Chapter 1

Introduction to photovoltaic technology and theoretical background of Dye Sensitized Solar Cells

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1.1. Introduction

In this modern technological era, energy has become the most important daily need of our life. With the increasing world population, spreading urbanization and technological advancement, matching the energy supply with the energy demand is the main challenging issue the world is facing these days. The total global energy consumption can be classified into different sources of energy. It is estimated that the primary sources of energy consist of petroleum 36.0%, coal 27.4%, and natural gas 23.0%, amounting to an 86.4% share of fossil fuels in the global primary energy consumption [1]. Burning fossil fuels produces many toxic and greenhouse gases, which affect our environment heavily. Although nuclear power is one feasible option for producing large-scale energy, it has some serious safety and waste management issues. To make it an alternative source of our energy demand, it is required to establish a 1GW nuclear fission power plant every day for the next 50 years on the earth [2]. This is almost impossible. Moreover, the weapon-grade uranium or plutonium fuels might be secretly derived from the nuclear power plants to make nuclear weapons and that could be used for mass destruction. This is another critical concern related to the use of nuclear fuels for power generation.

These environmental consequences related to extensive use of fossil fuels, safety related issues of nuclear power, ever-growing energy demand and depleting stock of fossil fuels have motivated the researchers to search for alternative economically and environmentally sustainable renewable energy sources. Among all the non-polluting and renewable energy sources such as Hydropower, Wind turbines, biomass-derived liquid fuels, biomass-fired electricity generation, solar cells, solar thermal, and geothermal heat, the photovoltaic technology utilizing solar energy has emerged as the most promising candidate. the annual solar energy that the earth receives is about 3×10^{24} J which is approximately 10^4 times more than the present global energy consumption. So covering 0.1% area of the earth surface with solar cells with an efficiency of 10% would satisfy our present needs. So we are in great need of technologies for efficient conversion, storage, and distribution of this energy [3].

1.2. Solar Cell Technologies

A solar cell is a type of semiconducting device that directly transforms solar energy into electrical energy. Photovoltaic electricity generation employs solar panels consisting of several solar cells. No harmful emission occurs in the process of conversion of solar energy to electricity in the solar cells. Thus it is environmentally sustainable. Aside from the abundance of potentially exploitable solar energy, photovoltaic cells have several other competitive features such as comparatively reduced maintenance, off-grid operation and zero noise pollution, making them ideal for use in remote locations and mobile applications.

Currently, the crystalline silicon modules (including mono-crystalline and large-grain polycrystalline Si) based on bulk wafers dominate the commercial PV module production. These devices are the typical members of a group referred to as the first generation of photovoltaic cells, which accounted for around 85% of the photovoltaic market [4].

1.2.1. Classical P-N junction silicon solar sells

The silicon based solar cell technology is basically rooted on the formation of *p-n* junction as shown in Fig. 1.1. This junction is formed by doping two different regions of the same semiconductor (Si) with trivalent and pentavalent impurities. An interface between p-type and n-type materials can be created in this manner. As a consequence of accumulation of donor and acceptor ions near the interface, a built in electric field is created in that region. In the so-called depletion layer, this inherent electric field facilitates charge separation.

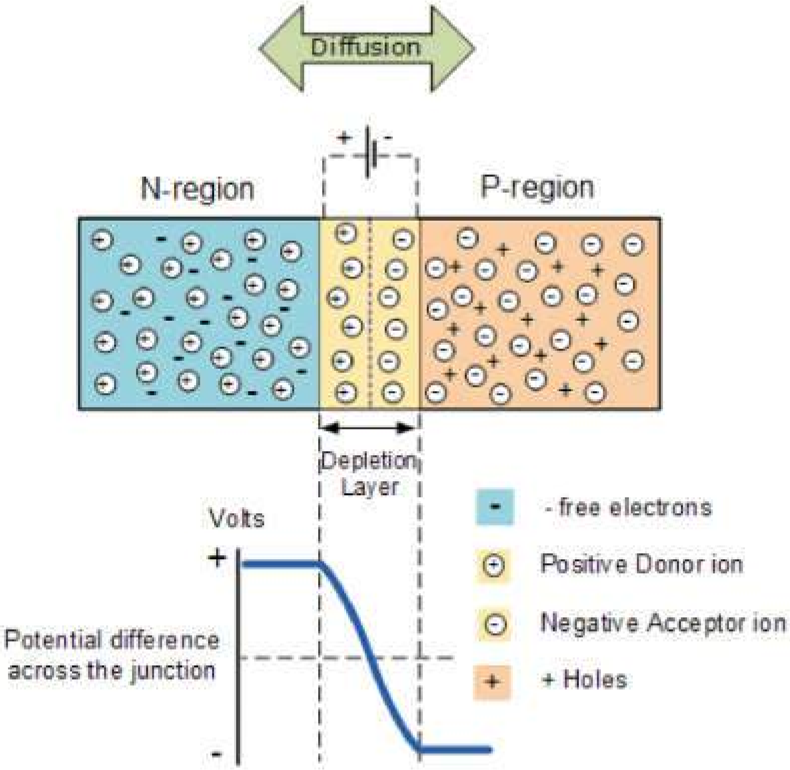


Figure 1.1 Construction of a *p-n* junction [5].

Electron-hole pairs are formed when photons with energies greater than the material's band gap energy incident at the depletion region. The strong built-in electric field existing in the depletion region favours the charge separation, and as a consequence, the electrons move to the *n* region and holes move to the *p* regions, respectively. In presence of an external load, connected across the cell, the accumulated excess electrons and holes pass through the load, creating electricity and ultimately recombining with each other (Fig.1.2).

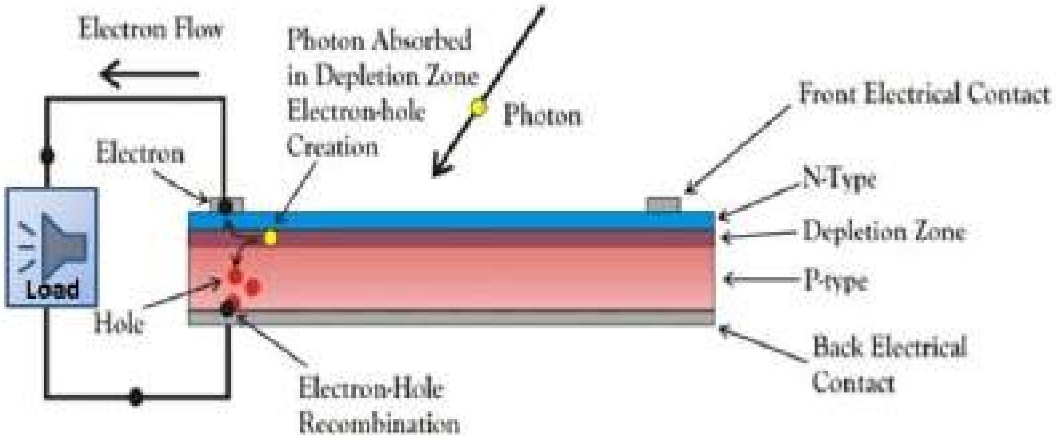


Figure 1.2 Working of a *p-n* junction solar cell [6].

Several theoretical calculations have been performed to estimate the highest power conversion efficiency that can be obtained from a single *p-n* junction Si solar cell. Shockley and Queisser calculated a theoretical upper limit of efficiency to be 33.7 % for a *p-n* junction solar cell based on a semiconductor with band gap energy (Eg) of 1.4 eV [7]. Poor maximum efficiency is caused mainly by two main factors. Firstly, the solar cells do not absorb photons with an energy of $E < E_g$. Secondly, even though the photons with an energy $E > E_g$ get absorbed, they can only transmit the band gap energy to the electric circuit, while the rest ($E - E_g$) amount of energy is lost as thermal dissipation [8]. The following requirements that are to be fulfilled by the solar cells to make it a realistic solution to our present and future energy crisis:

- Broad solar spectrum absorption
- High power conversion efficiency
- Economically cheap

- Can be fabricated using abundant and environment-friendly raw materials
- Should have long term stability

1.2.2. Photovoltaic Generation

On the basis of their performance, cost effectiveness and nature of materials used, the solar cell technologies are classified into three major generations (Fig. 1.3).

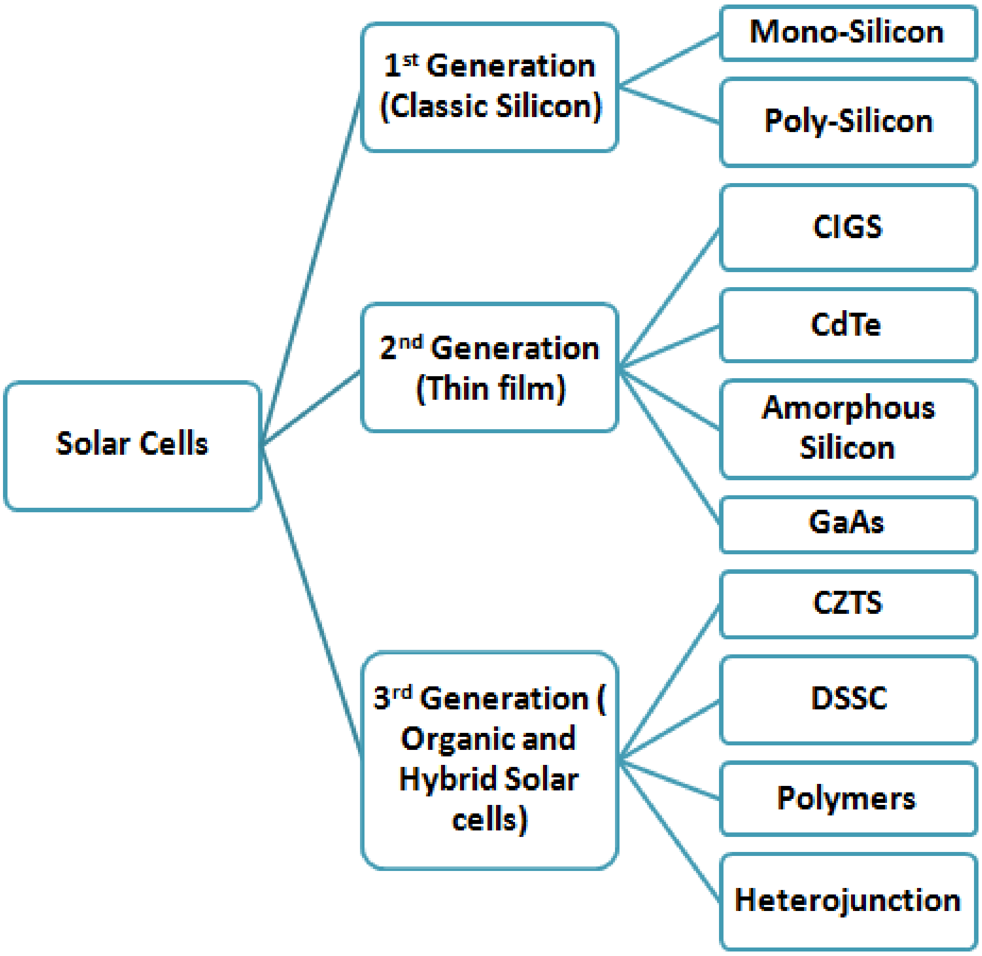


Figure 1.3 Generation wise classification of solar cells.

1.2.2.1. *1^st^ generation: Crystalline Silicon (Poly-silicon or mono-silicon) solar cells*

The first generation contains cells that use high-purity materials with low levels of structural flaws. These solar cells are basically silicon wafer-based and presently the most efficient cells but have high production cost. The working principle of these cells is mainly based on the following steps:

a. Photo excited generation of electron-hole pair.

b. Their separation and collection through the P-N junction of a doped semiconductor.

The efficiencies of these cells typically lie in the range of about 25 % [9]. However, despite being the most commonly used and researched material, silicon is not an ideal semiconductor for photovoltaic conversion. It has a low optical absorption coefficient as it is an indirect bandgap semiconductor. Consequently, Silicon substrates of larger thickness are required to effectively absorb the major portion of the incident light. This, combined with the high cost of silicon purification and crystallization, makes silicon solar cell manufacturing prohibitively expensive. As a result, while silicon based first-generation photovoltaics are a reliable and well-established PV technology, their cost-cutting potential appears to be limited. Furthermore, even though there is still opportunity for improvement, silicon solar cell efficiencies are still restricted by the theoretical Shockley-Queisser limit for a single-junction cell [10]. To address the issues with first-generation solar cells, two approaches have been taken: (a) to concentrate on to lowering the costs and (b) to boost the energy conversion efficiency and go beyond the Shockley–Queisser limit. The primary focus of the first approach is the development of thin-film solar cells. These devices are commonly known as second generation photovoltaics. On the other hand, third-generation PV technologies are based on approaches centred on devices that could theoretically overcome the Shockley-Queisser limit.

1.2.2.2. *2nd generation: Thin film Solar Cell (TFSC)*

The second generation of solar cells is mainly based on the use of thin film technology. Their constituent material has a thickness of less than 1 μm, which is much thinner than the first generation solar cells. Thin films are deposited on glass, metal or plastic substrate by applying various deposition techniques. The thickness of such films can be varied from a few nanometers to tens of micrometers. This is because thin film materials have a substantially higher absorption coefficient than silicon as they are direct band gap semiconductors. Since these cells use a single *p-n* junction, they also have a theoretical maximum efficiency restriction similar to first-generation photovoltaics. PV modules made of crystalline silicon must be constructed from individual cells. In contrast, a thin film of the semiconductor materials may be formed on the larger surfaces, which is advantageous for mass production of the devices. Examples of these kinds of materials include amorphous silicon, micro-crystalline silicon, polycrystalline silicon, copper indium selenide, and cadmium telluride.

Among the materials employed, the most established technique is that of amorphous silicon (a-Si), which is frequently utilized in so-called double- or triple-junction cells: these devices are made by assembling several cells with different band gaps, which absorb light in different wavelength regions. This material is used in photovoltaic applications where the power requirement is relatively low. Though these cells have relatively lower efficiency, they are much cheaper to fabricate. The major advantage of these solar cells is that they require only 1% of the silicon for solar cell production. As a result, the manufacturing cost of these solar cells is dramatically reduced. At the module level, the efficiency of these solar cells ranges between 4 and 8 percent. The low quantum efficiency of amorphous silicon solar cells is the reason behind their low efficiency. These solar cells have low quantum efficiency as a result of the low number of collected charge carriers per incident photon. The efficiency of these amorphous silicon solar cells has been enhanced using tandem and even triple layer devices that feature p-i-n cells stacked one on top of the other [11]. The low efficiency of these cells is due to the existence of many dangling bonds, which resulted as a consequence of the disordered structure of amorphous silicon. Acting like defects, these dangling bonds results in anomalous conductivity in the amorphous silicon material.

Another popular material used for thin-film solar cell fabrication is cadmium telluride (CdTe). It has photovoltaic capabilities very similar to crystalline Si, but with the added benefits of diffuse light absorption and stability to increasing temperature concerns [12]. The only photovoltaic technology based on the thin film which is able to outperform the crystalline silicon PV in terms of cost in the PV market is CdTe. It holds a record with laboratory efficiency as high as 20%, which has been validated at NREL [13]. The key advantage of these solar cells that are appropriate for wide-scale production is the availability of a broad range of manufacturing procedures. The use of rare and toxic materials like cadmium and telluride is the main concern of this technology. Further, Copper indium selenide (CIS) is a material with exceptional long-term stability and potential applications in building-integrated photovoltaics [14]. Another promising material in the field of thin-film solar cell technology is Copper Indium gallium selenide (CIGS). It has a high absorption coefficient and subsequently shows high absorption of light even with much thinner film thickness than other materials. One of the major advantages of CIGS based cells over other thin film based solar cells is its extended life span without showing any significant decline in its performance. It showed a certified efficiency of 23.35 % in the laboratory scale whereas in module form, it holds a record of efficiency of around 19.64 % [15] [16-18]. Due to low fabrication cost and high efficiency, CIGS cells are regarded as one of the most promising candidate of the thin film solar cell technology. Thin film solar cells also have the advantage of fitting the solar panels on flexible materials like textiles. [19-21].

The development of thin-film technology is still in its early phases, and the efficiencies of small-area laboratory cells do not always convert to large-scale module efficiencies. Aside from this, the usage of toxic compounds like cadmium and rare elements as telluride and indium is one of the major challenges that are encountered by this technology. The employment of toxic materials in a technology that is promoted as environmentally safe is highly controversial.

1.2.2.3. *3rd generation Solar Cells*

The third generation encompasses a wide range of technologies and is usually used to describe photovoltaic systems that are not part of the first or second generation solar cells and seek to exceed the Shockley-Queisser limit. This generation of photovoltaic cells relies on a variety of new and low-cost materials such as organic, conductive polymers, small molecules, and organic dye molecules. It uses low-cost fabrication methods that do not require severe temperatures, such as those required for pure silicon-based cells. The primary difference from earlier generations is that the device’s basic structure is no longer a *p-n* junction. Now, it possesses a multilayer structure wherein the charge carriers are exchanged. In contrast to their inorganic counterparts, newly discovered organic and polymeric materials emerged out to be very promising for photovoltaic application for various reasons, including low material consumption, lightweightness, flexibility, and low cost for large-scale manufacture. The areas of research in this field that have attracted the researchers' attention most are extremely thin absorber cells (ETA), organic heterojunction solar cells, hybrid solar cells and dye-sensitized solar cells.

The active layer of an organic heterojunction solar cell is made up of an n-type donor and a p-type acceptor material. Donor materials include polyphenylene vinylene derivatives and poly-alkyl thiophene, whereas some common acceptors include fullerene and its derivatives. The maximum efficiency that has been achieved to date for this class of devices is 5.15 %, check for the recent highest efficiency [22].

Entirely solid inorganic materials are used to fabricate three phase ETA solar cells. A very thin photon absorbing semiconductor material is placed in a sandwich manner in between two highly interpenetrated and transparent semiconductor nanomaterial layers acting as electron and hole transport materials. [23-25]. Semiconductors like TiO_2 and ZnO are generally used as electron conductors, whereas material like CuSCN is used as hole conducting material in these devices.

In contrast, the hybrid solar cells are composed of both the organic and inorganic semiconductor materials. Usually conjugated polymers are the most used organic materials used in these cells to absorb light as well as participate in hole transport. On the other hand, the inorganic material is mainly used as electron conduction material. These materials are mixed together, forming a heterojunction. Efficiencies above 5 % have been recorded for this kind of devices [26].

The breakthrough came in the third generation of solar cells with the discovery of Dye sensitized solar cells in 1991 by O'Regan and Grätzel with a significant energy conversion efficiency of 7.9 % [27]. These cells emerged as one of the leading runners in the race of non silicon based solar cells because of its novel fabrication concept derived from nature's principle (photosynthesis) and easy fabrication procedure using abundant materials and cost effectiveness [28, 29]. Working principle of these cells is often referred as artificial photosynthesis. These cells are usually made up of highly porous film of titanium dioxide nanoparticles photosensitized with dye molecules which absorb sunlight similar to the chlorophyll presents in plant leaves. The porous TiO_2 layer is submerged in a liquid electrolyte solution and a platinum based counter electrode is placed above it. Discovery of these cells opened a new scope in the field of photovoltaic research. Many research groups have been working in this field to improve its performance in terms of efficiency, stability, durability, flexibility and cost-effectiveness. Today, there are various similar solar cell approaches, including solid-state DSSCs [30], quantum dot sensitized solar cells [31, 32], p-type hole conductor-based DSSCs [33], and perovskite solar cells [34-37]. Since their discovery in 2012, perovskite solar cells have become a subject of growing interest among researchers worldwide. Alternatives to the liquid electrolyte in DSSC include gel electrolytes, ionic liquids, and in-situ polymerized hole conductors [38-43]. The outstanding consolidated efforts given by the research community throughout the last 30 years have not only improved the efficiencies of these cells but also uncovered various novel strategies to make rugged and stable DSSCs with satisfactory conversion efficiencies. This includes vigorous work on different semiconductor oxides and their morphologies, different inorganic and organic sensitizers, co-sensitization of different sensitizers, new red-ox electrolyte and counter electrode materials.

The key benefits of the Dye sensitized solar cells are inexpensive large-scale production capability with flexibility. The disadvantages are low efficiency, stability and strength compared to traditional non-organic PV cells. For the most part, organic photovoltaic technology is still in the research and development stages and is not ready for mass commercialization.

The efficiency trend of different generations of solar cells over the years in the form of laboratory research cells and as solar modules are summarized below in Fig. 1.4 and Fig. 1.5, respectively.

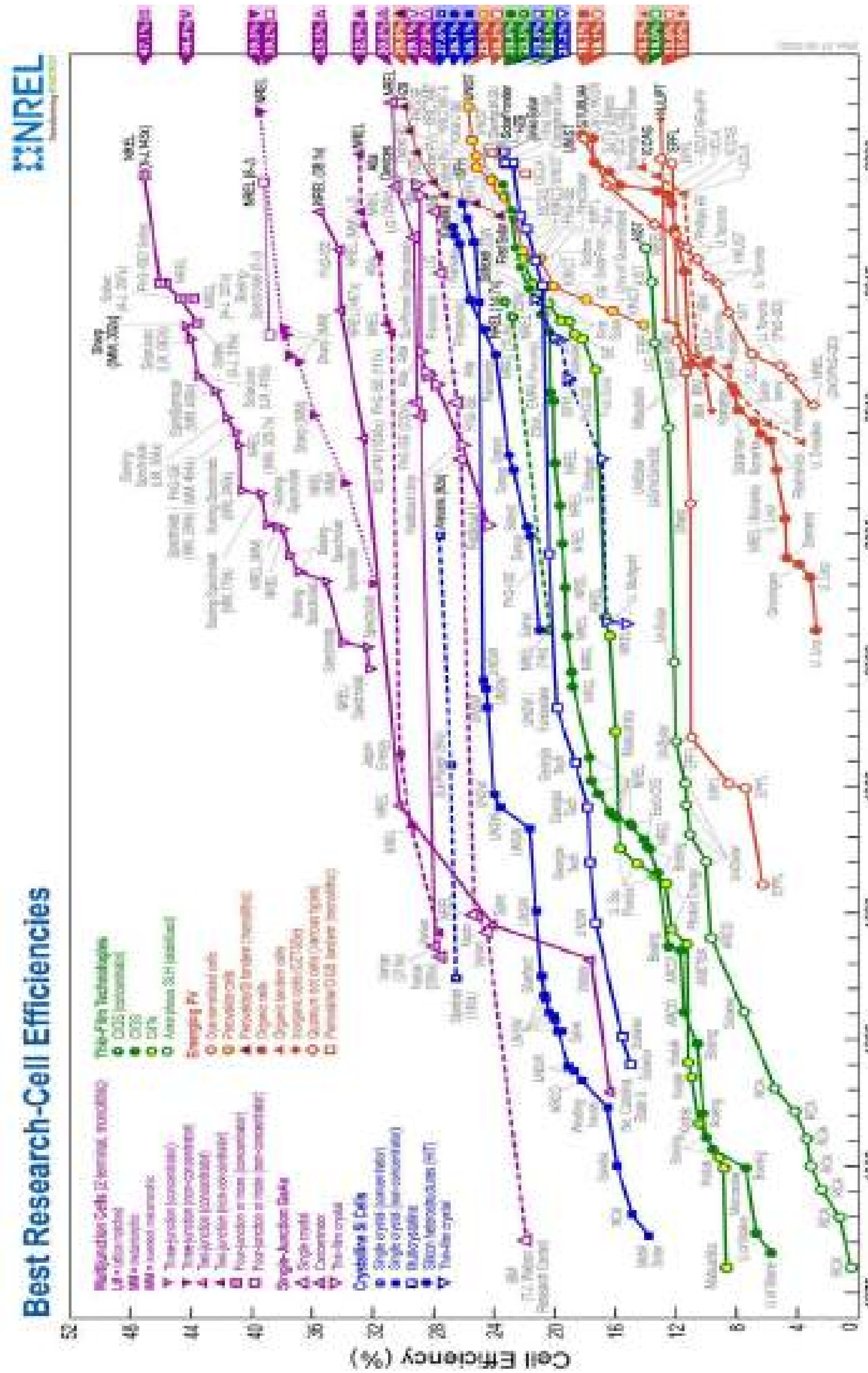


Figure 1.4 Reported timeline of best Research-Cell conversion efficiencies of different solar cell technologies (National Renewable Energy Laboratory, USA) (https://www.nrel.gov/pv/cell-efficiency.html).

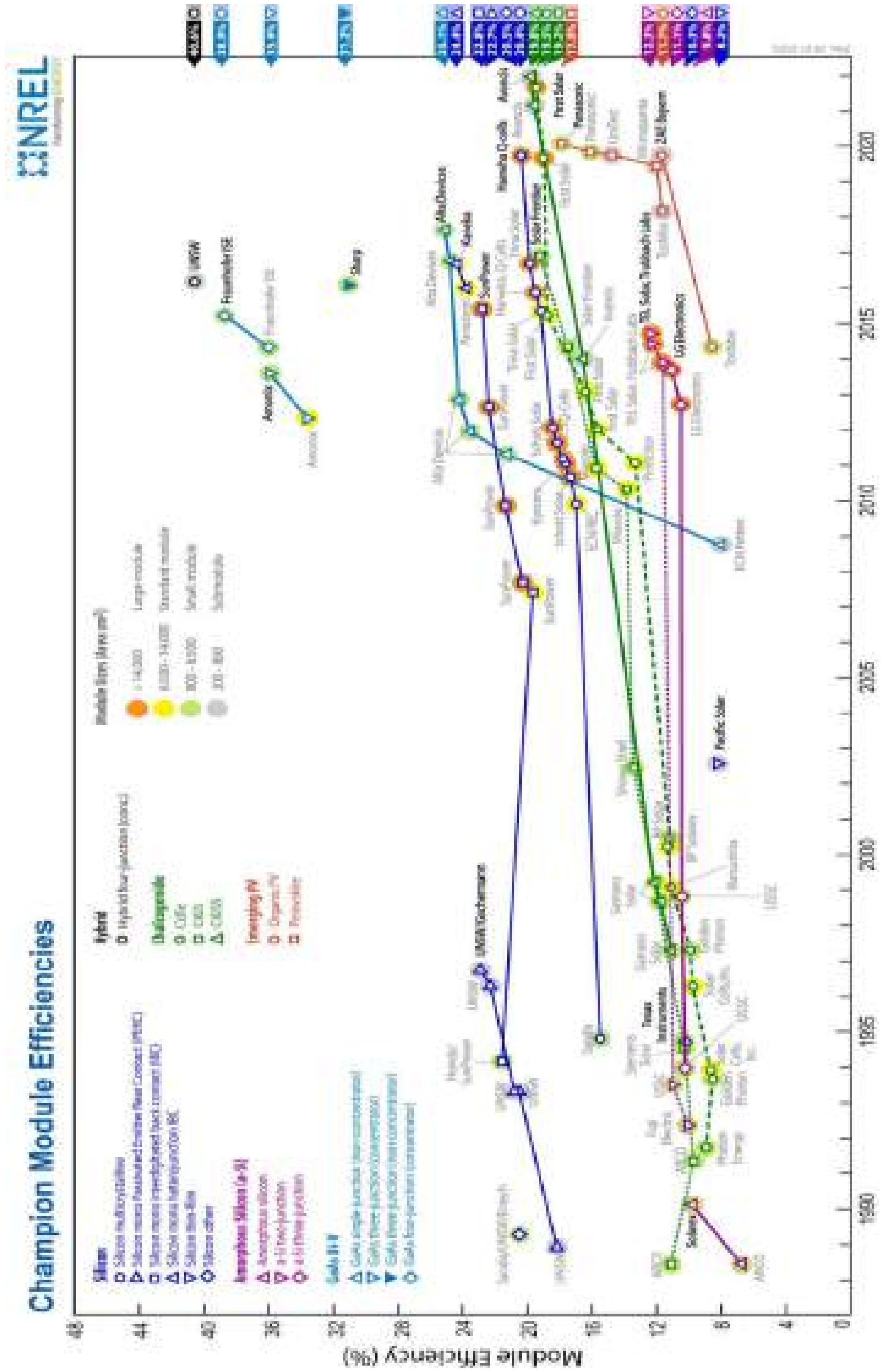


Figure 1.5 Reported timeline of Solar Module efficiencies of different solar cell technologies (National Renewable Energy Laboratory, USA) (https://www.nrel.gov/pv/module-efficiency.html)

1.3. Basic construction and different components of a Dye sensitized solar cell

The working of a DSSC is based on the sensitization of wide band gap semiconductors. A typical DSSC consists of five essential elements as follows:

a) Transparent conductive oxide coated glass substrate (FTO, ITO etc).

b) A photoelectrode with a thin layer of nanostructured wide band-gap semiconductor (usually TiO_2, ZnO, WO_3, SnO_2 or Nb_2O_5) attached to the conducting glass substrate.

c) A monolayer of dye deposited on the semiconductor's surface to absorb light.

d) An electrolyte containing a red-ox couple (typically I-/I3-) which acts as a source for electron replacement.

e) A counter electrode made of a glass sheet coated with a catalyst to facilitate electron collection (typically platinized FTO, ITO etc).

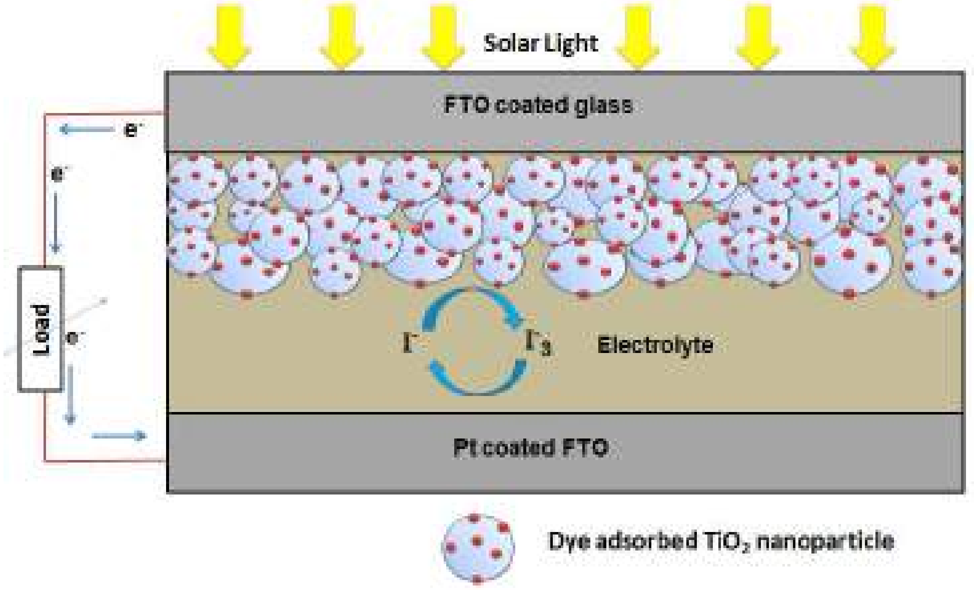


Figure 1.6 Basic structure of DSSC.

1.3.1. Transparent conducting oxide (TCO) coated glass substrate

The electrodes for a conventional DSSC are constructed on the TCO-coated glass substrates [44,45] and the cell is assembled between them. The performance of the DSSC is heavily influenced by the transparent conducting substrate. It serves the role of a current collector as well as a support structure for the semiconductor layer. It has two key characteristics: high optical transparency, which permits natural sunlight to penetrate through to the underlying active material without suffering any undesired solar spectrum absorption, and low electrical resistivity, which promotes electron transport and decreases energy loss.

Both inorganic as well as organic materials have been used to make transparent conducting coatings for photovoltaic usage. Indium tin oxide (ITO), fluorine-doped tin oxide (FTO), and doped zinc oxide [46–48] are examples of transparent conducting oxides (TCO) that are frequently utilized as a layer in inorganic films.. On the other hand, the organic layers have been developed employing grapheme and carbon nanotube networks, as well as networks of polymers like PEDOT [poly(3,4-ethylenedioxythiophene)] [49,50] and its derivatives[51-53]. A large varity of TCOs have been designed and researched extensively during the past thirty years. Among them, the most efficient TCO materials frequently utilized in solar applications are ITO and FTO coated glass substrates because of their easy fabrication process along with optimum electrical and optical properties. However, compared to ITO, FTO has better conductivity and better transparency to visible light. Furthermore, the electrical properties of ITO degrade at high temperatures and in the presence of oxygen, whereas FTO remains much more stable in such conditions. Moreover, FTO is cheaper as compared to ITO. Due to these reasons, FTO is mostly preferred over ITO in DSSC fabrications.

1.3.2. Photo electrode

The photoanode comprises of a wide bandgap metal oxide semiconductor coating over a TCO glass substrate, usually deposited via doctor blading, screen printing or dip-coating method. The semiconductors widely used to prepare mesoporous photoanode material are TiO_2 [154-58], ZnO [59-61], SnO_2 [62-64], WO_3 [65-68], Nb_2O_5 [69-71] etc. This layer acts as a dye adsorption surface, accepting electrons from the excited dye and conducting them to the TCO. TiO_2 has been and continues to be the most preferred choice as photoanode material for DSSCs. It has three different crystalline forms: anatase, rutile, and brookite. The brookite form is very difficult to synthesize. So it is not so popularly used to make photoanodes. Rutile (band gap = 3 eV, absorption edge at 413 nm) [72] is the most stable among all the three phases; however, it has a poor electron transfer rate, resulting in low current in DSSC. Moreover, it is not completely transparent in the UV-VIS range of the solar spectrum [73]. As a result, the anatase form of TiO_2 having band gap = 3.2 eV (absorption edge at 388 nm) [74] has been widely used in DSSC fabrication [75].

TiO_2 has certain special features that make it the favoured semiconductor for dye sensitised solar cells. Its conduction band edge is slightly lower than the excited state energy level (LUMO) of many dyes, which is one of the major requirements for the efficient electron injection from dye to semiconductor. Another advantage of TiO_2 is it's high dielectric constant (80 for anatase), which allows efficient electrostatic screening of the injected electron from the oxidized dye molecules anchored to the TiO_2 surface, lowering the possibility of recombination before the dye molecule gets reduced by the red-ox electrolyte. As discussed earlier, the larger band gap of anatase phase of TiO_2 makes it a better choice for dye-sensitized solar cells. It has the ability to absorb only ultraviolet light, leaving the rest of the visible and near-infrared spectrum of the solar light for the dye molecules attached to the surface, depending upon the sensitizers properties. Aside from this, the high refractive index of anatase TiO_2 ($n = 2.5$) enables effective diffuse scattering of the light inside the mesoporous photoanode and hence significantly enhances the light adsorption. As a result, by carefully controlling the TiO_2 surface, one may improve the light absorption and hence the photo anode's light harvesting efficiency.

If we consider a simple planar electrode TiO_2 surface covered with a sensitizer monolayer, only a small percentage of incident light may be absorbed, which is disadvantageous for the device performance. But when a nanocrystalline mesoporous TiO_2 film is used, the effective surface area may be enhanced to 1000 times the area of a planer film. As a result, the dye loading is also enhanced and ultimately increasing the light harvesting efficiency. Usually doctor- blading or screen printing method is to prepare the mesoporous nanostructured film over the TCO substrate. Subsequently, the nanoparticle film is sintered to improve its electronic interconnectivity and charge transfer to the substrate. TiO_2 cells exhibited a highest efficiency of 14.30 % till date [76]. The drawback of mesoporous nanostructured films is the lower charge transfer rate as a result of an extended electron diffusion pathway inside the semiconductor network. To address this significant drawback and provide improved charge transport capabilities, photoanode materials other than nanoparticles, such as 1-D nanostructures like nanotubes, nanorods, and nanowires, are gaining significant attention among researchers [77-83].

Recently, ZnO has emerged as a great potential alternative to TiO2 due to its fascinating electrical and optical properties along with a simple synthesis process. ZnO is a wide band gap semiconductor having a direct band gap of 3.37 eV, making it suitable as a photoanode material for DSSC [84, 85]. Moreover, it's conduction band edge is placed nearly at same level as that of TiO_2. Apart from this, ZnO is very easy to synthesize, abundant, inexpensive and poses higher electron mobility (200-300 $cm^2V^{-1}S^{-1}$for bulk material and 1000 $cm^2V^{-1}S^{-1}$ for nanowire) than that of TiO_2 nanoparticles (0.1-4$cm^2V^{-1}S^{-1}$) [86-88]. Furthermore, zinc oxide is popular for its ability to be grown easily with a wide range of nanostructural shapes, such as nanoparticles, nanorods or nanowires, nanotubes, nanoplants, nanosheets etc. Additionally, the 1-D single-crystalline rod-like structure of ZnO nanorods provides a higher surface-to-volume ratio enabling better dye loading [79]. These qualities of ZnO make it a potential alternative to TiO_2 for the fabrication of DSSCs. Currently, the highest efficiency of ZnO photoanode-based DSSCs lies in the range of 8 % [89, 90]. However, the main issue with ZnO is its stability, particularly in aqueous situations. ZnO gets dissolved easily in basic and acidic solutions and has a relatively narrow range of stability. Dissolution of ZnO by anchoring groups like carboxylic acid results in Zn^{+2} ions. These Zn^{+2} ions subsequently form insoluble complexes with ruthenium dyes like N3 and N719. These insoluble complexes formed in the mesoporous structure disrupt the charge transport process.

1.3.3. Dye sensitizer

The sensitizing dye serves as the heart of a DSSC. By absorbing photons, it generates electrons that are then injected into the conduction band of the metal oxide semiconductor. The characteristics of the dye have a significant impact on the light-harvesting efficiency, thus highly influencing the overall conversion efficiency of the device. A good sensitizer for DSSC must satisfy several criteria in order to achieve high conversion efficiency.

i. The longer the absorption range of the dye molecule, higher will be the conversion efficiency of the device. So the dye should absorb the sunlight ranging from UV to Infrared region.

ii. The dye must carry an anchoring group so that it can be anchored firmly to the surface of the metal oxide semiconductor material by forming a chemical bond. The charge transfer from the dye to the semiconductor occurs through this chemical bond. Good adsorption to the semiconductor surface, i.e., Good attachment to semiconductor nanoparticles, ensures rapid electron transfer.

iii. The excited state (LUMO) of the adsorbed dye molecule should be higher enough than the conduction band edge of the semiconductor oxide so that an energetic driving force can be provided for the electron injection process.

iv. The sensitizer's highest occupied orbital (HOMO) must be placed low enough so that it can accept electron donation from the electrolyte or a hole conducting material and, consequently, the oxidized could be regenerated.

v. The adsorbed dye molecule should be thermally and electrochemically stable enough in the working environment to sustain a long operation life under exposure to natural daylight. So it should also have high photostability.

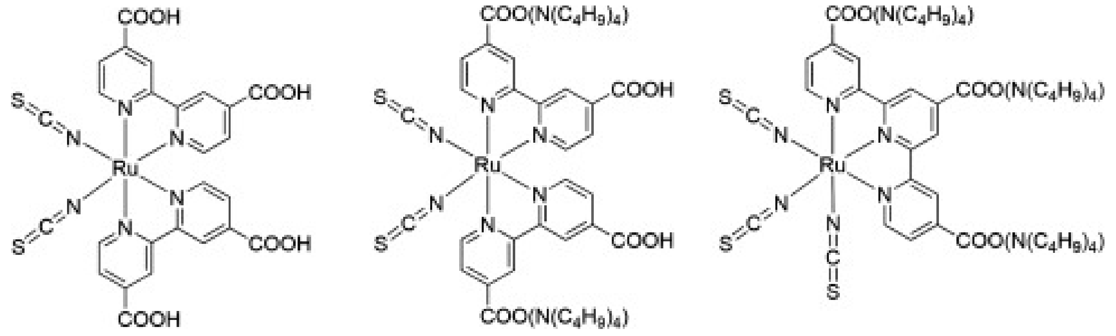
vi. It should possess high solubility to the solvent used in the dye impregnation.

vii. The band gap of the dye or HOMO-LUMO gap must be as small as possible while still maintaining a LUMO that is more negative than the conduction band of the semiconductor and HOMO that is more positive than the red-ox species. The HOMO-LUMO gap of the dye sensitizer determines the spectral range of light that it can absorb.

viii. Finally, the dye should not suffer aggregation. Dye molecules frequently tend to aggregate on the semiconductor oxide surface, increasing the decay from the excited to the fundamental state and, as a result, lowering electron injection into the semiconductor conduction band. Some additives, such as chenodeoxycholic acid (CDCA), are commonly used as co-adsorbents with the sensitizer in order to reduce the dye aggregation phenomena.

Several photosensitizers for DSSC applications have been studied over the last few decades: they are likely the most researched component of a DSSC device and have been thoroughly evaluated in multiple studies. The typical sensitizers are mainly classified into metal-complex dyes, metal-free organic dyes, and natural dyes [91-95].

Metal complex dye sensitizers, like polypyridyl complexes of Ruthenium (Ru), Osmium (Os), metal porphyrin and phthalocyanine are efficient and reliable dyes for DSSC application. Ruthenium-based metal complexes are the most popular among the metal complex dyes, owing to their excellent photovoltaic characteristics. So far, the most efficient sensitizers in DSSCs have been Ruthenizer 535-bisTBA (known as N719 dye), Ruthenizer 535(known as N3 dye) and N749 (known as black dye). Their exceptional photovoltaic activity stems from a broad absorption spectrum, well-aligned excited and ground states, and stability in the oxidized state, making them the most suited candidate for DSSC application [96]. However, their poor molar extinction coefficient, inadequate availability of noble metals, high cost, negative environmental impacts and complex synthesis and purification method have compelled researchers to look for metal-free organic dyes and natural dyes [97]. Chemical structures of some popular metal complex dyes are shown in Fig. 1.7.



N3 N719 N749 "black dye"

Figure 1.7 Chemical structure of some metal-complex dyes.

Over the last decade, several organic sensitizer families have been presented. Organic dye-based DSSCs have been advancing quite rapidly in recent years, and their conversion efficiencies are comparable to that of polypyridyl ruthenium dye-based cells. In addition, metal-free organic dyes are distinguished by their low cost, high molar extinction coefficients, and diversity of molecular architectures.

Coumarin, indoline, cyanine, merocyanine, hemocyanin, triphenylamine, phenothiazine, tetrahydroquinoline, dialkylaniline, and carbazole are some examples of dyes falling in this category. Fig. 1.8, Fig. 1.9 and Fig 1.10 show molecular structures of some common dyes belonging to this category. Hara et al. presented various coumarin derivatives and achieved an efficiency of 7.4 % [98], which was comparable to the performance of a cell fabricated using N719 dye under similar working conditions. In 2003, Horiuchi and co-workers, for the first time, reported the synthesis and application of indoline dye in DSSC and achieved a conversion efficiency of 6.1 %, which was slightly less than the 6.3 % efficiency obtained with N3 dye under the same experimental conditions [99]. Later in 2004, the same group reported a conversion effiency of 8 % for a new type of indoline structure [100]. In addition to its high photoconversion efficiencies, indoline dye was found to be highly stable to photodegradation procedures. Cyanine dyes are well known for having high molar extinction coefficients and have the ability to absorb light in the near-IR region [101, 102]. A novel cyanine dye featuring a triphenylamine as donor, carboxylic acid as acceptor and connected by a low-band-gap benzothiadiazole conjugation fragment had been developed and effectively used to sensitize TiO_2-based DSSC by Tian and his co-workers [103]. It showed an efficiency of 7.62 % under the illumination of 75 mW/cm^2. Liu et al. developed a novel isophorone sensitizer D-3 based on a donor–π–acceptor system and obtained a remarkable photoconversion efficiency of 7.41 % under 100 mW/cm^2 illumination.

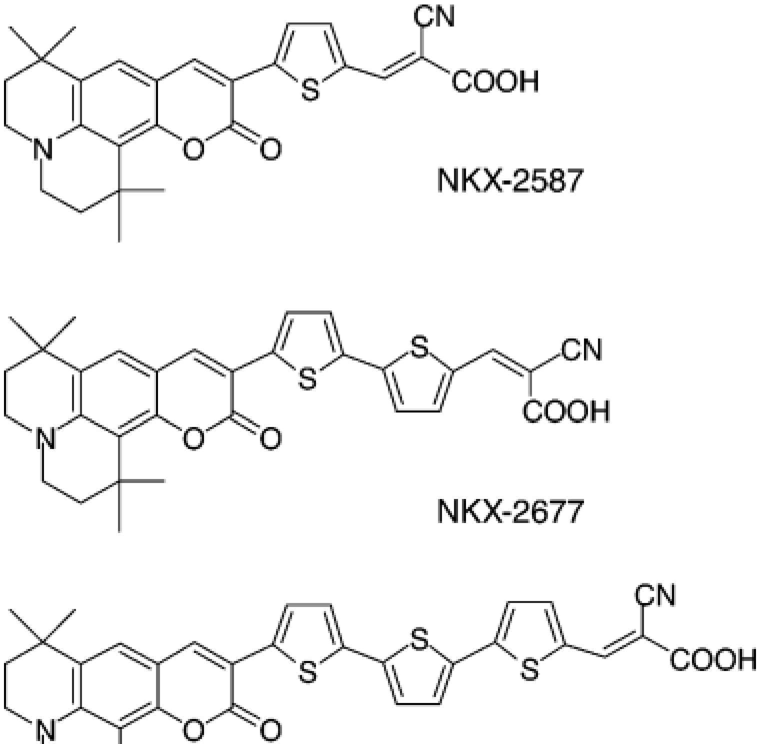


Figure 1.8 Molecular structure of Coumarine dyes.

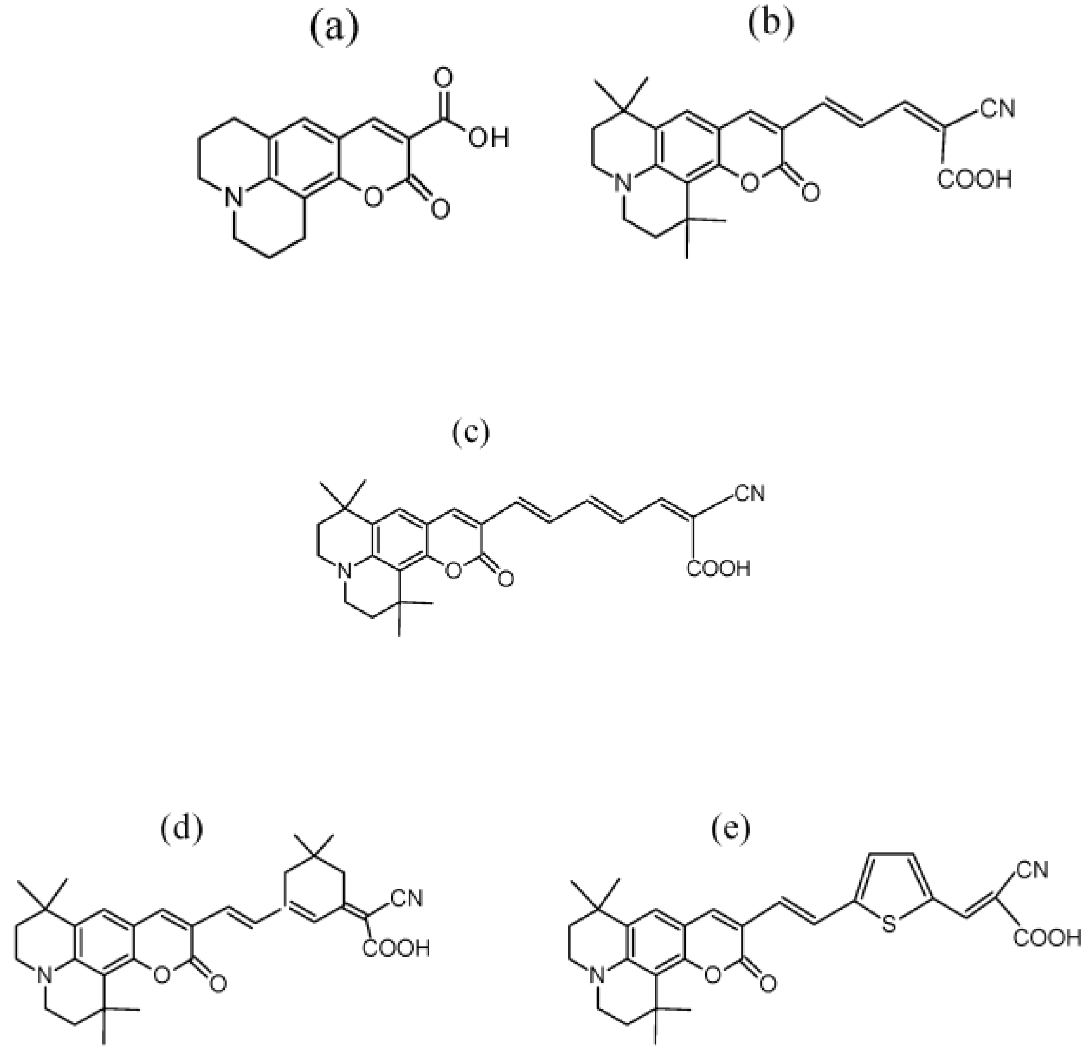
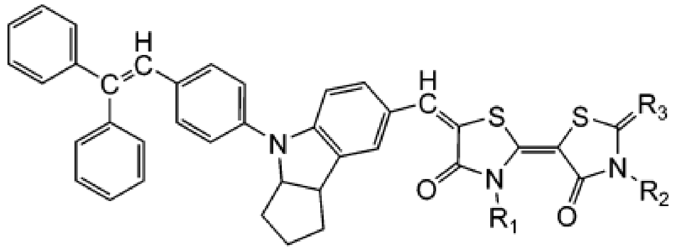


Figure 1.9 Coumarin dye structures: (a) C343, (b) NKX-2311, (c) NKX-2586, (d) NKX-2753 and (e) NKX-2593.



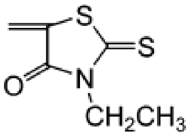
	R_1	R_2	R_3
Indoline Dye **1**	$-CH_2COOH$	$-CH_2CH_3$	$=S$
2	$-CH_2COOH$	$-CH_2COOH$	$=S$
3	$-CH_2CH_2COOH$	$-CH_2CH_3$	$=S$
4	$-CH_2COOH$	$-CH_2CH_3$	

Figure 1.10 Molecular structure of indoline dyes (1-4).

Exrensive research has been conducted over the years to determine the feasibility of replacing synthesized dyes with plant-based natural dyes. Various natural fruits, flowers and plant leaves have a variety of colours and contain a variety of pigments that can be extracted and used in DSSCs to harvest solar energy. Natural dyes have several advantages compared to the synthesized dyes. Natural dyes, unlike synthetic dyes, are widely available, simple to prepare, inexpensive, non-toxic, environment friendly, and fully biodegradable [104, 105]. Natural dyes are classified into four major families: chlorophyll, anthocyanin, carotenoids, and flavonoids. Figure 1.11 depicts a flow chart diagram representing the classification of pigments found in plants [106-108].

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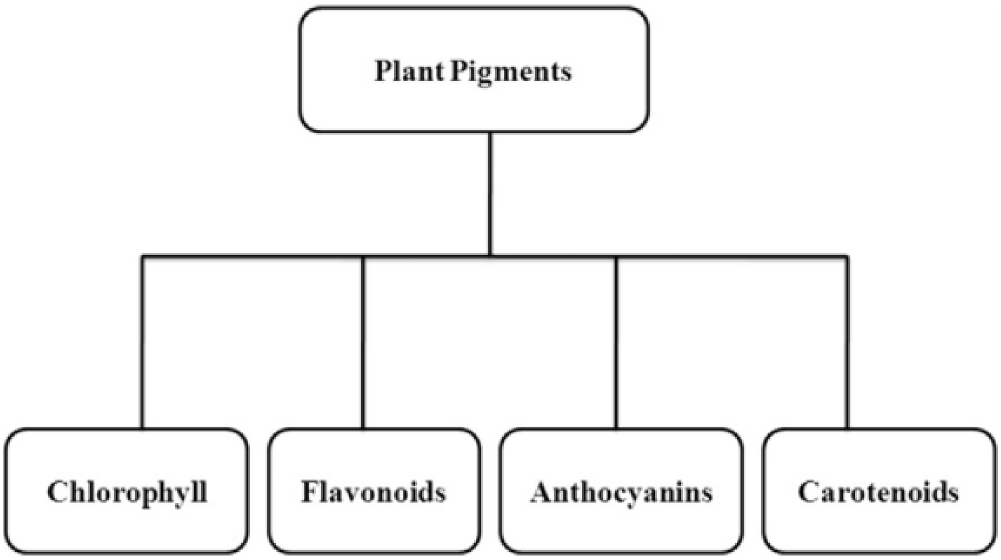

Figure 1.11 Classification of plant pigments.

Chlorophyll is abundant in the leaves of most green plants. It is the natural photosynthetic pigment that gives plants their green colour [109, 110]. The primary functions of chlorophyll are efficient harvesting of light energy and transduction of that energy for photosynthesis, which is primarily accomplished by their spectral properties. Chlorophyll ‘a’ and chlorophyll ‘b’ are the two major types of chlorophylls. Because of their ability to absorb blue and red light, chlorophylls and their derivatives are used as sensitizers in DSSC. The most effective is a chlorophyll a derivative (methyl trans-32-carboxy-pyropheophorbide) [111]. When compared to chlorophyll a, the absorbance spectrum of chlorophyll b has a distinct blue tinge and a red shift. Fig 1.12 depicts the chemical structure of chlorophyll a and chlorophyll b.

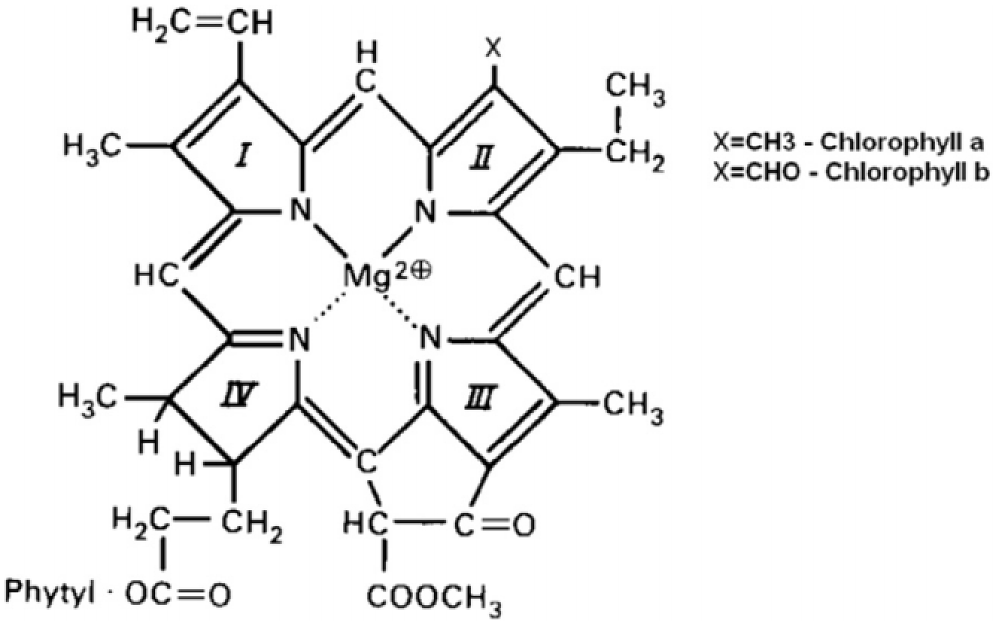

Figure 1.12 Chemical structure of Chlorophyll 'a' and chlorophyll 'b'. [112]

Flavonoids are the most common and biochemically active group of natural constituents that contribute to the colour of flowers [113, 114]. Geissman and Hinreiner coined the term "flavonoid" to describe all compounds whose structure is based on flavones with a basic C6–C3–C6 skeleton [115]. Flavone comprises two benzene rings connected by a ring that distinguishes one flavonoid compound from another. Despite their structural similarities, only a few flavonoids can absorb light in the visible range [111]. The basic chemical structure of a commonly occurring flavonoid is depicted in Fig. 1.13. The number of flavonoid structures found in nature is limited, and they range in oxidation state from flavan-3-ol to flavonols and anthocyanins. Flavonoids are also comprised of flavanones, flavanonols, and flavan-3, 4-diols [116]. Neoflavones or 4-phenyl coumarins, dihydrochalcones or 3-phenylpropiophenones, chalcones or phenyl styryl ketones, isoflavones or 3-phenyl chromones, and aurones or 2-benzylidine-3-coumaranones are also compounds. The orientation of hydroxy and methoxy groups and their numbers in these two benzene rings distinguish the individual compounds in each class [117]. Fig. 1.13 depicts the structure of commonly occurring flavonoid. [118]

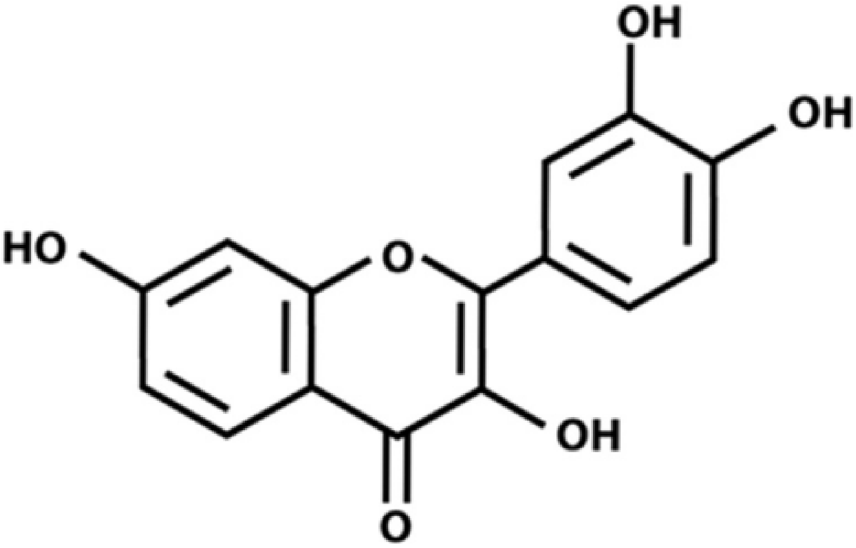

Figure 1.13 Chemical Structure of commonly occurring flavonoid.

Anthocyanins are the second most crucial group of pigments visible to the human eye after chlorophyll [104]. Anthocyanins also influence the amount and quality of light incident on chloroplasts [119]. The anthocyanins found in plants are so diverse that ornamental plants such as dianthus and petunia only have one type of anthocyanin, whereas tulipa, rosa, verbena, for example, has mixture of several. Some fruits, on the other hand, are rich in anthocyanins. Grapes contain a wide range of anthocyanins. Cyanidin is found in apples, cherries, figs, and peaches, while delphinidin is found in eggplant and pomegranate. Cherry sweet and cranberry contain both cyanidin and peonidin. Carbonyl and hydroxyl groups present in anthocyanin molecules from bonding with the TiO2 molecule, thereby promoting excitation and injection of electrons from the dye molecule to the conduction band of TiO_2. The basic chemical structure of anthocyanin pigment is shown in Fig. 1.14

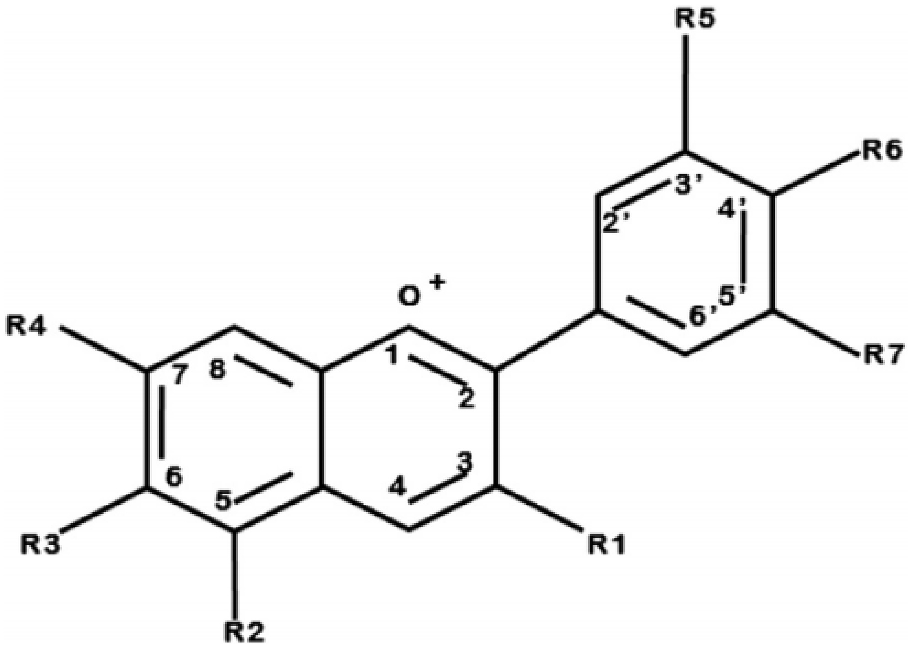

Figure 1.14 Basic chemical structure of anthocyanin pigment. Here ‘R’ could be replaced with H, OH or OCH_3 depending on the pigment. The numbers can be substituted with the hydroxyl group.

Carotenoids are a large family of isoprenoids (with more than 600 members) that give distinguishing red, orange, and yellow colours to many fruits and flowers. The presence of a C_{40} hydrocarbon backbone distinguishes carotenoids, causing structural and oxygenic changes. Fig. 1.15 shows the chemical structures of some pigments from the carotenoid class [120-122].

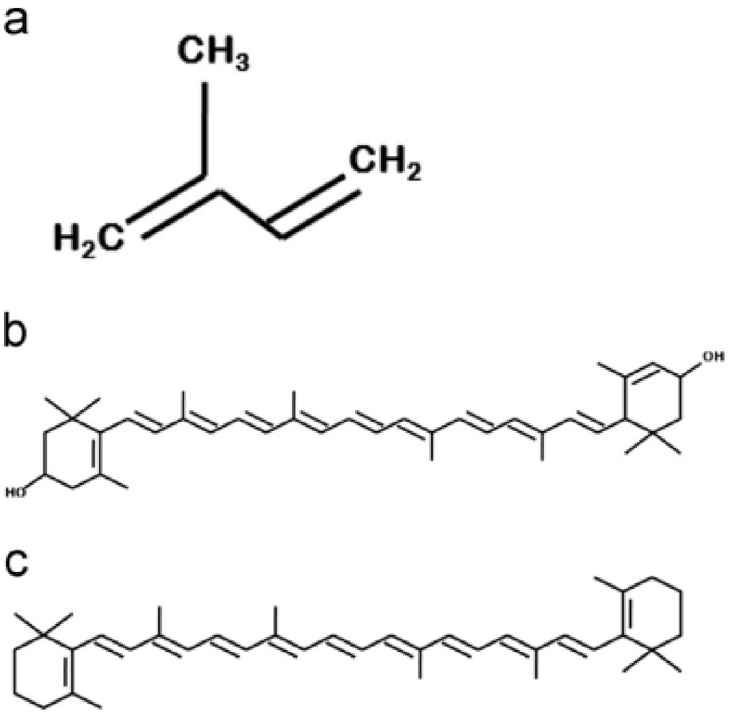

Figure 1.15 (a) Basic structure of an Isoprene unit, (b) Chemical structure of Xanthophylls, and (c) Chemical structure of Carotene.

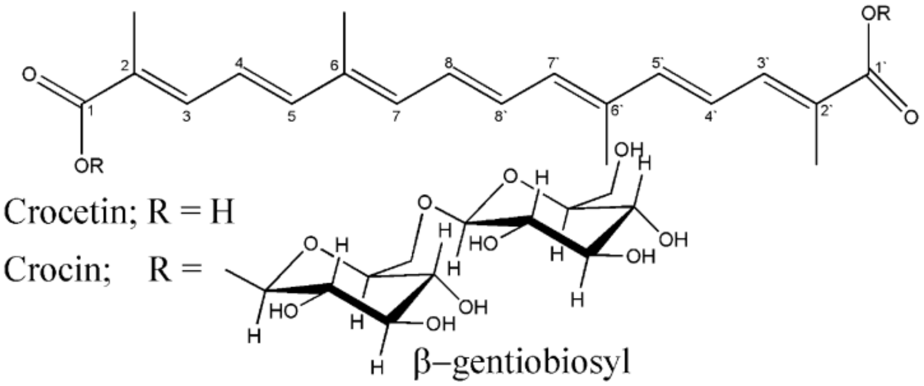

Figure 1.16 The molecular structures of crocetin and crocin.

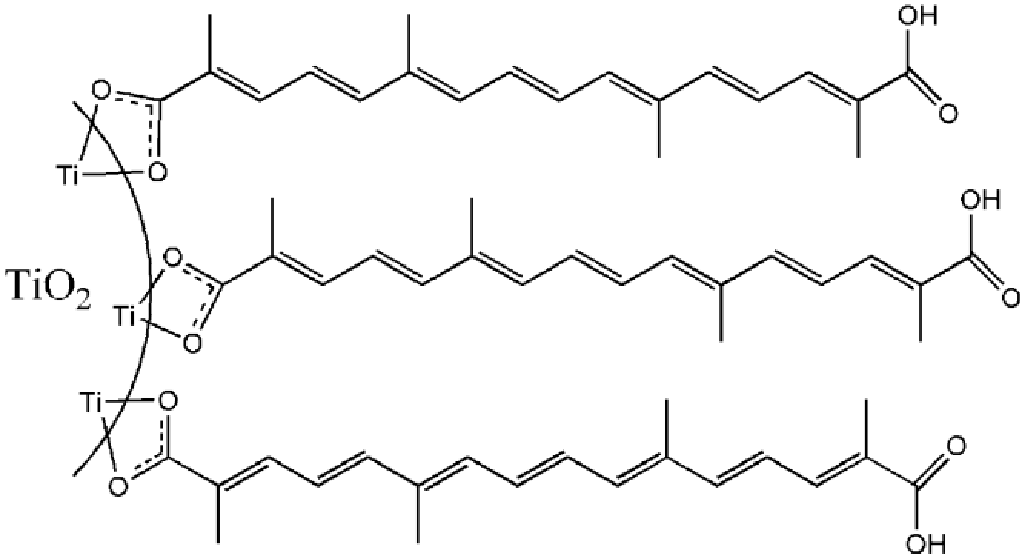

Figure 1.17 Possible mechanism of the binding between crocetin and TiO$_2$ surface.

Many investigations have been performed to explore all the classes of natural dyes mentioned earlier, such as chlorophyll [123-131], carotenoids [132-134], and flavonoids [135-139]. When compared to DSSCs sensitized with synthetic dyes, the overall cell efficiency of natural dye-based DSSCs is comparatively low. Comparative studies on the performances of DSSCs based on different types of natural dyes have been done by several researchers [105, 140, 141]. To improve the efficiencies of the natural dye based DSSCs further, different dye combinations have been investigated and reported in order to obtain a broader absorption spectrum. Using natural dyes in conjunction with an optimized extraction solvent improves solar light absorption by the dye molecules and allows for more efficient utilization of photon energy. As a result, DSSC sensitized with the dye mixture exhibits higher absorbance and cumulative absorption properties across the entire visible region than DSSC manufactured with single individual dyes [138, 142-147].

1.3.4. Electrolyte

One of the most crucial function in the light-to-electricity conversion process is played by the electrolyte. It acts as an electron transfer mediator, restoring the dye sensitizer molecules from their oxidized state. The following are the requirements for any electrolyte used in a dye-sensitized solar cell:

1. To prevent dye degradation from the oxide surface, the electrolyte must be chemically, thermally, optically, and electrochemically stable over time.
2. The charge carriers must be transported between the working electrode and the counter electrode by the electrolyte. The oxidized dye must be regenerated and restored to its ground state after the electrons are injected into the oxide material's conduction band. As a result, the electrolyte must be selected carefully, taking into account the redox potential and recombination properties of the dye.
3. The electrolyte must allow charge carriers to diffuse quickly into the device and maintain good contact with both the mesoporous nanocrystalline oxide surface and the counter electrode. In case of liquid electrolytes, it is necessary to prevent solution loss due to leakage or evaporation..
4. There should be no significant absorption of visible light by the electrolyte. As I_3^- has its own colour, it reduces visible light absorption by the dye. Additionally, I_3^- ions may react with the injected electrons leading to increased current. That is why the concentration of I^-/I_3^- must be optimized in the electrolytes containing I^-/I_3^- couple.

Depending upon the viscosity, the electrolytes are classified as liquid, quasi-solid, or solid. Electrolytes based on liquid organic solvents are the most common electrolytes used in DSSCs. They are typically made up of a redox couple dissolved in an organic solvent with a high dielectric constant; additional additives can be added to improve device performance.

Iodide/triiodide (I^-/I_3^-) is the most common redox couple, owing to the slow recombination reaction; these electrolytes are generally prepared by dissolving iodide salts with various cations (K^+, Li^+, Na^+, Mg^+) in a liquid solvent. The kinetics of the (I^-/I_3^-) redox couple with Ruthenium dye (N719) is depicted in Fig.1.18. The injection of phtogenerated electrons into the conduction band of TiO_2 takes place on the femtosecond time scale, which is much quicker than the electron recombination process with I_3^-, and the oxidized dye mainly reacts with I^- rather than the injected electrons. I_3^- diffuses to the cathode in the electrolyte to harvest electrons, producing I^-, which then diffuses in the opposite direction towards the TiO_2 electrode and consequently regenerates the dye molecules.

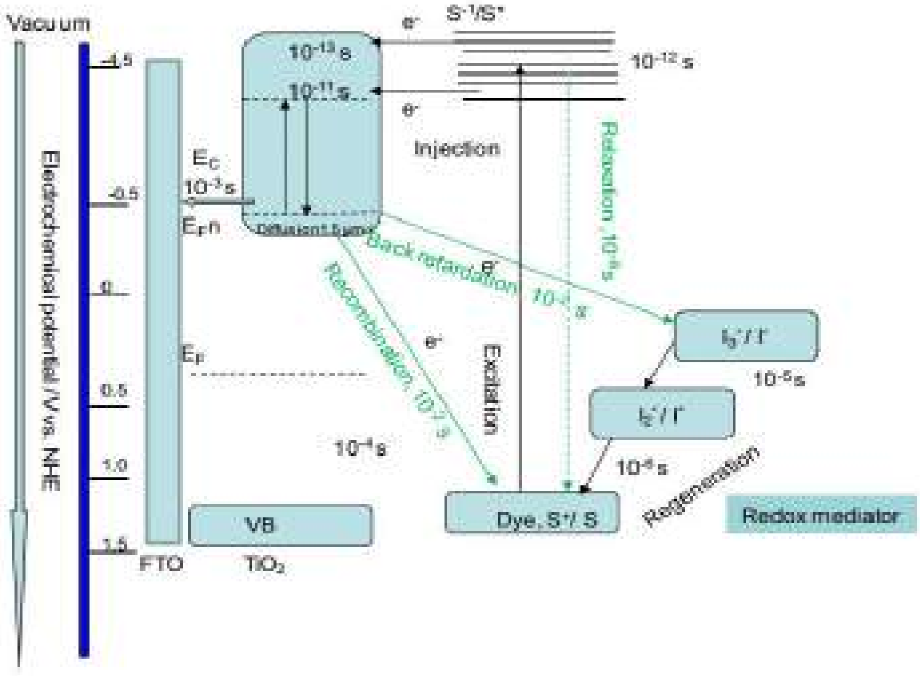

Figure 1.18 Charge transfer and recombination kinetics in DSSC.

(https://ro.uow.edu.au/theses/3415/)

However, because of iodine's corrosive properties, researchers have looked into alternative redox couples such as Br-/Br3- [148], SCN-/(SCN)3- [149], and SeCN-/(SeCN)3- [150], all of which have promising electrochemical and noncorrosive properties but are chemically unstable [151]. Copper and cobalt complexes can also function as redox mediators [152, 153].

Regarding the solvent, it should be chemically stable, have low volatility in the temperature range within which the DSSC is being operated, have a high dielectric constant to facilitate redox couple dissolution faster, low viscosity to promote rapid charge diffusion [151], and should allow for good solubility of the redox mediator and other additives in the electrolyte. It is also essential that the solvent does not cause dye, semiconductor desorption, or dissolve the sealing material into the solvent. Mostly used solvents are polar organic solvents. Acetonitrile (ACN) is the most common and effective solvent used in DSC research because of its excellent performance, stability, low viscosity, and ability to dissolve a wide range of salts and organic molecules. However, unfortunately, the boiling point of acetonitrile is low (78 °C), so 3-methoxypropionitrile (MPN), with a boiling point of 164 °C and low toxicity, is the preferred choice for the long-term stability of DSSCs.

Additives to the electrolyte such as 4-tert-butyl pyridine (4TBP), guanidiumthiocyanate, and methyl benzimidazole (MBI) have been found to be very effective in suppressing the recombination [154-156]. The most likely mechanism behind this reduction in recombination is that when the TiO2 surface absorbs these additives, they block reduction sites, preventing electron acceptor molecules from coming into contact. A variety of cations and compounds have been added to liquid electrolytes as additives and tested to improve the cell's photovoltaic performance. The most widely used additive is 4-tert-butylpyridine (TBP), which effectively suppresses the dark current and thus increases the fill factor and efficiency values by the introduction of coordination between N atoms and Ti ions on the TiO_2 surface, thereby limiting electron recombination [157]. When guanidinium thiocyanate (GuSCN) is added in the liquid electrolyte, it increases both the current and voltage due to a positive shift in the conduction band of TiO_2 and leads to a reduction in the charge recombination phenomena [158]. Li cations are another common additive. They can be readily adsorbed on the surface of TiO_2 nanoparticles, resulting in a significant increase in photocurrent density. This effect is caused by the capability of Li ions in lowering the acceptor states of TiO_2, modifying the flat band on the photoanode surface and consequently electron injection process becomes more energetically favourable [159]. When these cations are not present on the surface, the conduction band of the semiconductor shifts downward, lowering the V_{oc} of the cell [160]. These additives can thus enhance the efficiency and stability, even without participating in the fundamental photoelectrochemical processes. However, the concentration of LiI must be kept low because the small Li cations may bind to the TiO_2 matrix and act as recombination centers, reducing device performance [161]. The maximum voltage that can be obtained from the DSSC is theoretically determined by the difference between the quasi-Fermi energy level of TiO_2 and the redox potential of the electrolyte.

The major challenges with using liquid solvent-based electrolytes are their leakage problem, difficulty in sealing and limited long-term stability. These limitations prevent the utilization of the devices with high and consistent efficiency over time. Various alternative solutions have been proposed to address these shortcomings and are currently being researched. Quasi-solid electrolytes and solid electrolytes have attracted special consideration from researchers in this regard. Quasi-solid electrolytes can be derived from organic solvent-based or ionic liquid electrolytes that can be gelled, polymerized, and dispersed in a polymeric material [151, 162-164].

Conductive polymers, hole-conducting molecular solids, and organic p-type conductors, such as poly(3-hexylthiophene) (P3HT) [165] polypyrrole [166], poly(3,4-ethylene dioxythiophene) (PEDOT) [167], polyaniline (PANI) [168] and 2,2’7,7’-tetranis- (N,N-di-p-methoxyphenyl-amine)9,9’-spirobifluorene (spiro-OMeTAD) [169] are few examples of solid-state electrolytes. However, the photovoltaic performance of DSSCs based on all of these alternative electrolytes is currently lower than those based on liquid solvents, indicating that more research is needed in this field.

1.3.5. Counter electrode

The counter electrode is that important component of a DSSC where the reduction of the redox species occurs. In the case of solid-state DSSCs, the counter electrode collects the holes from the hole transporting material [170]. As the counter electrode, Pt-coated FTO obtained through thermal decomposition [171], sputtering [172] or chemical reduction [173] is typically used. However, due to the high cost and limited resources of Pt, considerable efforts have been made in recent years to replace this Pt catalyst with other low-cost, earth-abundant materials. Due to their excellent catalytic activity, materials such as graphite, carbon black, activated carbon on FTO-glass, and organic-ion doped conducting polymer of poly(3,4- ethylene dioxythiophene)(PEDOT) on both indium tin oxide (ITO) and FTO-glass have also been successfully used as counter electrode materials in DSSCs [174-178]. However, the main issue with the carbon counter electrodes is their adhesion to the substrate surface and their opaque nature.

1.4. Basic Operating Principle of DSSC

A DSSC is the only photovoltaic device with multiple electron transfer processes running in parallel and competition. It utilizes separate mediums for light absorption/carrier generation (dye) and carrier transport (TiO_2 nanoparticles and the electrolyte). In contrast, in a *p-n* junction semiconductor solar cell, the light absorption, charge separation and transport occur in the same material. Dye molecules play the same role as chlorophyll in leaves: they absorb incident photons and initiate the electron transfer process. The schematic diagram showing the basic working principle of a DSSC is shown in Fig. 1.19.

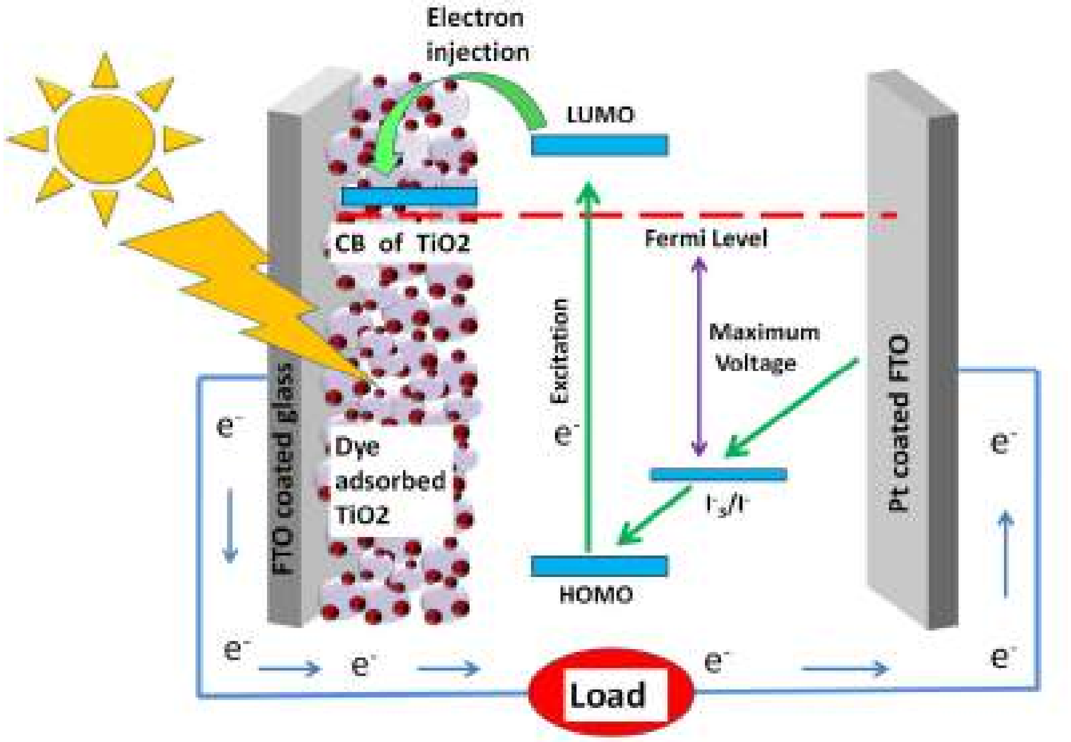

Figure 1.19 Schematic and basic working mechanism of DSSC.

The basic operation steps and electron transfer process occurring inside DSSC are as follows [179-181]:

a) When exposed to sunlight, photons are absorbed by the dye molecules and the electrons are excited from the HOMO-level to the LUMO-level, instantaneously. This process is known as photo-excitation.
b) These excited electrons are then injected into the conduction band of TiO_2, diffuse through it and are utilized at the external load before being collected by the electrolyte at the cathode surface to complete the cycle.
c) The dye molecule after losing one electron to the TiO2 gets oxidized. This means it has deficiency one electron. To recover its initial state, the dye molecule must obtain an electron. It To obtains this electron from the iodide electrolyte (I-) and the dye returns to the ground state. This procedure is known as dye regeneration..
d) This causes the iodide to become oxidized. When the original lost electron reaches the counter electrode, it returns the electron to the electrolyte. I- ion is regenerated in turn at the counter electrode by the reduction of I3- with electrons which have travelled through the external load.

There are also some reverse processes that decrease the overall cell performance. These are given below.

a) Relaxation of photo excited electron of dye molecule from excited state (LUMO) to ground state (HOMO), both by radiative and non-radiative processes.
b) Recombination of photo-injected electrons in the TiO_2 to the oxidized species (I_3^-) in the electrolyte.
c) Recombination of photo-injected electrons in the TiO_2 to the oxidized dye molecule.

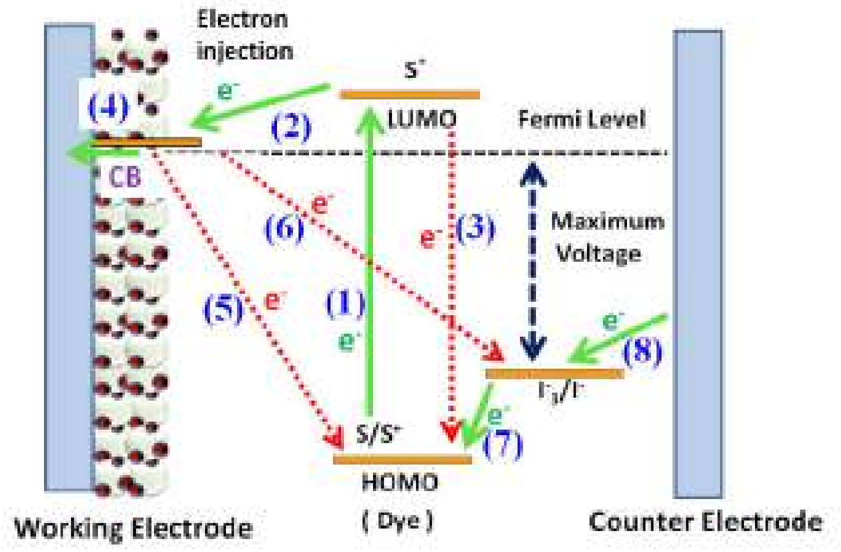

Figure 1.20 Fundamental processes inside dye-sensitized solar cell.

The following are the steps and corresponding equations involved in the cell operation [182,183]:

1. Photo excitation: S + hν (Photon) → S* (Excited)
2. Electron injection: S* (Excited) → $e^-_{(CB)}$ (SC) + S^+
3. Relaxation: S* → S + hν (Photon)
4. Electron transport: $e^-_{(CB)}$ (SC) → e^- (TCO)
5. Recombination with the dye: $S^+ + e^-_{(CB)}$ (SC) → S
6. Recombination: 2 $e^-_{(CB)}$ (SC) + $I_3^- \rightarrow 3I^-$
7. Dye regeneration: $2S^+ + 3I^- \rightarrow 2S + I_3^-$
8. Reaction at the counter electrode: $I_3^- + 2e^-(C) \rightarrow 3I^-$

S: Dye sensitizer; S*: excitation upon irradiation; S+: Oxidized dye; SC: Semiconductor; CB: Conduction band; C: Counter electrode.

The above processes are schematically illustrated in Fig. 1.20. The forward processes are depicted with green arrows, whereas red arrows represent combination and reverse processes. The maximum output voltage is determined by the difference between the Fermi energy level of the semiconductor and the red-ox potential levell of the mediator electrolyte [184]. Thus, the device can produce electricity from light without undergoing any permanent physical and chemical change.

References:

[1] Patel, Nikul K., and Shailesh N. Shah. "Biodiesel from plant oils." In Food, energy, and water, pp. 277-307. Elsevier, 2015.

[2] European Commission, The Energy Challenge of the 21st Century: The role of Nuclear Energy, http://europa.eu.int/comm/research/rtdinfoen.html

[3] M. Grätzel, Solar Energy Conversion by Dye-Sensitized Photovoltaic Cells, Inorg. Chem., 2005, 44(20), 6841–6851

[4] Song, Dengyuan, Jingfeng Xiong, Zhiyan Hu, Gaofei Li, Hongfang Wang, Haijiao An, Bo Yu et al. "Progress in n-type Si solar cell and module technology for high efficiency and low cost." In 2012 38th IEEE Photovoltaic Specialists Conference, pp. 003004-003008. IEEE, 2012.

[5] https://www.electronics-tutorials.ws/diode/diode_2.html

[6] Sharma, Divya, Rajesh Mehra, and Balwinder Raj. "Comparative analysis of photovoltaic technologies for high efficiency solar cell design." Superlattices and Microstructures 153 (2021): 106861.

[7] Shockley, William, and Hans J. Queisser. "Detailed balance limit of efficiency of p-n junction solar cells." Journal of applied physics 32, no. 3 (1961): 510-519.

[8] Hagfeldt, Anders, Gerrit Boschloo, Licheng Sun, Lars Kloo, and Henrik Pettersson. "Dye-sensitized solar cells." Chemical reviews 110, no. 11 (2010): 6595-6663.

[9] Battaglia, Corsin, Andres Cuevas, and Stefaan De Wolf. "High-efficiency crystalline silicon solar cells: status and perspectives." Energy & Environmental Science 9, no. 5 (2016): 1552-1576.

[10] Avrutin, V., N. Izyumskaya, and H. Morkoç. “Semiconductor solar cells: Recent progress in terrestrial applications.” Superlattices and Microstructures 49, no. 4 (2011): 337-364.

[11] Aberle, Armin G. “Thin-film solar cells.” Thin solid films 517, no. 17 (2009): 4706-4710.

[12] Pagliaro, Mario, Giovanni Palmisano, and Rosaria Ciriminna. Il nuovo fotovoltaico. Palermo: Dario Flaccovio Editore, 2008.

[13] Gloeckler, M., I. Sankin, and Z. Zhao. “CdTe solar cells at the threshold to 20% efficiency.” IEEE Journal of Photovoltaics 3, no. 4 (2013): 1389-1393.

[14] Pagliaro, Mario, Giovanni Palmisano, and Rosaria Ciriminna. Il nuovo fotovoltaico. Palermo: Dario Flaccovio Editore, 2008.

[15] https://www.pv-magazine.com/2021/03/04/avancis-claims-19-64-efficiency-for-cigs-module/

[16] Green, Martin, Ewan Dunlop, Jochen Hohl-Ebinger, Masahiro Yoshita, Nikos Kopidakis, and Xiaojing Hao. “Solar cell efficiency tables (version 57).” Progress in photovoltaics: research and applications 29, no. 1 (2021): 3-15.

[17] Nakamura, Motoshi, Koji Yamaguchi, Yoshinori Kimoto, Yusuke Yasaki, Takuya Kato, and Hiroki Sugimoto. “Cd-free Cu (In, Ga)(Se, S) 2 thin-film solar cell with record efficiency of 23.35%.” IEEE Journal of Photovoltaics 9, no. 6 (2019): 1863-1867.

[18] Jackson, Philip, Roland Wuerz, Dimitrios Hariskos, Erwin Lotter, Wolfram Witte, and Michael Powalla. “Effects of heavy alkali elements in Cu (In, Ga) Se2 solar cells with efficiencies up to 22.6%.” physica status solidi (RRL)–Rapid Research Letters 10, no. 8 (2016): 583-586.

[19] Plentz, Jonathan, Gudrun Andrä, Torsten Pliewischkies, Uwe Brückner, Björn Eisenhawer, and Fritz Falk. "Amorphous silicon thin-film solar cells on glass fiber textiles." Materials Science and Engineering: B 204 (2016): 34-37.

[20] Zhang, Yaokang, Sze-Wing Ng, Xi Lu, and Zijian Zheng. "Solution-processed transparent electrodes for emerging thin-film solar cells." Chemical Reviews 120, no. 4 (2020): 2049-2122.

[21] Arumugam, Sasikumar, Yi Li, Monika Glanc-Gostkiewicz, Russel N. Torah, and Stephen P. Beeby. "Solution processed organic solar cells on textiles." IEEE Journal of Photovoltaics 8, no. 6 (2018): 1710-1715.

[22] GREENY, Martin A., Keith Emery, Yoshihiro Hishikawa, and Wilhelm Warta. "Solar cell efficiency tables (version 37)." Progress in photovoltaics 19, no. 1 (2011): 84-92.

[23] Itzhaik, Yafit, Olivia Niitsoo, Miles Page, and Gary Hodes. "Sb2S3-sensitized nanoporous TiO2 solar cells." The Journal of Physical Chemistry C 113, no. 11 (2009): 4254-4256.

[24] Lévy-Clément, Claude. "Nanostructured ETA-solar cells." In Nanostructured Materials for Solar Energy Conversion, pp. 447-484. Elsevier, 2006.

[25] Lévy-Clément, Claude, Ramon Tena-Zaera, Margaret A. Ryan, Abou Katty, and Gary Hodes. "CdSe-sensitized p-CuSCN/nanowire n-ZnO heterojunctions." Advanced Materials 17, no. 12 (2005): 1512-1515.

[26] Chandrasekaran, J., D. Nithyaprakash, K. B. Ajjan, S. Maruthamuthu, D. Manoharan, and S. Kumar. "Hybrid solar cell based on blending of organic and inorganic materials—An overview." Renewable and Sustainable Energy Reviews 15, no. 2 (2011): 1228-1238.

[27] Chandrasekaran, J., D. Nithyaprakash, K. B. Ajjan, S. Maruthamuthu, D. Manoharan, and S. Kumar. "Hybrid solar cell based on blending of organic and inorganic materials—An overview.” Renewable and Sustainable Energy Reviews 15, no. 2 (2011): 1228-1238.

[28] Gong, Jiawei, Jing Liang, and K. Sumathy. “Review on dye-sensitized solar cells (DSSCs): fundamental concepts and novel materials.” Renewable and Sustainable Energy Reviews 16, no. 8 (2012): 5848-5860.

[29] Upadhyaya, Hari M., S. Senthilarasu, Min-Hung Hsu, and D. Kishore Kumar. “Recent progress and the status of dye-sensitised solar cell (DSSC) technology with state-of-the-art conversion efficiencies.” Solar Energy Materials and Solar Cells 119 (2013): 291-295.

[30] Bach, Udo, Donald Lupo, Pascal Comte, Jacques-E. Moser, F. Weissörtel, J. Salbeck, H. Spreitzer, and Michael Grätzel. "Solid-state dye-sensitized mesoporous TiO2 solar cells with high photon-to-electron conversion

[31] Kamat, Prashant V. “Boosting the efficiency of quantum dot sensitized solar cells through modulation of interfacial charge transfer.” Accounts of chemical research 45, no. 11 (2012): 1906-1915.

[32] Kramer, Illan J., and Edward H. Sargent. “The architecture of colloidal quantum dot solar cells: materials to devices.” Chemical reviews 114, no. 1 (2014): 863-882.

[33] Zhang, Xiao Li, Fuzhi Huang, Andrew Nattestad, Kun Wang, Dongchuan Fu, Amaresh Mishra, Peter Bäuerle, Udo Bach, and Yi-Bing Cheng. “Enhanced open-circuit voltage of p-type DSC with highly crystalline NiO nanoparticles.” Chemical Communications 47, no. 16 (2011): 4808-4810.

[34] Kojima, Akihiro, Kenjiro Teshima, Yasuo Shirai, and Tsutomu Miyasaka. “Organometal halide perovskites as visible-light sensitizers for photovoltaic cells." Journal of the american chemical society 131, no. 17 (2009): 6050-6051.

[35] Im, Jeong-Hyeok, Chang-Ryul Lee, Jin-Wook Lee, Sang-Won Park, and Nam-Gyu Park. "6.5% efficient perovskite quantum-dot-sensitized solar cell." Nanoscale 3, no. 10 (2011): 4088-4093.

[36] Kim, Hui-Seon, Chang-Ryul Lee, Jeong-Hyeok Im, Ki-Beom Lee, Thomas Moehl, Arianna Marchioro, Soo-Jin Moon et al. "Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%." Scientific reports 2, no. 1 (2012): 1-7.

[37] Park, Nam-Gyu. "Perovskite solar cells: an emerging photovoltaic technology." Materials today 18, no. 2 (2015): 65-72.

[38] Li, Bin, Liduo Wang, Bonan Kang, Peng Wang, and Yong Qiu. "Review of recent progress in solid-state dye-sensitized solar cells." Solar energy materials and solar cells 90, no. 5 (2006): 549-573.

[39] Li, Qinghua, Haiyan Chen, Lin Lin, Pinjiang Li, Yuancheng Qin, Mingjun Li, Benlin He, Lei Chu, and Qunwei Tang. "Quasi-solid-state dye-sensitized solar cell from polyaniline integrated poly (hexamethylene diisocyanate tripolymer/polyethylene glycol) gel electrolyte." Journal of Materials Chemistry A 1, no. 17 (2013): 5326-5332.

[40] Kawano, Ryuji, Hiroshi Matsui, Chizuru Matsuyama, Akihiro Sato, Md Abu Bin Hasan Susan, Nobuo Tanabe, and Masayoshi Watanabe. "High performance dye-sensitized solar cells using ionic liquids as their electrolytes." Journal of Photochemistry and Photobiology A: Chemistry 164, no. 1-3 (2004): 87-92.

[41] Angaiah, Subramania, Vignesh Murugadoss, Subasri Arunachalam, Pratheep Panneerselvam, and Sarathkumar Krishnan. "Influence of various ionic liquids embedded electrospun polymer membrane electrolytes on the photovoltaic performance of DSSC." Engineered Science 4, no. 16 (2018): 44-51.

[42] Saito, Yasuteru, Norihiro Fukuri, Rohan Senadeera, Takayuki Kitamura, Yuji Wada, and Shozo Yanagida. "Solid state dye sensitized solar cells using in situ polymerized PEDOTs as hole conductor." Electrochemistry communications 6, no. 1 (2004): 71-74.

[43] Wang, Yanping, Ke Yang, Seong-Cheol Kim, Ramaswamy Nagarajan, Lynne A. Samuelson, and Jayant Kumar. "In situ polymerized carboxylated diacetylene as a hole conductor in solid-state dye-sensitized solar cells." Chemistry of materials 18, no. 18 (2006): 4215-4217.

[44] Sima, Cornelia, Constantin Grigoriu, and Stefan Antohe. "Comparison of the dye-sensitized solar cells performances based on transparent conductive ITO and FTO." Thin Solid Films 519, no. 2 (2010): 595-597.

[45] Kawashima, Takuya, Tetsuya Ezure, Kenichi Okada, Hiroshi Matsui, Kenji Goto, and Nobuo Tanabe. "FTO/ITO double-layered transparent conductive oxide for dye-sensitized solar cells." Journal of Photochemistry and Photobiology A: Chemistry 164, no. 1-3 (2004): 199-202.

[46] Hirahara, N., B. Onwona-Agyeman, and M. Nakao. "Preparation of Al-doped ZnO thin films as transparent conductive substrate in dye-sensitized solar cell." Thin Solid Films 520, no. 6 (2012): 2123-2127.

[47] Pawar, Bhagwat N., Gangeri Cai, Dukho Ham, Rajaram S. Mane, T. Ganesh, Anil Ghule, Ramphal Sharma, K. D. Jadhava, and Sung-Hwan Han. "Preparation of transparent and conducting boron-doped ZnO electrode for its application in dye-sensitized solar cells." Solar Energy Materials and Solar Cells 93, no. 4 (2009): 524-527.

[48] Sarker, Subrata, Hyun Woo Seo, Young-Ku Jin, Md Abdul Aziz, and Dong Min Kim. "Transparent conducting oxides and their performance as substrates for counter electrodes of dye-sensitized solar cells." Materials Science in Semiconductor Processing 93 (2019): 28-35.

[49] Yeon, Changbong, Sun Jin Yun, Jumi Kim, and Jung Wook Lim. "PEDOT: PSS Films with Greatly Enhanced Conductivity via Nitric Acid Treatment at Room Temperature and Their Application as Pt/TCO-Free Counter Electrodes in Dye-Sensitized Solar Cells." Advanced Electronic Materials 1, no. 10 (2015): 1500121.

[50] Anothumakkool, Bihag, Ishita Agrawal, Siddheshwar N. Bhange, Roby Soni, Onkar Game, Satishchandra B. Ogale, and Sreekumar Kurungot. "Pt-and TCO-free flexible cathode for DSSC from highly conducting and flexible PEDOT paper prepared via in situ interfacial polymerization." ACS applied materials & interfaces 8, no. 1 (2016): 553-562.

[51] Weerasinghe, Hasitha C., Fuzhi Huang, and Yi-Bing Cheng. "Fabrication of flexible dye sensitized solar cells on plastic substrates." Nano Energy 2, no. 2 (2013): 174-189.

[52] Yun, Sining, Jilian Nei Freitas, Ana F. Nogueira, Yanmin Wang, Shahzada Ahmad, and Zhong-Sheng Wang. "Dye-sensitized solar cells employing polymers." Progress in Polymer Science 59 (2016): 1-40.

[53] Toivola, Minna, Janne Halme, Kati Miettunen, Kerttu Aitola, and Peter D. Lund. "Nanostructured dye solar cells on flexible substrates." International Journal of Energy Research 33, no. 13 (2009): 1145-1160.

[54] Sang, Lixia, Yixin Zhao, and Clemens Burda. “TiO2 nanoparticles as functional building blocks.” Chemical reviews 114, no. 19 (2014): 9283-9318.

[55] Gupta, Shipra Mital, and Manoj Tripathi. “A review of TiO2 nanoparticles.” chinese science bulletin 56, no. 16 (2011): 1639-1657.

[56] Hegazy, Aiat, Natacha Kinadjian, Bahareh Sadeghimakki, Siva Sivoththaman, Nageh K. Allam, and Eric Prouzet. “TiO2 nanoparticles optimized for photoanodes tested in large area Dye-sensitized solar cells (DSSC).” Solar Energy Materials and Solar Cells 153 (2016): 108-116.

[57] Agrawal, Anupam, Shahbaz A. Siddiqui, Amit Soni, Kanupriya Khandelwal, and Ganesh D. Sharma. “Performance analysis of TiO2 based dye sensitized solar cell prepared by screen printing and doctor blade deposition techniques.” Solar Energy 226 (2021): 9-19.

[58] Baek, In Chan, Muga Vithal, Jeong Ah Chang, Jun-Ho Yum, Md K. Nazeeruddin, Michael Grätzel, Yong-Chae Chung, and Sang Il Seok. “Facile preparation of large aspect ratio ellipsoidal anatase TiO2 nanoparticles and their application to dye-sensitized solar cell.” Electrochemistry Communications 11, no. 4 (2009): 909-912.

[59] Meulenkamp, Eric A. “Synthesis and growth of ZnO nanoparticles.” The Journal of Physical Chemistry B 102, no. 29 (1998): 5566-5572.

[60] Vittal, R., and Kuo-Chuan Ho. “Zinc oxide based dye-sensitized solar cells: A review.” Renewable and Sustainable energy reviews 70 (2017): 920-935.

[61] Lin, Chia-Yu, Yi-Hsuan Lai, Hsin-Wei Chen, Jian-Ging Chen, Chung-Wei Kung, L. R. Vittal, and Kuo-Chuan Ho. “Highly efficient dye-sensitized solar cell with a ZnO nanosheet-based photoanode.” Energy & Environmental Science 4, no. 9 (2011): 3448-3455.

[62] Gubbala, Suresh, Vidhya Chakrapani, Vivekanand Kumar, and Mahendra K. Sunkara. “Band-edge engineered hybrid structures for dye-sensitized solar cells based on SnO2 nanowires.” Advanced Functional Materials 18, no. 16 (2008): 2411-2418.

[63] Li, Zhengdao, Yong Zhou, Ruzhong Sun, Yan Xiong, Haiquan Xie, and Zhigang Zou. “Nanostructured SnO2 photoanode-based dye-sensitized solar cells.” Chinese Science Bulletin 59, no. 18 (2014): 2122-2134.

[64] Basu, Kaustubh, Daniele Benetti, Haiguang Zhao, Lei Jin, Fiorenzo Vetrone, Alberto Vomiero, and Federico Rosei. “Enhanced photovoltaic properties in dye sensitized solar cells by surface treatment of SnO2 photoanodes.” Scientific reports 6, no. 1 (2016): 1-10.

[65] Zheng, Haidong, Yasuhiro Tachibana, and Kourosh Kalantar-Zadeh. “Dye-sensitized solar cells based on WO3.” Langmuir 26, no. 24 (2010): 19148-19152.

[66] Yong, Seok-Min, Tsvetkov Nikolay, Byung Tae Ahn, and Do Kyung Kim. “One-dimensional WO3 nanorods as photoelectrodes for dye-sensitized solar cells.” Journal of Alloys and Compounds 547 (2013): 113-117.

[67] Rashad, M. M., and A. E. Shalan. “Hydrothermal synthesis of hierarchical WO3 nanostructures for dye-sensitized solar cells.” Applied Physics A 116, no. 2 (2014): 781-788.

[68] Biswas, Rajat, and Suman Chatterjee. “Effect of surface modification via sol-gel spin coating of ZnO nanoparticles on the performance of WO3 photoanode based dye sensitized solar cells.” Optik 212 (2020): 164142.

[69] Le Viet, A., R. Jose, M. V. Reddy, B. V. R. Chowdari, and S. Ramakrishna. “Nb2O5 photoelectrodes for dye-sensitized solar cells: choice of the polymorph.” The Journal of Physical Chemistry C 114, no. 49 (2010): 21795-21800.

[70] Nunes, Barbara N., Leandro A. Faustino, Andressa V. Muller, Andre S. Polo, and Antonio Otavio T. Patrocinio. “Nb2O5 dye-sensitized solar cells.” Nanomaterials for solar cell applications (2019): 287-322.

[71] Ghosh, Rudresh, M. Kyle Brennaman, Tim Uher, Myoung-Ryul Ok, Edward T. Samulski, L. E. McNeil, Thomas J. Meyer, and Rene Lopez. “Nanoforest Nb2O5 photoanodes for dye-sensitized solar cells by pulsed laser deposition.” ACS Applied Materials & Interfaces 3, no. 10 (2011): 3929-3935.

[72] Pascual, J., J. Camassel, and H. Mathieu. “Fine structure in the intrinsic absorption edge of ti o 2.” Physical Review B 18, no. 10 (1978): 5606.

[73] Pfeifer, Verena, Paul Erhart, Shunyi Li, Karsten Rachut, Jan Morasch, Joachim Brötz, Philip Reckers et al. "Energy band alignment between anatase and rutile TiO2." The Journal of Physical Chemistry Letters 4, no. 23 (2013): 4182-4187.

[74] Tang, H., H. Berger, P. E. Schmid, F. Levy, and G. Burri. “Photoluminescence in TiO2 anatase single crystals.” Solid State Communications 87, no. 9 (1993): 847-850.

[75] Pfeifer, Verena, Paul Erhart, Shunyi Li, Karsten Rachut, Jan Morasch, Joachim Brötz, Philip Reckers et al. "Energy band alignment between anatase and rutile TiO2." The Journal of Physical Chemistry Letters 4, no. 23 (2013): 4182-4187.

[76] Kakiage, Kenji, Yohei Aoyama, Toru Yano, Keiji Oya, Jun-ichi Fujisawa, and Minoru Hanaya. “Highly-efficient dye-sensitized solar cells with collaborative sensitization by silyl-anchor and carboxyanchor dyes." Chemical communications 51, no. 88 (2015): 15894-15897.

[77] Han, Jingbin, Fengru Fan, Chen Xu, Shisheng Lin, Min Wei, Xue Duan, and Zhong Lin Wang. "ZnO nanotube-based dye-sensitized solar cell and its application in self-powered devices." Nanotechnology 21, no. 40 (2010): 405203.

[78] Maheswari, D., and P. Venkatachalam. "Enhancing the performance of dye-sensitized solar cells based on organic dye sensitized TiO2 nanoparticles/nanowires composite photoanodes with ionic liquid electrolyte." Measurement 60 (2015): 146-154.

[79] Nayeri, Fatemeh Dehghan, Mohammadreza Kolahdouz, Ebrahim Asl-Soleimani, and S. Mohajerzadeh. "Low temperature carving of ZnO nanorods into nanotubes for dye-sensitized solar cell application." Journal of Alloys and Compounds 633 (2015): 359-365.

[80] Liu, Bin, and Eray S. Aydil. "Growth of oriented single-crystalline rutile TiO2 nanorods on transparent conducting substrates for dye-sensitized solar cells." Journal of the American Chemical Society 131, no. 11 (2009): 3985-3990.

[81] Boercker, J. E., E. Enache-Pommer, and E. S. Aydil. "Growth mechanism of titanium dioxide nanowires for dye-sensitized solar cells." Nanotechnology 19, no. 9 (2008): 095604.

[82] Kandasamy, M., M. Selvaraj, C. Kumarappan, and S. Murugesan. "Plasmonic Ag nanoparticles anchored ethylenediamine modified TiO2 nanowires@ graphene oxide composites for dye-sensitized solar cell." Journal of Alloys and Compounds 902 (2022): 163743.

[83] Ko, Seung Hwan, Daeho Lee, Hyun Wook Kang, Koo Hyun Nam, Joon Yeob Yeo, Suk Joon Hong, Costas P. Grigoropoulos, and Hyung Jin Sung. "Nanoforest of hydrothermally grown hierarchical ZnO nanowires for a high efficiency dye-sensitized solar cell." Nano letters 11, no. 2 (2011): 666-671.

[84] Gupta, Ram K., K. Ghosh, R. Patel, S. R. Mishra, and Pawan K. Kahol. "Band gap engineering of ZnO thin films by In2O3 incorporation." Journal of crystal growth 310, no. 12 (2008): 3019-3023.

[85] Tan, Swee Tiam, B. J. Chen, X. W. Sun, W. J. Fan, Hoi Sing Kwok, X. H. Zhang, and S. J. Chua. "Blueshift of optical band gap in ZnO thin films grown by metal-organic chemical-vapor deposition." Journal of Applied Physics 98, no. 1 (2005): 013505.

[86] Özgür, Ümit, Ya I. Alivov, Chunli Liu, Ali Teke, MAn Reshchikov, S. Doğan, V. C. S. J. Avrutin, S-J. Cho, and and H. Morkoç. "A comprehensive review of ZnO materials and devices." Journal of applied physics 98, no. 4 (2005): 11.

[87] Bae, H. S., M. H. Yoon, J. H. Kim, and Seongil Im. "Photodetecting properties of ZnO-based thin-film transistors." Applied Physics Letters 83, no. 25 (2003): 5313-5315.

[88] Zhang, Qifeng, Christopher S. Dandeneau, Xiaoyuan Zhou, and Guozhong Cao. "ZnO nanostructures for dye-sensitized solar cells." Advanced materials 21, no. 41 (2009): 4087-4108.

[89] He, Yitao, Jing Hu, and Yahong Xie. "High-efficiency dye-sensitized solar cells of up to 8.03% by air plasma treatment of ZnO nanostructures." Chemical Communications 51, no. 90 (2015): 16229-16232.

[90] Xie, Yahong, Xiaofeng Zhou, Hongyu Mi, Junhong Ma, Jianya Yang, and Jian Cheng. "High efficiency ZnO-based dye-sensitized solar cells with a 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane chain barrier for cutting on interfacial recombination." Applied Surface Science 434 (2018): 1144-1152.

[91] Mishra, Amaresh, Markus KR Fischer, and Peter Bäuerle. “Metal-free organic dyes for dye-sensitized solar cells: From structure: Property relationships to design rules.” Angewandte Chemie International Edition 48, no. 14 (2009): 2474-2499.

[92] Albero, Josep, Pedro Atienzar, Avelino Corma, and Hermenegildo Garcia. “Efficiency Records in Mesoscopic Dye-Sensitized Solar Cells.” The Chemical Record 15, no. 4 (2015): 803-828.

[93] Ito, Seigo. “Investigation of dyes for dye-sensitized solar cells: Ruthenium-complex dyes, metal-free dyes, metal-complex porphyrin dyes and natural dyes.” Solar Cells-Dye-Sensitized Devices (2011): 19-48.

[94] Shalini, Status, R. Balasundaraprabhu, T. Satish Kumar, N. Prabavathy, S. Senthilarasu, and S. Prasanna. “Status and outlook of sensitizers/dyes used in dye sensitized solar cells (DSSC): a review.” International journal of energy research 40, no. 10 (2016): 1303-1320.

[95] Higashino, Tomohiro, and Hiroshi Imahori. “Porphyrins as excellent dyes for dye-sensitized solar cells: recent developments and insights.” Dalton transactions 44, no. 2 (2015): 448-463.

[96] Hagfeldt, Anders, Gerrit Boschloo, Licheng Sun, Lars Kloo, and Henrik Pettersson. "Dye-sensitized solar cells." Chemical reviews 110, no. 11 (2010): 6595-6663.

[97] Ito, Seigo. “Investigation of dyes for dye-sensitized solar cells: Ruthenium-complex dyes, metal-free dyes, metal-complex porphyrin dyes and natural dyes.” Solar Cells-Dye-Sensitized Devices (2011): 19-48.

[98] Hara, Kohjiro, Zhong-Sheng Wang, Tadatake Sato, Akihiro Furube, Ryuzi Katoh, Hideki Sugihara, Yasufumi Dan-Oh, Chiaki Kasada, Akira Shinpo, and Sadaharu Suga. “Oligothiophene-containing coumarin dyes for efficient dye-sensitized solar cells.” The Journal of Physical Chemistry B 109, no. 32 (2005): 15476-15482.

[99] Hara, Kohjiro, Zhong-Sheng Wang, Tadatake Sato, Akihiro Furube, Ryuzi Katoh, Hideki Sugihara, Yasufumi Dan-Oh, Chiaki Kasada, Akira Shinpo, and Sadaharu Suga. “Oligothiophene-containing coumarin dyes for efficient dye-sensitized solar cells.” The Journal of Physical Chemistry B 109, no. 32 (2005): 15476-15482.

[100] Horiuchi, Tamotsu, Hidetoshi Miura, Kouichi Sumioka, and Satoshi Uchida. “High efficiency of dye-sensitized solar cells based on metal-free indoline dyes.” Journal of the American Chemical Society 126, no. 39 (2004): 12218-12219.

[101] Delaey, Els, Frederik van Laar, Dirk De Vos, A. Kamuhabwa, Pierre Jacobs, and Peter de Witte. “A comparative study of the photosensitizing characteristics of some cyanine dyes.” Journal of Photochemistry and Photobiology B: Biology 55, no. 1 (2000): 27-36.

[102] Benson, Richard C., and Henry A. Kues. “Absorption and fluorescence properties of cyanine dyes.” Journal of Chemical and Engineering Data 22, no. 4 (1977): 379-383.

[103] Ma, Xuemei, Jianli Hua, Wenjun Wu, Yinghua Jin, Fanshun Meng, Wenhai Zhan, and He Tian. “A high-efficiency cyanine dye for dye-sensitized solar cells.” Tetrahedron 64, no. 2 (2008): 345-350.

[104] Shalini, S., S. Prasanna, Tapas K. Mallick, and S. Senthilarasu. “Review on natural dye sensitized solar cells: Operation, materials and methods.” Renewable and Sustainable Energy Reviews 51 (2015): 1306-1325.

[105] Richhariya, Geetam, Anil Kumar, Perapong Tekasakul, and Bhupendra Gupta. “Natural dyes for dye sensitized solar cell: A review.” Renewable and Sustainable Energy Reviews 69 (2017): 705-718.

[106] Shalini, S., S. Prasanna, Tapas K. Mallick, and S. Senthilarasu. "Review on natural dye sensitized solar cells: Operation, materials and methods." Renewable and Sustainable Energy Reviews 51 (2015): 1306-1325.

[107] Narayan, Monishka Rita. "Dye sensitized solar cells based on natural photosensitizers." Renewable and sustainable energy reviews 16, no. 1 (2012): 208-215.

[108] Kumara, N. T. R. N., Andery Lim, Chee Ming Lim, Mohamad Iskandar Petra, and Piyasiri Ekanayake. "Recent progress and utilization of natural pigments in dye sensitized solar cells: A review." Renewable and Sustainable Energy Reviews 78 (2017): 301-317.

[109] Wang, Xiao-Feng, Junfeng Xiang, Peng Wang, Yasushi Koyama, Shozo Yanagida, Yuji Wada, Kazunori Hamada, Shin-ichi Sasaki, and Hitoshi Tamiaki. "Dye-sensitized solar cells using a chlorophyll a derivative as the sensitizer and carotenoids having different conjugation lengths as redox spacers." Chemical physics letters 408, no. 4-6 (2005): 409-414.

[110] Green, Beverley, William W. Parson, and William W. Parson, eds. Light-harvesting antennas in photosynthesis. Vol. 13. Springer Science & Business Media, 2003.

[111] Lee, David. "Plant pigments and their manipulation. Annual Plant Reviews Vol 12. Davies KM, ed. 2004. Oxford/Boca Raton: Blackwell Publishing/CRC Press, Boca Raton.£ 110 (hardback). 352 pp." (2005): 1332-1333.

[112] Wang, Xiao-Feng, Junfeng Xiang, Peng Wang, Yasushi Koyama, Shozo Yanagida, Yuji Wada, Kazunori Hamada, Shin-ichi Sasaki, and Hitoshi Tamiaki. "Dye-sensitized solar cells using a chlorophyll a derivative as the sensitizer and carotenoids having different conjugation lengths as redox spacers.” Chemical physics letters 408, no. 4-6 (2005): 409-414.

[113] Harborne, Jeffrey B. “The flavonoids: advances in research since 1980.” (2013).

[114] Golden, J. H., R. P. Linstead, and G. H. Whitham. “355. Chlorophyll and related compounds. Part VII. The structure of bacteriochlorophyll.” Journal of the Chemical Society (Resumed) (1958): 1725-1732.

[115] Geissman, T. A., and Elly Hinreiner. “Theories of the biogenesis of flavonoid compounds (Part II).” The Botanical Review 18, no. 3 (1952): 165-244.

[116] Goodwin, Trevor Walworth. “Chemistry and biochemistry of plant pigments.” Chemistry and biochemistry of plant pigments. (1965).

[117] Caula S. A, Villar S. I., Martino V. S., Coussio 1. D., Ferraro G. E. (1991) Polyphenols isolated from Eupatorium buniifolium. Rev. Latinoamer. Quim. 22: 1-3.

[118] Butt, V. S. "Chemistry and biochemistry of plant pigments: Edited by TW Goodwin Academic Press; London, 1976 Volume 1: xvi+ 870 pages.£ 26.50, $65.75 Volume 2: xiii+ 373 pages.£ 12.00, $29.75." (1977): 155.

[119] Steyn, W. J卌 , S. J. E. Wand, D. M. Holcroft, and G. J. N. P. Jacobs. “Anthocyanins in vegetative tissues: a proposed unified function in photoprotection.” New Phytologist 155, no. 3 (2002): 349-361.

[120] Yamazaki, Eiji, Masaki Murayama, Naomi Nishikawa, Noritsugu Hashimoto, Masashi Shoyama, and Osamu Kurita. “Utilization of natural carotenoids as photosensitizers for dye-sensitized solar cells.” Solar energy 81, no. 4 (2007): 512-516.

[121] Hug, Hubert, Michael Bader, Peter Mair, and Thilo Glatzel. “Biophotovoltaics: natural pigments in dye-sensitized solar cells.” Applied Energy 115 (2014): 216-225.

[122] Hussain, Syed Arshad. “Development of dye sensitized solar cells using Botuje green leaves (Jathopha Curcas Linn).” Science Journal of Physics 2013 (2013).

[123] Hao, Sancun, Jihuai Wu, Yunfang Huang, and Jianming Lin. “Natural dyes as photosensitizers for dye-sensitized solar cell.” Solar energy 80, no. 2 (2006): 209-214.

[124] Kumara, G. R. A., S. Kaneko, M. Okuya, B. Onwona-Agyeman, A. Konno, and K. Tennakone. “Shiso leaf pigments for dye-sensitized solid-state solar cell.” Solar Energy Materials and Solar Cells 90, no. 9 (2006): 1220-1226.

[125] Hernández-Martínez, A. R., S. Vargas, M. Estevez, and R. Rodríguez. "Dye-sensitized solar cells from extracted bracts bougainvillea betalain pigments." In 1st International Congress on Instrumentation and Applied Sciences, vol. 1, p. 15. 2010.

[126] Chang, Ho, H. M. Wu, T. L. Chen, K. D. Huang, C. S. Jwo, and Y. J. Lo. “Dye-sensitized solar cell using natural dyes extracted from spinach and ipomoea.” Journal of Alloys and Compounds 495, no. 2 (2010): 606-610.

[127] Hao, Sancun, Jihuai Wu, Yunfang Huang, and Jianming Lin. “Natural dyes as photosensitizers for dye-sensitized solar cell.” Solar energy 80, no. 2 (2006): 209-214.

[128] Dai, Qing, and Joseph Rabani. “Photosensitization of nanocrystalline TiO2 films by anthocyanin dyes.” Journal of Photochemistry and Photobiology A: Chemistry 148, no. 1-3 (2002): 17-24.

[129] Dai, Qing, and Joseph Rabani. “Photosensitization of nanocrystalline TiO2 films by pomegranate pigments with unusually high efficiency in aqueous medium.” Chemical Communications 20 (2001): 2142-2143.

[130] Zhou, Huizhi, Liqiong Wu, Yurong Gao, and Tingli Ma. “Dye-sensitized solar cells using 20 natural dyes as sensitizers.” Journal of Photochemistry and Photobiology A: Chemistry 219, no. 2-3 (2011): 188-194.

[131] Wongcharee, Khwanchit, Vissanu Meeyoo, and Sumaeth Chavadej. “Dye-sensitized solar cell using natural dyes extracted from rosella and blue pea flowers.” Solar Energy Materials and Solar Cells 91, no. 7 (2007): 566-571.

[132] Yamazaki, Eiji, Masaki Murayama, Naomi Nishikawa, Noritsugu Hashimoto, Masashi Shoyama, and Osamu Kurita. “Utilization of natural carotenoids as photosensitizers for dye-sensitized solar cells.” Solar energy 81, no. 4 (2007): 512-516.

[133] Hao, Sancun, Jihuai Wu, Yunfang Huang, and Jianming Lin. “Natural dyes as photosensitizers for dye-sensitized solar cell.” Solar energy 80, no. 2 (2006): 209-214.

[134] Supriyanto, A., F. Nurosyid, and A. H. Ahliha. “Carotenoid pigment as sensitizers for applications of dye-sensitized solar cell (DSSC).” In IOP Conference Series: Materials Science and Engineering, vol. 432, no. 1, p. 012060. IOP Publishing, 2018.

[135] Ludin, Norasikin A., AM Al-Alwani Mahmoud, Abu Bakar Mohamad, Abd Amir H. Kadhum, Kamaruzzaman Sopian, and Nor Shazlinah Abdul Karim. “Review on the development of natural dye photosensitizer for dye-sensitized solar cells.” Renewable and Sustainable Energy Reviews 31 (2014): 386-396.

[136] Sabagh, Samira, Mohammad Izadyar, and Foroogh Arkan. “Photovoltaic properties of the flavonoid-based photosensitizers: Molecular-scale perspective on the natural dye solar cells.” International Journal of Quantum Chemistry 120, no. 10 (2020): e26171.

[137] Omar, Azimah, Mohd Syukri Ali, and Nasrudin Abd Rahim. “Electron transport properties analysis of titanium dioxide dye-sensitized solar cells (TiO2-DSSCs) based natural dyes using electrochemical impedance spectroscopy concept: A review.” Solar Energy 207 (2020): 1088-1121.

[138] Ghann, William, Hyeonggon Kang, Tajbik Sheikh, Sunil Yadav, Tulio Chavez-Gil, Fred Nesbitt, and Jamal Uddin. “Fabrication, optimization and characterization of natural dye sensitized solar cell.” Scientific reports 7, no. 1 (2017): 1-12.

[139] Hug, Hubert, Michael Bader, Peter Mair, and Thilo Glatzel. “Biophotovoltaics: natural pigments in dye-sensitized solar cells.” Applied Energy 115 (2014): 216-225.

[140] Shalini, S., S. Prasanna, Tapas K. Mallick, and S. Senthilarasu. “Review on natural dye sensitized solar cells: Operation, materials and methods.” Renewable and Sustainable Energy Reviews 51 (2015): 1306-1325.

[141] Baby, Ruby, Peter Daniel Nixon, Nallapaneni Manoj Kumar, M. S. P. Subathra, and Nallamuthu Ananthi. “A comprehensive review of dye-sensitized solar cell optimal fabrication conditions, natural dye selection, and application-based future perspectives.” Environmental Science and Pollution Research (2021): 1-34.

[142] Kabir, Fahmid, Syed Nazmus Sakib, Sheikh Shehab Uddin, Erteza Tawsif Efaz, and Md Tahmid Farhan Himel. “Enhance cell performance of DSSC by dye mixture, carbon nanotube and post TiCl4 treatment along with degradation study." Sustainable Energy Technologies and Assessments 35 (2019): 298-307.

[143] Kabir, F., M. M. H. Bhuiyan, M. S. Manir, M. S. Rahaman, M. A. Khan, and T. Ikegami. "Development of dye-sensitized solar cell based on combination of natural dyes extracted from Malabar spinach and red spinach." Results in Physics 14 (2019): 102474.

[144] Kabir, Fahmid, Md Mosharraf H. Bhuiyan, Md Robiul Hossain, Humayra Bashar, Md Saifur Rahaman, Md Serajum Manir, Ruhul A. Khan, and Tomoaki Ikegami. "Effect of combination of natural dyes and post-TiCl4 treatment in improving the photovoltaic performance of dye-sensitized solar cells." Comptes Rendus Chimie 22, no. 9-10 (2019): 659-666.

[145] Pratiwi, D. D., F. Nurosyid, A. Supriyanto, and R. Suryana. "Performance improvement of dye-sensitized solar cells (DSSC) by using dyes mixture from chlorophyll and anthocyanin." In Journal of Physics: Conference Series, vol. 909, no. 1, p. 012025. IOP Publishing, 2017.

[146] Bashar, H., M. M. H. Bhuiyan, M. R. Hossain, F. Kabir, M. S. Rahaman, M. S. Manir, and T. Ikegami. "Study on combination of natural red and green dyes to improve the power conversion efficiency of dye sensitized solar cells." Optik 185 (2019): 620-625.

[147] Kabir, F., M. M. H. Bhuiyan, M. R. Hossain, H. Bashar, M. S. Rahaman, M. S. Manir, S. M. Ullah et al. "Improvement of efficiency of dye sensitized solar cells by optimizing the combination ratio of natural red and yellow dyes." Optik 179 (2019): 252-258.

[148] Ferrere, Suzanne, Arie Zaban, and Brian A. Gregg. "Dye sensitization of nanocrystalline tin oxide by perylene derivatives." The Journal of Physical Chemistry B 101, no. 23 (1997): 4490-4493.

[149] Oskam, Gerko, Bryan V. Bergeron, Gerald J. Meyer, and Peter C. Searson. "Pseudohalogens for dye-sensitized TiO2 photoelectrochemical cells." The Journal of Physical Chemistry B 105, no. 29 (2001): 6867-6873.

[150] Wang, Peng, Shaik M. Zakeeruddin, Jacques-E. Moser, Robin Humphry-Baker, and Michael Grätzel. "A solvent-free, SeCN-/(SeCN) 3-based ionic liquid electrolyte for high-efficiency dye-sensitized nanocrystalline solar cells." Journal of the American Chemical Society 126, no. 23 (2004): 7164-7165.

[151] Hagfeldt, Anders, Gerrit Boschloo, Licheng Sun, Lars Kloo, and Henrik Pettersson. "Dye-sensitized solar cells." Chemical reviews 110, no. 11 (2010): 6595-6663.

[152] Sapp, Shawn A., C. Michael Elliott, Cristiano Contado, Stefano Caramori, and Carlo A. Bignozzi. "Substituted polypyridine complexes of cobalt (II/III) as efficient electron-transfer mediators in dye-sensitized solar cells." Journal of the American Chemical Society 124, no. 37 (2002): 11215-11222.

[153] Hattori, Shigeki, Yuji Wada, Shozo Yanagida, and Shunichi Fukuzumi. "Blue copper model complexes with distorted tetragonal geometry acting as effective electron-transfer mediators in dye-sensitized solar cells." Journal of the American Chemical Society 127, no. 26 (2005): 9648-9654.

[154] Choi, Hyunbong, Chul Baik, Sang Ook Kang, Jaejung Ko, Moon-Sung Kang, Md K. Nazeeruddin, and Michael Grätzel. "Highly efficient and thermally stable organic sensitizers for solvent-free dye-sensitized solar cells." Angewandte Chemie International Edition 47, no. 2 (2008): 327-330.

[155] Kopidakis, Nikos, Nathan R. Neale, and Arthur J. Frank. "Effect of an adsorbent on recombination and band-edge movement in dye-sensitized TiO2 solar cells: evidence for surface passivation." The journal of physical chemistry B 110, no. 25 (2006): 12485-12489.

[156] Figgemeier, Egbert, and Anders Hagfeldt. "Are dye-sensitized nanostructured solar cells stable? An overview of device testing and component analyses." International journal of photoenergy 6, no. 3 (2004): 127-140.

[157] Hao, Sancun, Jihuai Wu, Leqing Fan, Yunfang Huang, Jianming Lin, and Yelin Wei. "The influence of acid treatment of TiO2 porous film electrode on photoelectric performance of dye-sensitized solar cell." Solar energy 76, no. 6 (2004): 745-750.

[158] Zhang, Changneng, Yang Huang, Zhipeng Huo, Shuanghong Chen, and Songyuan Dai. "Photoelectrochemical effects of guanidinium thiocyanate on dye-sensitized solar cell performance and stability." The Journal of Physical Chemistry C 113, no. 52 (2009): 21779-21783.

[159] Kelly, Craig A., Fereshteh Farzad, David W. Thompson, Jeremy M. Stipkala, and Gerald J. Meyer. "Cation-controlled interfacial charge injection in sensitized nanocrystalline TiO2." Langmuir 15, no. 20 (1999): 7047-7054.

[160] Zakeeruddin, Shaik M., and Michael Grätzel. "Solvent-free ionic liquid electrolytes for mesoscopic dye-sensitized solar cells." Advanced Functional Materials 19, no. 14 (2009): 2187-2202.

[161] Wang, Peng, Shaik M. Zakeeruddin, Jacques-E. Moser, Robin Humphry-Baker, and Michael Grätzel. "A solvent-free, SeCN-/(SeCN) 3-based ionic liquid electrolyte for high-efficiency dye-sensitized nanocrystalline solar cells." Journal of the American Chemical Society 126, no. 23 (2004): 7164-7165.

[162] Gunasekaran, Ahalya, Andrea Sorrentino, Abdullah M. Asiri, and Sambandam Anandan. "Guar gum-based polymer gel electrolyte for dye-sensitized solar cell applications." Solar Energy 208 (2020): 160-165.

[163] Saidi, Norshahirah M., Fatin Saiha Omar, Arshid Numan, David C. Apperley, Mohammed M. Algaradah, Ramesh Kasi, Alyssa-Jennifer Avestro, and Ramesh T. Subramaniam. "Enhancing the efficiency of a dye-sensitized solar cell based on a metal oxide nanocomposite gel polymer electrolyte." ACS applied materials & interfaces 11, no. 33 (2019): 30185-30196.

[164] Su'ait, Mohd Sukor, Mohd Yusri Abd Rahman, and Azizan Ahmad. "Review on polymer electrolyte in dye-sensitized solar cells (DSSCs)." Solar Energy 115 (2015): 452-470.

[165] Ravirajan, Punniamoorthy, Ana M. Peiró, Mohammad K. Nazeeruddin, Michael Graetzel, Donal DC Bradley, James R. Durrant, and Jenny Nelson. "Hybrid polymer/zinc oxide photovoltaic devices with vertically oriented ZnO nanorods and an amphiphilic molecular interface layer." The Journal of Physical Chemistry B 110, no. 15 (2006): 7635-7639.

[166] Murakoshi, Kei, Ryuichiro Kogure, Yuji Wada, and Shozo Yanagida. "Solid state dye-sensitized TiO2 solar cell with polypyrrole as hole transport layer." Chemistry letters 26, no. 5 (1997): 471-472.

[167] Saito, Yasuteru, Takayuki Kitamura, Yuji Wada, and Shozo Yanagida. "Poly (3, 4-ethylenedioxythiophene) as a hole conductor in solid state dye sensitized solar cells." Synthetic Metals 131, no. 1-3 (2002): 185-187.

[168] Somani, Prakash R., and S. Radhakrishnan. “Solid state electrochemical reaction in photocells made using conducting polyaniline and sensitized with methylene blue.” Journal of Solid State Electrochemistry 7, no. 3 (2003): 166-170.

[169] Cai, Ning, Soo-Jin Moon, Lê Cevey-Ha, Thomas Moehl, Robin Humphry-Baker, Peng Wang, Shaik M. Zakeeruddin, and Michael Grätzel. “An organic D-π-A dye for record efficiency solid-state sensitized heterojunction solar cells.” Nano letters 11, no. 4 (2011): 1452-1456.

[170] Chung, In, Byunghong Lee, Jiaqing He, Robert PH Chang, and Mercouri G. Kanatzidis. “All-solid-state dye-sensitized solar cells with high efficiency.” Nature 485, no. 7399 (2012): 486-489.

[171] Siqian, L. I., Jie HUANG, X. I. E. Jian, Jun ZHANG, Y. E. Cong, and W. A. N. G. Hao. “High Efficient Pt Counter Electrode Prepared by One-step Thermal Decomposition for Dye-sensitized Solar Cell.” Chinese Journal of Materials Research 29, no. 9 (2015): 656-662.

[172] Chang, H. C., H. H. Huang, C. Y. Wu, R. Q. Hsu, and C. Y. Hsu. “The photocatalytic activity and compact layer characteristics of TiO2 films prepared using radio frequency magnetron sputtering.” International Journal of Photoenergy 2014 (2014).

[173] Popoola, Idris K., Mohammed A. Gondal, Jwaher M. AlGhamdi, and Talal F. Qahtan. “Photofabrication of highly transparent platinum counter electrodes at ambient temperature for bifacial dye sensitized solar cells.” Scientific reports 8, no. 1 (2018): 1-12.

[174] Murakami, Takurou N., Seigo Ito, Qing Wang, Md Khaja Nazeeruddin, Takeru Bessho, Ilkay Cesar, Paul Liska et al. “Highly efficient dye-sensitized solar cells based on carbon black counter electrodes." Journal of the Electrochemical Society 153, no. 12 (2006): A2255.

[175] Veerappan, Ganapathy, Karunagaran Bojan, and Shi-Woo Rhee. "Sub-micrometer-sized graphite as a conducting and catalytic counter electrode for dye-sensitized solar cells." ACS applied materials & interfaces 3, no. 3 (2011): 857-862.

[176] Li, Yu-Yan, Chun-Ting Li, Min-Hsin Yeh, Kuan-Chieh Huang, Ping-Wei Chen, R. Vittal, and Kuo-Chuan Ho. "Graphite with different structures as catalysts for counter electrodes in dye-sensitized solar cells." Electrochimica Acta 179 (2015): 211-219.

[177] Imoto, Kiyoaki, Kohshin Takahashi, Takahiro Yamaguchi, Teruhisa Komura, Jun-ichi Nakamura, and Kazuhiko Murata. "High-performance carbon counter electrode for dye-sensitized solar cells." Solar Energy Materials and Solar Cells 79, no. 4 (2003): 459-469.

[178] Wei, Wei, Hui Wang, and Yun Hang Hu. "A review on PEDOT-based counter electrodes for dye-sensitized solar cells." International Journal of Energy Research 38, no. 9 (2014): 1099-1111.

[179] Wu, Jihuai, Zhang Lan, Jianming Lin, Miaoliang Huang, Yunfang Huang, Leqing Fan, Genggeng Luo, Yu Lin, Yimin Xie, and Yuelin Wei. "Counter electrodes in dye-sensitized solar cells." Chemical Society Reviews 46, no. 19 (2017): 5975-6023.

[180] Gregg, Brian A., Francois Pichot, Suzanne Ferrere, and Clark L. Fields. "Interfacial recombination processes in dye-sensitized solar cells and methods to passivate the interfaces." The Journal of Physical Chemistry B 105, no. 7 (2001): 1422-1429.

[181] Gregg, Brian A. "Interfacial processes in the dye-sensitized solar cell." Coordination Chemistry Reviews 248, no. 13-14 (2004): 1215-1224.

[182] Sharma, Khushboo, Vinay Sharma, and S. S. Sharma. “Dye-sensitized solar cells: fundamentals and current status.” Nanoscale research letters 13, no. 1 (2018): 1-46.

[183] Nazeeruddin, Md K., Etienne Baranoff, and Michael Grätzel. "Dye-sensitized solar cells: A brief overview." Solar energy 85, no. 6 (2011): 1172-1178.

[184] Baviskar, Prashant K., and Babasaheb R. Sankapal. “Dye-sensitized solar cells.” In Energy Materials, pp. 179-211. Elsevier, 2021.