charge separation process in a DSSC consists of the following steps [1].

- (i) Photoanode absorbs incident solar energy. Upon absorption of photo energy, the electrons in the dye become excited from ground state to the excited state.
- (ii) Due to the difference in energy levels of the electronic states, electrons from the excited state are injected to the conduction band of the semiconductor. As a result the dye becomes oxidized.
- (iii) The electrolyte, which is in contact with the dye, then donates electrons to the dye restoring it to the initial state.
- (iv) Electrolyte then diffuses towards the catalytic electrode where the reduction reaction takes place and electrolyte restores its initial state by accepting electrons from the external circuit.
- (v) In addition to these forward charge transfer processes, backward charge transfer processes also occur in one complete cycle. These backward electron transfer processes drastically reduce the efficiency of DSSCs. These include the following:
  - (a) transfer of electrons from the semiconductor to the oxidized dye,
  - (b) recombination of injected electrons with the electrolyte (dark current),
  - (c) transfer of electrons from the dye in its excited state to the dye in the ground state.

The following should be fulfilled to reduce the effects of the backward transfer processes.

- (i) Charge transfer to semiconductor must occur with a quantum yield [12].
- (ii) The lowest unoccupied molecular orbital (LUMO) of the photosensitizer should be more negative than the conduction band of the semiconductor and the highest occupied molecular orbital (HOMO) should be more positive than the redox potential of the electrolyte [13].
- (iii) Electron injection rate to the semiconductor should be higher than the rate of decay of electrons from the excited state of the dye to its ground state [14].

## 2. Components of Dye-Sensitized Solar Cell

*2.1. Transparent Conductive Substrate.* DSSCs are typically constructed with two sheets of conductive transparent materials, which provide a substrate for the deposition of the semiconductor and catalyst, acting also as current collectors. Substrates must be highly transparent (transparency > 80%) to allow the passage of maximum sunlight to the active area of the cell. The electrical conductivity of the substrates should also be high for efficient charge transfer and to minimize energy loss. These two characteristics of substrate dictate the efficiency of DSSCs [3].

Typically, FTO (fluorine tin oxide,  $\text{SnO}_2\text{:F}$ ) and ITO (indium tin oxide,  $\text{In}_2\text{O}_3\text{:Sn}$ ) are used as the conductive substrate. FTO and ITO substrates consist of soda lime glass coated with fluorine tin oxide and indium tin oxide layers, respectively. ITO films have a transmittance of over 80% and sheet resistance  $18 \Omega/\text{cm}^2$ , while FTO films exhibit a transmittance of about 75% in the visible region and sheet resistance of  $8.5/\text{cm}^2$ . Sima et al. conducted a study to compare FTO and ITO based DSSCs [15]. Photoanodes based on FTO and ITO glass substrates were sintered at  $450^\circ\text{C}$  for 2 h in an oxygen atmosphere. They found that the sheet resistance of FTO remained constant, while that of ITO increased from  $18 \Omega/\text{cm}^2$  to  $52 \Omega/\text{cm}^2$  upon sintering. The overall  $\eta$  of a DSSC based on FTO is 9.4%, while for an identical cell based on ITO it is 2.4%. Thus, FTO is highly recommended for DSSCs due to its low and temperature-stable sheet resistance.

Polymers can also be used as an alternative to glass substrates because of their flexibility and low cost. Murakami et al. used PET (polyethylene terephthalate) coated with ITO and found an efficiency of 3.8% [16]. Polyethylene naphthalate (PEN) coated with ITO was used by Ito et al. and reported an efficiency of 7.8% [17]. However, limitations in the range of usability temperature restrict the use of polymers as substrates in DSSCs [18]. Metals such as stainless steel, tungsten, and titanium that can form a conducting layer have also been used as substrates. Although Jun et al. demonstrated an efficiency of 6.1% using a stainless steel as the substrate

[19], the high cost and corrosion caused by the electrolyte prohibit the use of metals as substrates [20].

**2.2. Mesoporous Semiconductor.** The semiconductor, which provides a surface area for the adsorption of the dye, accepts electrons from the excited dye and conducts them to the external circuit to produce an electric current [21]. The electron transport rate, which highly depends on the crystallinity, morphology, and the surface area of semiconductors, affects the efficiency of DSSCs. Metal oxides like titanium oxide ( $\text{TiO}_2$ ), zinc oxide ( $\text{ZnO}$ ) [22], and stannic oxide ( $\text{SnO}_2$ ) [23] have been used as the semiconductor material. However, experiments show that DSSCs based on  $\text{ZnO}$  and  $\text{SnO}_2$  yield a lower efficiency in comparison to those based on nanocrystalline  $\text{TiO}_2$  [23–25]. The latter has been considered as an ideal semiconductor material for DSSCs since 1991 due to this and its better morphological and photovoltaic properties when compared to other semiconductors [8].

Of the two crystalline forms of  $\text{TiO}_2$ , anatase and rutile, the former is preferred because of its high conduction band edge energy (3.2 eV) when compared to rutile (~3 eV). High band gap energy makes anatase chemically more stable [26]. The electron transport process in rutile is also slow when compared to anatase due to the high packing density. Short circuit photo current of an anatase-based DSSC is 30% more than that of a rutile-based DSSC with the same film thickness. Owing to the smaller surface area per unit volume, rutile absorbs less dye and therefore rutile-based DSSCs are less efficient [27].

The main loss path in DSSCs is the recombination of injected electrons with the electrolyte. This phenomenon, the resulting current of which is known as the dark current, diminishes the efficiency of DSSCs, and it can be minimized by employing structural changes, use of insulating layers, or surface treatment of  $\text{TiO}_2$  [28]. Many morphologies of anatase  $\text{TiO}_2$  from nanoparticles, nanofibers [29], nanowires [30], hollow spheres [31], hollow hemispheres [32], nanotubes [33], and hierarchical spheres to ellipsoid spheres [34] have been fruitfully fabricated via solvothermal reactions of titanium *n*-butoxide and acetic acid. A DSSC with a photoelectrode based on the hierarchical anatase  $\text{TiO}_2$  spheres has an overall  $\eta$  of 9.35%, with a  $J_{sc}$  of  $17.94 \text{ mA cm}^{-2}$ ,  $V_{oc}$  of 803 mV, and FF of 0.65. Its overall  $\eta$  is much higher than that of a DSSC based on nanoparticles (7.37%), nanofibers (8.15%), and ellipsoid  $\text{TiO}_2$  spheres (7.93%) [35]. The substantial improvement of short- $J_{sc}$  and  $\eta$  for the hierarchical sphere-based DSSC when compared to other nanostructure-based DSSCs is mainly due to the larger dye loading, higher light scattering ability, faster charge transport, and longer electron lifetime [36, 37]. Another approach to minimize the charge recombination is the deposition of an insulating layer on the semiconductor electrode. Many metal oxides like  $\text{ZnO}$  [38], niobium pentoxide ( $\text{Nb}_2\text{O}_5$ ) [39],  $\text{Al}_2\text{O}_3$  [40], and  $\text{SiO}_2$  [41] have been used as an energy barrier for retarding the charge recombination owing to their insulating properties. These insulating layers reduce the interaction between the electrons injected to the semiconductor and the electrolyte solution [42]. Similarly, surface treatment of  $\text{TiO}_2$  with  $\text{TiCl}_4$  also reduces the charge recombination process by increasing the

interfacial charge-transfer resistance of the TCO/electrolyte interface [43, 44]. Recently, Melhem et al. synthesized a nitrogen-doped  $\text{TiO}_2$  electrode (optically active electrode) by laser pyrolysis [45]. They found that the short-circuit current density of DSSC based on an N-doped electrode increased by more than 10% when compared to that of a DSSC based on pure anatase. This progress is associated with electronic and optical properties of the starting nanopowder.

**2.3. Dye (Photosensitizer).** The function of dye is to absorb light and transfer electrons to the conduction band of the semiconductor. It is chemically bonded to the porous surface of the semiconductor. An efficient photosensitizer should

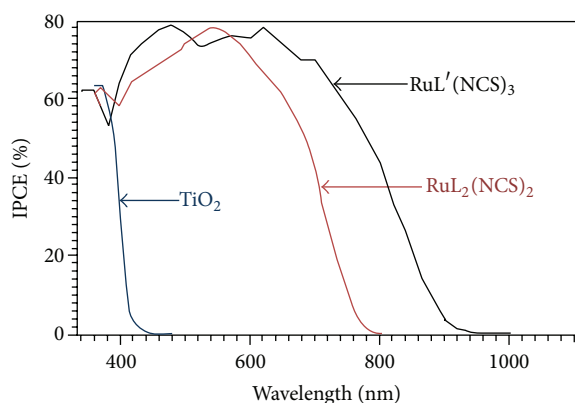
- (i) show intense absorption in the visible region (400 nm to 700 nm),
- (ii) adsorb strongly on the surface of the semiconductor,
- (iii) possess a high extinction coefficient,
- (iv) be stable in its oxidized form allowing it to be rereduced by an electrolyte,
- (v) be stable enough to carry out  $\sim 10^8$  turnovers, which typically correspond to 20 years of cell operation,
- (vi) possess more negative LUMO than the CB of the semiconductor and more positive HOMO than the redox potential of the electrolyte.

In addition, the performance of DSSCs highly depends on the molecular structure of the sensitizers. Many chemical compounds, such as the phthalocyanines [47–49], coumarin-343 [50–52], carboxylated derivatives of anthracene [53, 54], and porphyrins [55–57] have been used for the sensitization of semiconductors. However, photosensitizers based on transition metals have been shown to be the best so far [46]. There are three classes of photosensitizers: metal complex sensitizers, metal-free organic sensitizers, and natural sensitizers.

**2.3.1. Metal Complex Sensitizers.** Metal complex sensitizers comprise of both anchoring ligands (ACLs) and ancillary ligands (ALLs). The adhesion of photosensitizers to the semiconductor is strongly dependent on the properties of ACLs. While ALLs can be used for the tuning of the overall properties of sensitizers, polypyridinic complexes of  $d^6$  metal ions possess intense metal to ligand charge transfer (MLCT) bands in the visible region which is shown by polypyridinic complexes of  $d^6$  metal ions. Modification of ACLs as well as changing the ALLs or its substituents can alter the energies of the MLCT states. Many metal complex sensitizers have been prepared by changing the ALLs. However, ruthenium (II) polypyridyl complexes show better light to electricity conversion efficiency [58] because of their good spectroscopic, photostability, redox, and excited state properties in the final device [59, 60]. The general representation of carboxylic acid based sensitizers is  $[\text{Ru}(\text{dcbH}_2)_2\text{LL}']$ , while  $\text{dcbH}_2$  and  $\text{L}$  and/or  $\text{L}'$  represent anchoring ligands and ancillary ligands, respectively. An example of a high performance carboxylic acid based sensitizer is *cis*- $[\text{Ru}(\text{dcbH}_2)_2(\text{NCS})_2]$ , which is also known as the  $\text{N}_3$  dye [61]. Efficient performance has also

TABLE 1: Record efficiencies achieved for DSSCs of varying surface area [46].

No.	Dye	Surface (cm <sup>2</sup> )	$\eta$ (%)	$V_{oc}$ (V)	$I_{sc}$ (mA/cm <sup>2</sup> )	FF (%)
1	N-719	<1	11.2	0.84	17.73	74
2	N-749	0.219	11.1	0.736	20.9	72
3	N-749	1.004	10.4	0.72	21.8	65
4	N-719	1.310	10.1	0.82	17.0	72
5	N-3	2.360	8.2	0.76	15.8	71



L = 4, 4'-COOH-2, 2'-bipyridine

L' = 4, 4', 4''-COOH-2, 2':6', 2''-terbipyridine

FIGURE 2: IPCE of efficient dyes and their chemical structures [75].

been predicted for other ruthenium based photosensitizers such as  $[\text{Ru}(\text{tcterpy})(\text{NCS})_3]^-$ , which is also known as the black dye. Figure 2 shows that a cell based on black dye is more efficient than that of cell based on red dye in the near infrared region and attained an efficiency of 10.4% [4]. Record efficiencies of DSSCs with varying surface area and the structure of the photosensitizers are shown in Table 1 and Figure 3, respectively. Although record efficiency and stability have been achieved with ruthenium-based sensitizers, the high cost and scarcity of ruthenium have necessitated the consideration of other options.

**2.3.2. Metal-Free Photosensitizers.** Metal-free organic sensitizers have been used not only to replace the expensive ruthenium based sensitizers but also to improve the electronic properties of devices. However, the efficiency of these sensitizers is still low when compared to devices based on ruthenium-based dyes. But the efficiency and performance can be improved by the proper selection or tuning of the designing components. The general design mechanism of metal-free organic dye sensitized photoanode is shown in Figure 4. Substituents acting as the donor and the acceptor are separated by a  $\pi$ -conjugated spacer.

The photoelectric properties of these dyes can be tuned by altering or matching different substituents within the D- $\pi$ -A structure. The literature shows that the efficiency of such dyes depends on the chemistry of the electrolytes. For example, efficiencies of metal-free organic dyes in liquid, ionic, and solid state electrolytes are greater than 8%, 6%, and

4%, respectively [77]. These results suggest that the donor groups to form efficient sensitizers should be selected from the electron rich aryl amines family including phenylamine, aminocoumarin, indoline, and (difluorenyl)triphenylamine. The  $\pi$ -conjugated connector must be selected from compounds containing thiophene units, for example, oligothiophenes, thienylenevinylenes, or dithienothiophene due to their outstanding charge transfer characteristics. Acrylic acid group is considered the best acceptor moiety. However, the efficiency of DSSCs based on metal-free organic sensitizers is still low for industrial applications. Some important metal free photosensitizers and their photoelectric properties are summarized in Table 2.

**2.3.3. Natural Sensitizers.** Natural dyes have also been used in DSSCs because of their low cost, easy extraction, nontoxicity, and the environmentally benign nature [78].

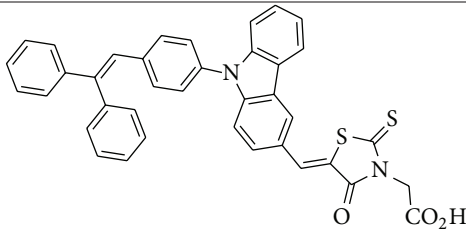
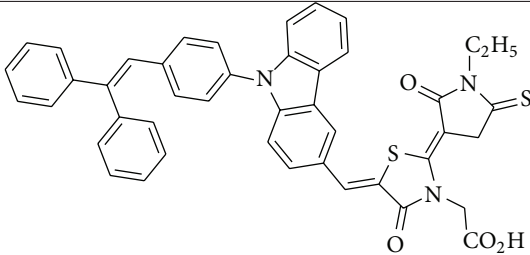
There are two classes of plant pigments, namely, carotenoids and flavonoids. In addition, there are three subclasses of flavonoids: anthocyanins, proanthocyanidins, and flavonols. But only anthocyanins of the flavonoid group are responsible for cyanic colors, which range from salmon pink through red and violet to dark blue of most flowers, fruits, and leaves. Anthocyanins is the group most extensively investigated as natural sensitizers and their extracts show maximum absorption in the range of 510 to 548 nm, depending on the fruit or solvent used [79]. The basic chemical structures of most abundant anthocyanins are shown in Figure 5.

The chain length of the substituent R also affects the performance of anthocyanins. The performance of a dye containing an R group with a long chain length will be lower due to steric hindrance, which restricts the transfer of electrons from dye molecules to the conduction band of the semiconductor. The efficiency of natural dyes is very low because of the weak interaction between the semiconductor ( $\text{TiO}_2$ ) and dyes. Dye aggregation on the nanocrystalline film is another important cause of low efficiency. Some important natural dyes and their photoelectric properties are summarized in Table 3. Calogero et al. demonstrated that red turnip yields the highest efficiency [67].

**2.4. Electrolyte.** The function of the electrolyte is to regenerate the dye after it injects electrons into the conduction band of the semiconductor. The electrolyte also acts as a charge transport medium to transfer positive charges toward the counter electrodes. The long-term stability of DSSCs depends on the properties of electrolyte. Therefore, the electrolyte must have the following characteristics [80, 81]:



TABLE 2: Metal free organic photosensitizers with different electrolytes.

No.	Compound	$\eta$ (%)	$V_{oc}$	$J_{sc}$	FF (%)	References	Electrolyte*
1		6.1	0.6	17.8	57	[62]	O.E
		4.9	0.67	9.7	74	[63]	I.L
		4.1	0.87	7.7	61	[64]	S.S
2		9.0	0.65	20	69.4	[65]	O.E
		6.4	0.71	12.5	72	[63]	I.E
		4.2	0.55	14.1	54	[66]	S.S

Electrolyte\*: O.E: organic electrolyte, I.E: ionic liquid, S.S: solid state.

TABLE 3: Photoelectric parameters of DSSCs based on natural dyes.

No.	Dye	$\eta$ (%)	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	References
1	Red turnip	1.7	0.43	9.50	0.37	[67]
2	<i>Rhoeo spathacea</i>	1.49	0.5	10.9	0.27	[68]
3	Shisonin	1.31	0.53	4.80	0.51	[69]
4	Wild sicilian	1.19	0.38	8.2	0.38	[67]
5	Mangosteen	1.17	0.67	2.69	0.63	[70]

- (i) a high electrical conductivity and low viscosity for faster diffusion of electrons,
- (ii) good interfacial contact with the nanocrystalline semiconductor and the counter electrode,
- (iii) not causing desorption of the dye from the oxidized surface and the degradation of the dye,
- (iv) not absorbing light in the visible region.

Electrolytes for DSSCs are classified into three types: liquid electrolytes, solid state electrolytes, and quasisolid state electrolytes.

**2.4.1. Liquid Electrolytes.** Liquid electrolytes are further classified into two types: organic solvent based electrolytes and room temperature ionic liquid electrolytes (RTIL) depending on the solvent used.

**(1) Organic Electrolytes.** Each component of organic electrolytes such as the redox couple, solvent, and additives affects the performance of DSSCs. The major component of organic electrolyte is the redox couple. Many types of redox couples such as  $\text{Br}^-/\text{Br}_3$  [82],  $\text{SCN}^-/(\text{SCN})_2$ ,  $\text{SeCN}^-/(\text{SeCN})_2$  [83, 84], and substituted bipyridyl cobalt (III/II) [85] have been investigated. But  $\text{I}_3^-/\text{I}^-$  is considered an ideal redox couple [86] because of its good solubility, rapid dye regeneration, low

absorbance of light in the visible region, suitable redox potential, and very slow recombination kinetics between injected electrons into the semiconductor and triiodide ( $\text{I}_3$ ) [87].

Another basic component of the liquid electrolyte is the organic solvent. It is responsible for the diffusion and the dissolution of the iodide/triiodide ions. Many types of solvents such as acrylonitrile (AcN), ethylenecarbonate (EC), propylene carbonate (PC), 3-methoxypropionitrile (MePN), and N-methylpyrrolidone (NMP), which yield reliable performance, have been investigated [88, 89]. The photoelectric performance of DSSCs depends on the donor number (DN) of the solvents. Using solvents with high DN increases the  $V_{oc}$  and decreases  $J_{sc}$  Values [90] due to the lower concentration of triiodide, which in turn reduces the dark current and therefore yields a high photovoltage ( $V_{oc}$ ). The photovoltaic properties of DSSCs can be optimized by employing electric additives. The most efficient additives are 4-*tert*-butylpyridine (TBP), N-methylbenzimidazole (NMBI), and guanidinium thiocyanate (GuNCS) [91]. These additives adsorb on the photoelectrode/electrolyte interface and prevent the recombination of injected electrons with the tri-iodide ions. Another important parameter is the concentration of  $\text{I}_3^-/\text{I}^-$  in the mixture when used as a redox couple. If the concentration is low, then it will be difficult to maintain the required conductivity. But if the concentration is high then it will absorb light in the visible region [3]. Therefore, the concentration of  $\text{I}_3^-/\text{I}^-$  electrolyte must be optimized.

TABLE 4: ILs and their efficiencies in DSSC applications.

No.	Ionic liquids	$\eta$ (%)	References
1	1-hexyl-3-methylimidazolium iodide	5	[71]
2	1-methyl-3-(3,3,4,4,5,5,6,6,6,-nonafluorohexyl) imidazolium	5.1	[72]
3	1-butyl-3-methylimidazolium iodide	4.6	[72]
4	S-propyltetrahydrothiophenium iodide	3.51	[73]
5	Eutectic mixture of glycerol and choline iodide	3.88	[74]

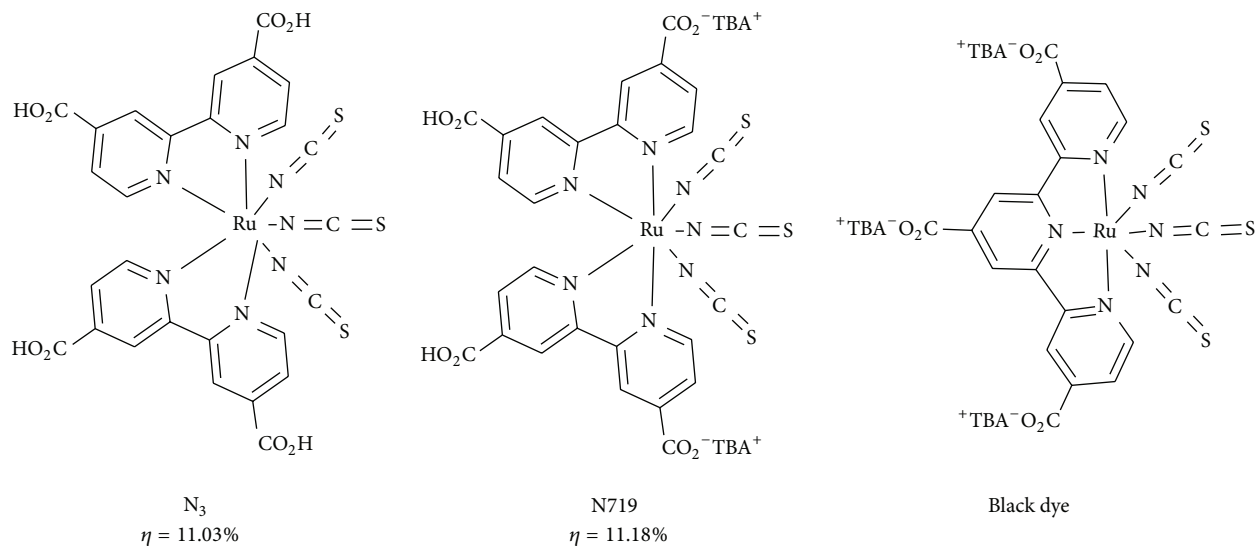
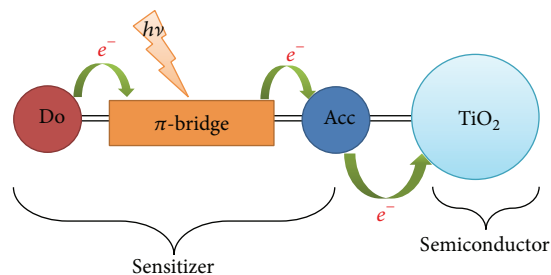


FIGURE 3: Structure of some efficient Ru-based photosensitizers [76].

FIGURE 4: Design mechanism of the use of an organic dye for  $TiO_2$  photoanodes in DSSCs [77].

(2) *Ionic Electrolytes*. Although covalent electrolytes show record efficiency, they have a high evaporation rate due to high volatility. High evaporation rates and leakage limit the long-term stability of DSSCs based on covalent electrolytes. In order to minimize these problems, room temperature ionic liquids (RTIL) have been employed successfully. They are a group of organic salts containing cations such as pyridinium, imidazolium, and anions from the halide or pseudohalide family [92]. They act simultaneously as an iodine source and as a solvent. The most commonly used ionic liquid (IL) for DSSC applications is N, N' bis-alkyl-substituted imidazolium iodides [93]. It has been found that the viscosity of these salts decrease with decreasing alkyl chain length due to the decrease of van der Waals forces. Therefore, the

conductivity of IL electrolytes decreases because an increase in viscosity limits the diffusion of charges in the liquid [71]. The preferred counter ions for alkyl imidazolium based ILs are  $I^-$ ,  $N(CN)_2^-$ ,  $B(CN)_4^-$ ,  $(CF_3COO)_2N^-$ ,  $BF_4^-$ ,  $PF_6^-$ , and  $NCS^-$ . In addition to alkyl imidazolium based ILs, alkyl pyridinium and trialkylmethylsulfonium based ILs have also been developed for DSSCs applications. Some ILs and their efficiencies in DSSC applications are presented in Table 4. However, low efficiency due to the high viscosity limits their application as electrolytes in DSSCs.

2.4.2. *Solid-State Electrolytes*. Leakage is a key problem in liquid-electrolyte based DSSCs, which drastically reduce the long-term stability of solar cells. In order to improve the performance and stability, solid state electrolytes have been developed [94]. They replace the liquid electrolyte with a p-type semiconductor or a hole transfer material (HTM). The band gap structure of the p-type semiconductor must be compatible with the HOMO level of the photosensitizer and the conduction band of the n-type semiconductor ( $TiO_2$ ) [3]. Copper based compounds such as CuI, CuBr, and CuSCN have been employed as inorganic HTMs because of their good conductivity [86]. Organic HTMs have advantages over inorganic HTMs because of their low cost and easy deposition. The pioneer compound of this class is 2,2',7,7'-tetrakis (N,N-di-p-methoxyphenylamine) 9,9'-spirobifluorene (OMeTAD) which has an efficiency of only 0.74% (under white-light illumination of  $4 \text{ mW/cm}^2$ ) [95]. Its efficiency was

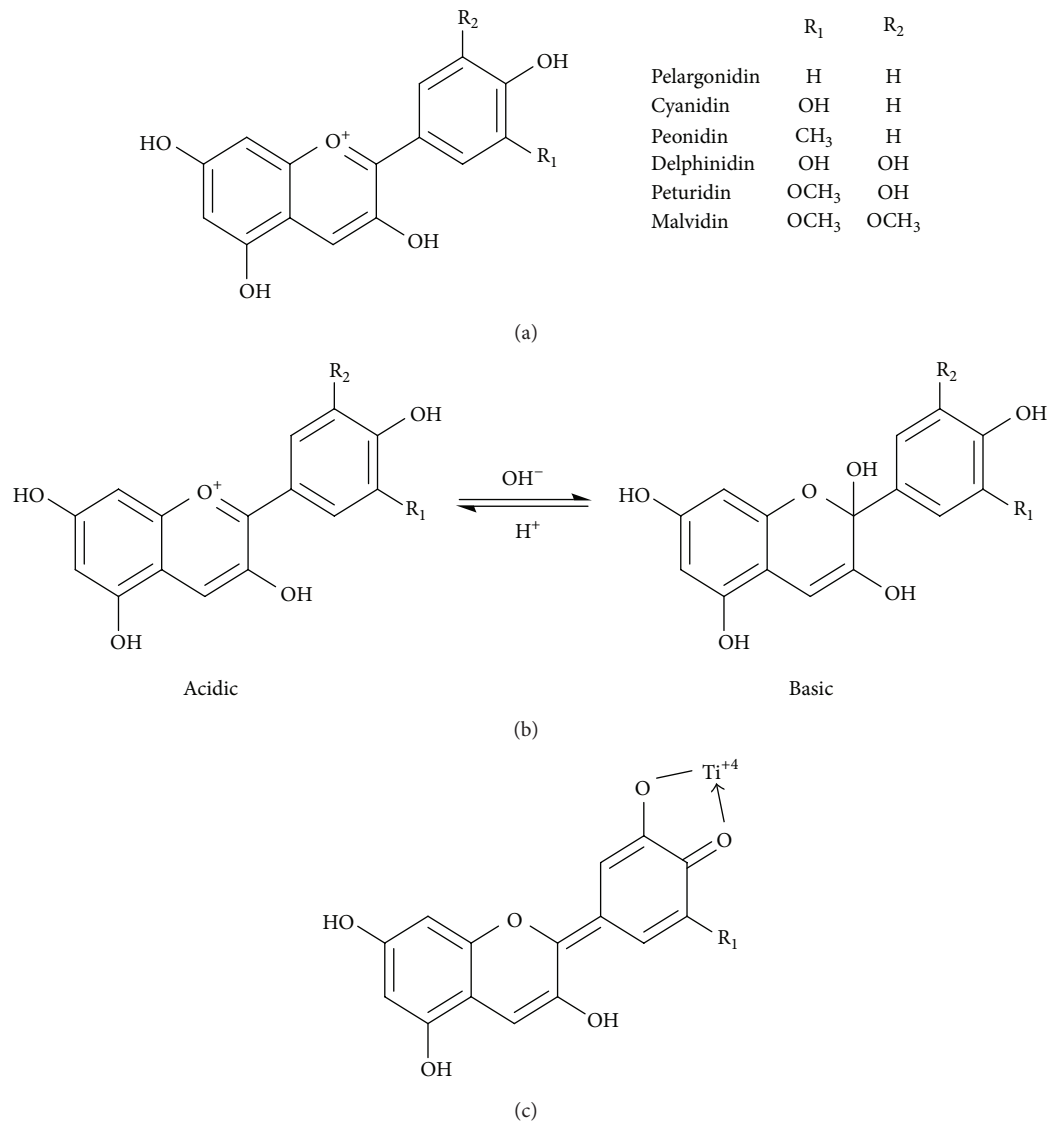


FIGURE 5: (a) Chemical structures of anthocyanins. (b) Structure in acidic and basic media. (c) Chelation mechanism with TiO<sub>2</sub> [79].

increased to 3.2% by improving dye adsorption by the presence of silver ions in the dye solution [96]. Solid state electrolyte based DSSCs have very low light-to-electricity conversion efficiency due to the poor intimate contact between the photoelectrode-HTMs and high rate of charge recombination between the semiconductor and the HTM. However, light-to-electricity conversion efficiency can be improved by introducing a redox couple into the solid state electrolyte, which acts as a transport medium. Some common HTMs and their efficiencies in DSSCs are presented in Table 5.

**2.4.3. Quasisolid State Electrolytes.** Though the leakage problem can be solved by using solid state electrolytes, contact between the mesoporous semiconductor and the HTM is weak. As solid-state electrolytes do not penetrate into the pores of the semiconductor, the above problem was solved using quasisolid state electrolytes. A quasisolid state electrolyte is a composite of a polymer and a liquid electrolyte

TABLE 5: Performance of different HTMs in DSSCs.

No.	HTMs	$\eta$ [%]	References
1	CuI	2.4	[97]
2	CuI	3.8	[98]
3	CuSCN	1.5	[99]
4	Spiro-OMeTAD	3.2	[96]
5	Polyaniline	1.15	[100]

[101, 108]. Because of the unique network structure of polymers, quasisolid state electrolytes show better long-term stability, high electrical conductivity, and good interfacial contact when compared to liquid electrolytes [101, 108]. The conductivity of the quasisolid state electrolytes depends on the molecular weight and the morphology of the polymer because of the higher mobility of charges in the amorphous phase of polymers when compared to the crystalline

TABLE 6: Polymer electrolytes and their performance in DSSC applications.

No.	Polymer	Solvent	$\eta$ (%)	References
1	1,3:2,4-Di-O-benzylidene-D-sorbitol	3-methoxypropionitrile	6.1	[101]
2	5 poly (acrylic acid)-poly(ethylene glycol)	N-Methyl-2-pyrrolidone + $\gamma$ -butyrolactone	6.1	[102]
3	Low molecular weight gelator	1-Hexyl-3-methylimidazoliumiodide, iodine	5	[103]
4	Poly(acrylonitrile-co-styrene)	4- <i>tert</i> -Butylpyridine + NaI + I <sub>2</sub>	2.75	[104]
5	Poly(ethylene glycol) (PEG)	Propylene carbonate + potassium Iodide, Iodine	7.2	[105]
6	Poly(ethylene oxide-co-propylene oxide)trimethacrylate	EC + GBL	8.1	[106]
7	Poly(vinylidene-fluoride-co-hexafluoropropylene)	1,2-Dimethyl-3-propyl imidazoliumiodide, iodine	>6	[107]

phase. The performance of polymer-electrolyte based DSSCs strongly depends on the working temperature because an increase of temperature causes a phase transformation from a gel state to a solution state [86]. Some important polymer electrolytes are summarized in Table 6.

**2.5. Counter Electrode.** The counter electrode is used for the regeneration of the electrolyte. The oxidized electrolyte diffuses towards the counter electrode where it accepts electrons from the external circuit. A catalyst is required to accelerate the reduction reaction and platinum (Pt) is considered a preferred catalyst because of its high exchange current density, good catalytic activity, and transparency. The performance of the CE depends on the method of Pt deposition on TCO substrate. Among the deposition methods are thermal decomposition of hexachloroplatinic salt in isopropanol [109], electrodeposition [110], sputtering [111], vapor deposition [112], and screen printing [112]. It has been found that the activity of the Pt catalyst decreases with time in the presence of iodide/tri-iodide redox couple [113]. Experiments show that two major factors are responsible for the deactivation of the Pt counter electrode: alteration of its electrocatalytic properties and the removal of Pt from the substrate [109].

Although the Pt catalyst possesses high catalytic activity, the high cost of Pt is a disadvantage.

Therefore, graphene and conductive polymers have also been used as alternative materials for counter electrode [1]. But their electrical efficiencies were very low when compared to the Pt catalyst.

### 3. Key Challenges and Recommendations

Low efficiency and low stability are the major challenges for the commercial deployment of DSSCs. The following factors are responsible for the low efficiency and stability of DSSCs:

- (i) nonoptimized dark current,
- (ii) poor performance of dyes in the NIR region,
- (iii) poor contact between the electrodes,
- (iv) low volatility and high viscosity of electrolytes,
- (v) degradation of electrolyte properties due to UV absorption of light.

The following steps can be recommended in order to enhance the efficiency and stability of DSSCs:

- (i) improvement in the morphology of semiconductors to reduce the dark current,

- (ii) improvement in the dye design to absorb radiation in the NIR region,
- (iii) developing low volatile and less viscous electrolytes to improve the charge transfer rate,
- (iv) improvement in the mechanical contact or adhesion between the two electrodes,
- (v) use of additives for dyes and electrolytes that enhance their properties.

However, the efficiency and stability of DSSCs do not depend on a single factor. There must be trade off among different factors to improve the performance of DSSCs.

### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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