CHAPTER – I

INTRODUCTION
1.1 Importance of energy

Energy is the fundamental need for maintaining every aspect of life in this universe. It is needed at all steps of our life for maintaining ourselves as well as for our comfort.

*Energy is explained as the ability/capacity to perform the task or work.*

Cars, planes, trolleys, boats and machinery also transform energy into work. Work means moving or lifting something, warming or lighting something. There are many sources of energy that help to run the various machines invented by human being. The discovery of fire by man led to the possibility of burning wood for cooking and heating thereby using energy. For several thousand years human energy demands were met only by renewable energy sources sun, biomass (wood, leaves, and twigs), hydel (water) and wind power. As early as 4000–3500 BC, the first sailing ships and windmills were developed harnessing wind energy. With the use of hydropower through water mills or irrigation systems, things began to move faster. With the advent of the Industrial revolution, the use of energy in the form of fossil fuels began growing as more and more industries were planted. This occurred in stages, from the exploitation of coal deposits to the exploitation of oil and natural gas fields. It has been only half a century since nuclear power began being used as an energy source. In the past century, it became apparent that the expenditure of non-renewable sources of energy had caused more environmental damage than any other human activity. Electricity generated from fossil fuels such as coal and crude oil has led to high concentrations of harmful gases in the atmosphere. This has in turn led to problems such as ozone depletion and global warming. There has been a massive increase in the demand for energy since the middle of the last century due to industrial development and population growth. Total commercial energy consumption has been growing tremendously since last two decade. The demand of energy consumption in low-income countries has increased more than double (per capita commercial energy). The limited supply of today’s main energy sources (oil, coal, uranium) will force us sooner or later to replace most of the currently used power plants with renewable energy sources. According to recent predictions, the inevitable permanent decline in the global oil production rate is expected to start within the next 10-20 years [1]. Worldwide, oil demand rising considerably high, force to introduction of various renewable energy sources such as
solar cells, hydroelectric and wind power systems. However, the combustion of fossil fuels in the past has already harmful effects on the delicate balance of nature on our planet in the sense of global warming due to enormous amount of CO_2 emission.

The huge amount of CO_2 release is not absorbed by environment (i.e. Plant kingdom). According to the International Energy Administration (IEA), the climate goal of limiting warming to 2°C is becoming more difficult and more costly with each year that passes [2]. According to the reports, almost four-fifths of the CO_2 emissions allowable by 2035 are already locked in by the existing power plants, factories, buildings, etc. If action to reduce CO_2 emissions is not taken before 2017, all the allowable CO_2 emissions would be locked in by energy infrastructure existing at that time [3]. Due to the problems associated with the use of fossil fuels, alternative sources of energy have become important and relevant in today's world. The energy sources i.e. hydel, wind and the sun can never be exhausted so known as renewable energy sources. These are also known as non-conventional sources of energy; they cause less emission and are available locally. Their use can significantly reduce chemical, radioactive and thermal pollution. Most of the renewable sources of energy are fairly non-polluting, limitless and considered clean. In light of these concerns, solar energy can easily be considered the most attractive renewable source of energy as it is abundant, clean and safe and allows for energy generation in remote areas. Solar radiation is unevenly distributed around the globe; however, it varies in intensity from geographic location to another depending upon the latitude, season and time of day. Some of this massive amount of radiation is reflected back into space as it passes through the atmosphere, absorbed by clouds and the air mass, driving the dynamics of the atmosphere. Even when these three radiation losses are accounted for the amount of solar radiation that actually reaches the surface of the earth amounts to no less than 120,000 TW (tera watt), while the total demand of energy consumption of world is 15TW in a year.

Energy is the driving force of the nature. The biggest challenge that humanity would face over the next 50-100 years is Energy. In 2006, the world primary energy consumption was estimated to be about 14 TW yr and by 2030, the Figure is estimated to touch 20 TW yr. Figure 1.1 shows the World energy consumption reported by EIA (Energy Information Administration). According to the report of the International Energy Outlook 2013 (IEO2013), the world energy consumption is expected to show 56% growth between 2010 and 2040. This growth would be marked by a rise from 524 to 630 quadrillion Btu (British Thermal Unit) between 2010 and 2020, and from 630 to 820 quadrillion Btu, between 2020
and 2040 [www.eia.gov/ieo]. Environmental concern is coupled with growing demand for energy. Over 80% of current usage comes from carbon sources such as oil, coal and natural gas as comparison of which is given in Figure 1.2. The heat content and CO₂ release of these sources are shown in Figure 1.3. These carbon sources produce CO₂, a greenhouse gas with a long atmospheric residence time, the increased concentration of which is known to be closely linked to global warming. The consequence of global warming is likely to worsen with the increasing world’s population influencing the climate zones and disturbing the ecological systems.

1.2 Why solar energy?

The electricity is produced from the fossil fuels (natural gas, oil and coal). The conventional resources of energy faces challenges of increasing price, increasing pollution, climate change risk, etc. As a result, there is an increasing support from government, businesses and consumers in the research of other energy resources and new techniques for power production. Renewable power resources, which include solar, wind, hydroelectric, geothermal and bio-mass have emerged as potential alternatives as these energy sources are unlimited in availability. Among these renewable energy sources, solar energy is abundantly available at no cost. It is pollution free, maintenance free, saves natural resources and available everywhere. The earth receives only 2% of total radiation emitted by the Sun which is 1527 KW hr, 10,000 times more than our yearly requirement. Currently, the energy requirement worldwide is 15 Terawatts (TW) and it is expected to increase by another 10 TW in next 40 years. The amount of sunlight reaching the earth's surface is 120,000 TW. In other words, 20 minute of sunlight is sufficient to meet the energy requirement of whole world for one year. Among the viable sources: carbon/fuel based sources, nuclear power and renewable sources, the main criticism on carbon based energies is its impact on environment and on the

![Figure 1.1 World’s Energy consumption](image1)

![Figure 1.2 Energy consumption sources](image2)
Figure 1.3 Heat content and amount of CO$_2$ release 
(Series 1: Heat content/Glt$^{-1}$, Series 2: CO$_2$ release/KgGlt$^{-1}$)

nuclear fronts, power needs would require hundreds of gigawatt-level nuclear power stations to be built, which would entail disposal of hazardous nuclear fuel wastes. Thus, the choice of renewable energy based on sun as the source, is very attractive and promising [4].

1.3 Solar energy and Solar cells

A.E. Becquerel (1830s) explained the solar energy generation under enlightenment with platinum or silver chloride electrode with an electrolyte [5]. The first p-n junction cell was designed by Russel Ohl in 1941 [6]. In 1954 the first silicon solar cell was constructed by Chaplin et al., [7] with an initial efficiency of 6.0 which rapidly increased to 10.0. Public attention on alternate energy sources grew in 1970s as oil prices grew as a result of war.

Figure 1.4 Solar radiations available in earth’s atmosphere
Among the renewable energy sources, solar power became much more competent due to the apprehensions attached with global warming, pollution and largely due to IPCC (Intergovernmental Panel on Climate Change) report. Only 0.05% of the world’s energy production is from solar energy [8]. Solar energy is inexpensive as compared to coal and fossil fuels. Solar cells can be made efficient by making use of the solar spectrum which has the highest photon density between wavelength range 400 to 1100 nm. The sun is considered as a black body which behaves as a perfect emitter of radiation at a temperature close to 5800 K (Figure. 1.4). The sun emits electromagnetic radiations with wavelengths corresponding to Infrared (more than 800 nm), Visible (400-800) and UV (less than 400).

1.4 Types of solar cell depend upon used materials
Based on the nature of materials, maximum conversion of effectiveness obtained and the linked price of photovoltaic power, Martin Green has grouped various photovoltaic solar cells in three major categories. Development in photovoltaic solar cells year wise shown in Figure 1.5.

1.4.1 First Generation Photovoltaic cells
1.4.1.1 Silicon Single-crystal based solar cells
Single-crystal silicon based photovoltaic cells are the most common. The key procedure used for developing the Single-crystal silicon based photovoltaic cells is the Czochralski (CZ) process. Superb pure polycrystalline material is melted into the quartz crucible. A single-crystal silicon seed is dipped in the molten mass of polycrystalline. The pit is gradually pulled from the melt; the single-crystal block is produced. Then ingots are refined in to the lean wafers of ~200-400 µm. These fine wafers are further polished, coated, interconnected and reassembled into modules and then arrays.

Single-crystal silicon has homogeneous structure. Smooth high uniformity consequences the higher conversion efficiency i.e. power-output divided by power-input. The conversion efficiency of the single-silicon based commercial modules is ~15-20. These are effectively used for the outdoor electricity applications. The process of wafering is costly, time-consuming and tedious for shaping them into lean wafers ~200 micrometers thick. If the prepared silicon wafers are too slim then complete wafer would crack in successive processing. Hence due to the condition of thickness, a solar cell needs a considerable quantity of raw silicon and maximum expensive material is vanished as sawdust in wafering [9].
1.4.1.2 Polycrystalline silicon based solar cells
Polycrystalline photovoltaic cells are less proficient than single-crystalline silicon cells. These devices are made up of small grains of single-crystal silicon. The grain boundaries of polycrystalline silicon hinder the flow of electrons which reduce the power output of the solar device. The conversion efficiency of commercial module of polycrystalline silicon is 10 to 14. The polycrystalline silicon solar cells are produced to carve thin wafers from blocks of cast polycrystalline silicon. Another method is the ribbon growth process (edge defined film-fed growth) in which silicon is grown directly as thin ribbons or sheets with the suitable thickness for making solar cells. Compared to single-crystalline silicon, polycrystalline silicon material is stronger and can be cut into one-third the thickness of single-crystal material. It also has slightly lower wafer cost and less strict growth requirements. However, their lower manufacturing cost is compensating the lower cell efficiency.

1.4.1.3 Gallium Arsenide (GaAs) based solar cells
GaAs has a semiconductor crystal structure similar to that of silicon which is made up with gallium and arsenic. It has effective light absorptivity. GaAs needs only few micrometers thick layer while crystalline silicon wafer need ~200-300 micrometers thickness for
absorbing the same sunlight. It also has much superior energy conversion efficiency than crystal silicon that can be obtained up to 25 to 30. GaAs has high resistance to high temperature which made it a perfect selection for concentrator systems. Due to this it is also trendy in space applications in which strong resistance against radiation damage and high cell efficiency are needed. Only disadvantage of GaAs is its high price so it is applied in solar concentrator systems of small area [10].

1.4.2 Second Generation solar cell
These thin films of solar materials are usually fabricated on the low cost sustaining layer such as glass or plastic or metal substrate. These thin-film materials have effective higher absorptivities than the crystalline materials. The fabricated film of solar materials is enormously thin ~few micrometers (amorphous cell ~0.3 micrometer). Thinner layers of materials made these devices more reasonable. The solar materials are directly sprayed onto glass or plastic substrate for making device cheaper and faster. The drawback of thin layer based photovoltaic cells reduced cell conversion efficiency. If we increase the larger array areas for increasing the conversion efficiency then area-related costs get increased on fabrication. Various chemicals applied for thin film solar cells are given below:

1.4.2.1 Amorphous Silicon (a-Si) based solar cell
Amorphous silicon is a non-crystalline form of silicon in which silicon atoms are present disorderly in structure. These amorphous silicons have high capacity of light absorption~ 40 times more than that of single-crystal silicon. Hence a fine film (1 micrometer thick) of amorphous silicon is suitable for building photovoltaic cells. Amorphous silicon can be suitably deposited on low-cost substrates i.e glass or steel or plastic etc and also needs low temperature. The material and manufacturing costs are cheaper (per unit area) than crystalline silicon photovoltaic cells. However amorphous silicon has two big shortcomings i.e. low conversion efficiency (5-9) and another is its outdoor reliability problem which means the efficiency of photovoltaic cell degrades in a few months with the exposure to solar radiations (reduction upto 10 to 15)

1.4.2.2 Cadmium Telluride (CdTe) based solar cell
Cadmium telluride is a polycrystalline material prepared with Cd and Te. It has superb light absorption capacity in a micrometer thickness of layer which can absorb 90% of the solar spectrum. The fabrication of thin film of these materials is relatively easy and cheaper due to
high-rate evaporation, spraying or screen printing processes. The solar conversion efficiency of the CdTe based solar module is nearly 7.0 equivalents to the amorphous silicon device. These CdTe based photovoltaic devices are unstable and having less performance. These devices are also having highly toxic chemicals. Hence special care is a focus on the production of the CdTe based photovoltaic cell because of toxic effect of As/Cd.

1.4.2.3 Copper Indium Diselenide (CuInSe₂, or CIS) based solar cell
Copper Indium Diselenide (CIS) is a polycrystalline material made up of Cu, In and Se. This solar material has been an important study areas of thin layer based solar cell industry. CIS has more attention due to maximum conversion efficiency (17.7 in 1996 i.e very close to solar efficiency of polycrystalline silicon photovoltaic device 18). Copper Indium Diselenide based solar cells has good outdoor stability. It can absorb 90% of the solar spectrum with 0.5 μm thickness. Copper Indium Diselenide material is one of the important light-absorbent (0.5 micrometers film effectively absorb the 90% of solar spectrum). It is a composite material so complex for manufacturing of device. Safety issues are main worry in the manufacturing of Copper Indium Diselenide material as it involves hydrogen selenide (highly toxic gas).

1.4.3 Third Generation Photovoltaic
This generation of solar cells is being made from variety of new materials besides silicon, including nano-tubes, inorganic composites, silicon wires, organic dyes, and conductive polymers. Third-generation photovoltaic cells have potentially to overcome the Shockley–Queisser limit of 31–41 power efficiency for single band gap solar cells. These devices can be operated in extensive range of lighting conditions which make them suitable for a various array of shaded and diffused light locations, without suffering from angular dependence of sunlight or light. The performances of these solar cells are not affected by temperature, direct sunlight, climate etc. the main advantages of these solar cells are highly efficient, low cost, easy fabrication and eco-friendly. The indoor modules are highly flexible, durable and lightweight. As a result they are very versatile and can be incorporated into a wide variety of products.

1.4.3.1 Copper zinc tin sulfide solar cell (CZTS), and derivates CZTSe and CZTSSe
Copper zinc tin sulfide (CZTS) is a quaternary semiconducting compound which has received increasing interest since the late 2000s for applications in solar cells. CZTS offers favorable
optical and electronic properties similar to CIGS (copper indium gallium selenide) making it well suited for use as a thin-film solar cell absorber layer, but unlike CIGS (or other thin films such as CdTe), CZTS is composed of abundant and non-toxic elements. Concerns with the price and availability of indium in CIGS and tellurium in CdTe, as well as toxicity of cadmium have been a large motivator to search for alternative thin film solar cell materials. The maximum efficiency has been reported in CZTSSe solar cell is 12.6 jointly by Tokyo Ohka Kogyo, IBM and Solar Frontier [11].

1.4.3.2 Organic solar cell
The molecules used in organic solar cells are cheap [12]. Combined with the flexibility of organic molecules, organic solar cells are potentially cost-effective for photovoltaic applications. Molecular engineering (e.g. changing the length and functional group of polymers) can change the band gap, allowing for electronic tune-ability. The optical absorption coefficient of organic molecules is high, so a large amount of light can be absorbed with a small amount of materials, usually on the order of hundreds of nanometers. Further advances in modifying the electron acceptor has resulted in a device with a power conversion efficiency of 10.61 with a blend of PC$_{71}$BM as the electron acceptor and PTB7-Th as the electron donor [13].

1.4.3.3 Perovskite solar cell
A perovskite solar cell is a type of solar cell which includes a perovskite structure compound, most commonly a hybrid organic-inorganic lead or tin halide-based material, as the light-harvesting active layer [14]. Perovskite materials such as methyl ammonium lead halides are cheap to produce and simple to manufacture. Solar cell efficiencies of devices using these materials have increased from 3.8 [15] to 20.1 during 2009-2015, making this the fastest-advancing solar technology to date [15]. According to detailed analysis [16], the efficiency limit of perovskite solar cells is about 31, which approaches the Shockley–Queisser limit of gallium arsenide (33). Their high efficiencies and low production costs make perovskite solar cells a commercially attractive option.

In 2014, at the 6th World Conference on Photovoltaic Energy Conversion at Kyoto, Japan, the achievement of a single-junction perovskite solar cell with a power-conversion efficiency of 24 was mentioned [17].
1.4.3.4 Quantum dot solar cell

A quantum dot solar cell is a solar cell design that uses quantum dots as the absorbing photovoltaic material. It attempts to replace bulk materials such as silicon, copper indium gallium selenide (CIGS) or CdTe. Quantum dots have band gaps that are tunable across a wide range of energy levels by changing the dots’ size. In bulk materials the band gap is fixed by the choice of material(s). This property makes quantum dots attractive for multi-junction solar cells, where a variety of materials are used to improve efficiency by harvesting multiple portions of the solar spectrum. A three-layer InGaAs/GaAs/InGaP cells (band gaps 0.94/1.42/1.89 eV) claim the efficiency of 42.3 [18-19].

1.4.3.5 Dye Sensitized Solar Cell (DSSC) or Gratzel Solar Cell

The history of DSSCs goes back to 1972 with the finding that photo-current can be generated when a chlorophyll-sensitized zinc oxide electrode is exposed to light irradiation [19]. In the following years, a limited success was attained in the improvement of device efficiency. Poor photon-to-electricity conversion efficiency was attributed to the low photo-absorption ability of the dye molecules on the flat semiconductor. Although an improved photo-absorption was achieved by stacking dye molecules each other, charge separation just occurred at the interface between a semiconductor and a dye molecule contacting with the semiconductor directly. Porous ZnO particles with increased surface area were prepared and adopted to fabricate a photoanode for DSSCs in 1976 [20-23]. Progress thereafter was slow concerning substrate roughness and morphology, dye photophysics and electrolyte redox chemistry, until the announcement in 1991 of a sensitized electrochemical photovoltaic device with an energy conversion efficiency of 7.1 under solar illumination [24]. That evolution has continued progressively since then, with efficiencies now over 15.

Titanium dioxide (TiO2) was the first choice of semiconductor for the photoelectrode on account of its many advantages for sensitized photochemistry and photoelectron chemistry. TiO2 is a low-cost, non-toxic and biocompatible material, and as such is even used in healthcare products as well as industrial applications such as paints. The inherent electronic nature of semiconductor metal oxides can directly interact with molecular excited states in a manner not energetically possible with insulators. More specifically, an excited sensitizer, S*, may transfer an electron to the semiconductor forming a charge separated pair, [Eq-1 and II]

\[ \text{TiO}_2/\text{S} + h\nu \rightarrow \text{TiO}_2/\text{S}^* \]  \hspace{1cm} \text{(Eq. I)}

\[ \text{TiO}_2/\text{S}^* \rightarrow \text{TiO}_2/\text{S}^+ + e_{cb} \]  \hspace{1cm} \text{(Eq. II)}
A fundamental goal, therefore, is to form interfacial charge separated states with long lifetimes. A particular advantage of interfacial charge separated states at semiconductor materials is that the injected electrons can be collected as an electrical response. Initial studies of the TiO$_2$-based DSSC employed tris-bipyridyl ruthenium (II) dyes, which are excellent sensitizers for photochemical studies, functionalized by the addition of carboxylate groups to attach the chromophore to the oxide substrate by chemisorption.

Table 1.1. Shows the confirmed conversion efficiencies for various solar cell systems

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Photovoltaic Material</th>
<th>Lab, Year</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Si (crystalline)</td>
<td>Sandia National lab, 1999</td>
<td>25.0±0.5</td>
</tr>
<tr>
<td>2</td>
<td>Si (multicrystalline)</td>
<td>National Renewable Energy Laboratory (NREL), 2004</td>
<td>20.4±0.4</td>
</tr>
<tr>
<td>3</td>
<td>Si (thin film)</td>
<td>Fraunhofer Institute for Solar Energy Systems(FhG-ISC), 2007</td>
<td>10.5±0.3</td>
</tr>
<tr>
<td>4</td>
<td>GaAs(crystalline)</td>
<td>Fraunhofer Institute for Solar Energy Systems(FhG-ISC), 2007</td>
<td>26.1±0.8</td>
</tr>
<tr>
<td>5</td>
<td>GaAs(thin film)</td>
<td>Fraunhofer Institute for Solar Energy Systems(FhG-ISC), 2008</td>
<td>26.1±0.8</td>
</tr>
<tr>
<td>6</td>
<td>GaAs(multicrystalline)</td>
<td>National Renewable Energy Laboratory (NREL), 1995</td>
<td>18.4±0.5</td>
</tr>
<tr>
<td>7</td>
<td>InP(crystalline)</td>
<td>National Renewable Energy Laboratory (NREL), 1996</td>
<td>22.1±0.7</td>
</tr>
<tr>
<td>8</td>
<td>CIGS (cell)</td>
<td>National Renewable Energy Laboratory (NREL), 2008</td>
<td>19.4±0.6</td>
</tr>
<tr>
<td>9</td>
<td>CIGS(Sub-module)</td>
<td>Fraunhofer Institute for Solar Energy Systems(FhG-ISC), 2000</td>
<td>16.7±0.4</td>
</tr>
<tr>
<td>10</td>
<td>CdTe(cell)</td>
<td>National Renewable Energy Laboratory (NREL), 2001</td>
<td>16.7±0.5</td>
</tr>
<tr>
<td>11</td>
<td>Si (amorphous)</td>
<td>National Renewable Energy Laboratory (NREL), 2003</td>
<td>9.5±0.3</td>
</tr>
<tr>
<td>12</td>
<td>Si (nanocrystalline)</td>
<td>Japan Quality Assurance, 1997</td>
<td>10.1±0.2</td>
</tr>
<tr>
<td>13</td>
<td>Dye sensitized solar cells (DSSC)</td>
<td>National Institute of Advanced Industrial Science and Technology -SONY, 2008</td>
<td>8.2</td>
</tr>
<tr>
<td>14</td>
<td>Organic polymer</td>
<td>National Renewable Energy Laboratory (NREL), 2006</td>
<td>5.15</td>
</tr>
</tbody>
</table>
1.5 DSSC operation

DSSC is a photovoltaic device which converts solar energy into electric current. General dye-sensitized solar cell is shown in Figure 1.6. n-TiO$_2$ is the most employed semiconductor material in dye-sensitized photoelectrochemical solar cells due to its favorable energetic, good stability, low cost and facile processing [25-28].

![Figure 1.6 Sandwich type assembly of DSSCs.](image)

In a regenerative DSSC, visible light is transformed into electricity devoid of any stable chemical transform (Figure 1.7). The processes involved in the functioning of such cells in general have been summarized below.

\[
\begin{align*}
\text{TiO}_2/S + hv & \rightarrow \text{TiO}_2/S^* \quad \text{(Eq. I)} \\
\text{TiO}_2/S^* & \rightarrow \text{TiO}_2/S^+ + e_{cb} \quad \text{(Eq. II)} \\
\text{TiO}_2/S^+ + e_{cb} & \rightarrow \text{TiO}_2/S \quad \text{(Eq. III)} \\
\text{TiO}_2/S^+ + (3/2)I^- & \rightarrow \text{TiO}_2/S + (1/2)I_3^- \quad \text{(Eq. IV)} \\
(1/2)I_3^- + e_{\text{carbon}} & \rightarrow (3/2)I^- \quad \text{(Eq. V)}
\end{align*}
\]

The layer of dye (S) which is absorbed with TiO$_2$ material directly absorb the photon of light and get excited which is shown in Eq. (I). After getting excited (S*) the dye transfers an electron to the TiO$_2$ material through the injection process (Eq. (II)). The efficiency of solar cell directly depends upon the relative energy levels and the kinetics of electron transfer processes present at the liquid junction of the sensitized TiO$_2$ material /electrolyte interface. For proficient operation of the DSSC, the rate of electron injection must be more rapidly than the separation of the electron from the excited state of dye. Also, the rate of re-reduction of the oxidized dye sensitizer cation by the electron donor in the electrolyte [Eq. (IV)] must be higher than the rate of back reaction of the injected electrons with the dye cation [Eq. (III)].
as well as the rate of reaction of injected electrons with the electron acceptor in the electrolyte [Eq. (V)]. Finally, the kinetics of the reaction at the counter electrode must also assure the rapid regeneration of charge mediator [Eq. (V)] [29-32].

![Figure 1.7 Mechanisms of DSSCs.](image)

### 1.6 Components of DSSCs

The main components in dye sensitized solar cells are:

- Transparent conducting substrate
- Photoanode
- Photosensitizer
- Electrolyte
- Counter electrode

#### 1.6.1 Transparent conducting substrate

Transparent material having conductive nature plays a significant function in the functioning of Dye Sensitized Solar Cell. These materials are having fine film which works as photocurrent collector and hold the semiconductor film of solar cells. These have two significant characteristics:

(i) The best optical transparency that helps photonic radiation to go through the dynamic photoactive substrate exclusive of unnecessary absorption of solar radiation of present in the range.

(ii) The low electrical resistivity that helps in the facilitation of electron transfer process which reduces the energy loss.
Tin doped indium oxide film (In$_2$O$_3$:Sn; ITO) is having excellent transmittance more than 80% and low resistivity ($10^{-4}$ Ω cm at room temp.). Hence these are extensively used as transparent conducting substrate for optoelectronic apparatus. These ITO films are having efficient electrical characteristics. These are prepared with In$_2$(SO$_4$)$_3$.nH$_2$O and SnSO$_4$ through dipping technique [33] which has the resistivity in range of 6–8x10$^{-4}$ Ω cm. The low resistivity of formed film is due to availability of high free carrier densities developed due to (a) changeover of indium by tin atom producing one extra electron; (b) oxygen vacancies performing as two e donors [34-35].

The transparent SnO$_2$:F or Fluoride-doped tin oxide film is having the equivalent structure, conducting properties and functioning as transparent ITO. FTO-deposited substrates have 70–80% high transmittance having the thickness of 750 nm (~ 10% lesser than that of ITO glass materials). The resistance of FTO deposited glass sheet is <12 Ω/cm i.e nearly 20% lesser than the ITO deposited glass (15 Ω/cm). But the FTO-deposited are cheaper than the ITO-deposited substrate [36].

Now a day’s fine graphene film has also been applied in solar cell as a conducting substrate. The graphene films are produced by reducing the graphite oxide directly on substrates [37] which has a superb conductivity of 550 S/cm [38].

1.6.2 Photoelectrodes

The excitons developed at the dye are separated into free carriers at the dye photo-electrode boundary. There are following driving forces responsible for this charge separation:

(a) The charge partition is actively preferred because the conduction band of the metal oxide is having lower energy than the lowest unoccupied molecular orbital of the dye.

(b) The charge partition is actively preferred due to the larger density of electronic energy states of the conduction band of a crystal than the molecular orbital of a dye [39].

Metal oxides (ZnO, TiO$_2$, ZrO$_2$, Fe$_2$O$_3$, Nb$_2$O$_5$, Al$_2$O$_3$, CeO$_2$, Zn$_2$SnO$_4$ and SrTiO$_3$) have been used as photo electrodes in photovoltaic cells. Al$_2$O$_3$ is a oxide of p-block metal, ZnO and TiO$_2$, are oxides of 3d transition metal, ZrO$_2$ and Nb$_2$O$_5$ are oxide of 4d transition metal and CeO$_2$ is a oxide of f-block metal. ZrO$_2$, Al$_2$O$_3$, and Nb$_2$O$_5$ behave as insulators at room temperature having band gaps ~5, 6.6 and ~3.5 eV, correspondingly. These materials have conductivities of few mS/cm. Nb$_2$O$_5$ behave as n-type material at lower oxygen content and Nb$_2$O$_{4.978}$ has ~3x10$^3$ S/cm conductivity [40]. TiO$_2$, ZnO, and Nb$_2$O$_5$ have been the mainly accepted photo electrodes of solar cells. Hard work has developed the optimization of nanostructured electrodes, organized arrays of nanotubes and single crystalline nanorods.
1.6.2.1 Titanium oxide (TiO$_2$)

TiO$_2$ material is non-poisonous, chemically stable compound having refractive index 2.4 which is commonly applied in paints, toothpastes and various sunscreens. TiO$_2$ exists in different crystalline form such as anatase, rutile and brookite. Thermodynamically the TiO$_2$-rutile form is found most stable. While the TiO$_2$-anatase form is highly useful for the photovoltaic cells which have wide band gap (3.2 eV) as well as high conduction band energy ($E_{cb}$). Many authors [41-42] explained the transfer of the electron with nano-TiO$_2$ in pure form as well as in presence of a redox electrolyte. The electron transfer with any material is managed with the band structure. The titanium is an ionic material having strong electron–phonon coupling (polarons). The interactions are effective between small polarons and self-trapped electrons. Hence electron transportation happening via thermally activated hopping from one electronic state to the next. The large polarons exist for weaker coupling strength which exhibited band-type interactions.

Development of TiO$_2$ as a photovoltaic electrode material has been investigated since 1991. The DSSCs have been developed in terms of light absorption, light scattering, charge transport and suppression of charge recombination. The efficient and essential development of TiO$_2$ material as an electrode is given below:

(a) TiO$_2$-layer (50nm) helps as blocking-layer between redox electrolyte and the FTO coated substrate. The layer can be applied using different techniques i.e. chemical deposition, sputtering and spray pyrolysis etc [43-46].

(b) The TiO$_2$-layer helps in effective electron transportations.

Mixed form of TiO$_2$ brookite (having 25% anatase) as electrode when applied to the DSSCs enhances the efficiencies to 4.1 [47]. Therefore now a day’s mixed of TiO$_2$ layer is used for the various photovoltaic applications. TiO$_2$ nanotube based DSSCs on the titanium substrate have a photoconversion efficiency of 6.9 with N719 dye [48]. The nano-tubes developed on the FTO material (1.1 µm) produced solar efficiency of 4.1 with TiCl$_4$ after treatment having the strongly absorption of dye [49]. Researcher also investigated on fast electron transportation, their trapping and transfer of electron through nano-tubes based photovoltaic cells [50-51].

1.6.2.2 Zinc oxide (ZnO)

Zinc oxide is a semiconductor material that exists ($E_g$$\approx$3.37 eV) in cubic or hexagonal structure. The wurtzite structure is having lowest energy. The zinc oxide is having conduction band energy $\approx$4.45 eV equivalent to TiO$_2$. ZnO-Hexagonal has been applied as electrodes for
various photovoltaic applications [53-56]. The band gap as well as conduction band edge of ZnO is equivalent to TiO\textsubscript{2}-anatase. While the zinc oxide has high electron mobility than TiO\textsubscript{2}, that must favor the electron mobility. However, chemically the ZnO is less stable than TiO\textsubscript{2}. ZnO usually get dissolved in acidic and basic media. The main benefit is easy mode of its preparation in the high crystalline form of ZnO in various morphologies i.e branched nanostructures, nano-particles, nano-rods, nanotubes, nanowires, nanoflowers, tetrapods, nanosheets etc. Mesoporous-ZnO electrodes could be applied using ZnO nano-particles with doctor-blading/screen printing on the FTO materials with sintering process. The excellent outcome so far was reported with commercial ZnO-powder (20 nm) with 90 min dye-adsorption duration at 60 °C (0.3 mM N719 in ethanol solvent) having the efficiency 6.6 at AM 1.5 G (100 mW cm\textsuperscript{-2}) [57]. Nguyen et al. obtained the efficiency of photovoltaic cell 4.0. Which was designed with a Ru-complex have one carboxylated bipyridyl ligand onto the ZnO-electrode [58]. Park his team obtained a high stable ZnO form with SiO\textsubscript{2} core-shell [59]. The SiO\textsubscript{2}-coated ZnO-films used for the solar cells with an efficiency 5.2 then the compared with <1 for the initial ZnO at the same experimental situation.

ZnO is directly electrodeposited at low-temperature deposition on the glass substrate. Yoshida and coworkers successfully deposited the ZnO from aqueous zinc solutions in the presence of oxidants and water-soluble dye molecules using the cathodic electro-deposition [60]. The porous nanostructures of ZnO was formed which are appropriate for DSSCs. DSSC of high efficiency of 5.6 have been found with the electro-deposition of ZnO-films with the combination of organic dye D149 [60]. ZnO-nanorods can be deposited with gas-phase deposition and chemical bath deposition technique. Law et al. developed the DSSCs based on ZnO nano-wires of ~20 \( \mu \)m with chemical bath technique having the efficiencies of 1.5 [61-62]. ZnO nano-rod, nano-wire, and nano-tube based photovoltaic cells are so far analyzed with relatively low fill factors (<0.6).

1.6.2.3 Niobium pentoxide (Nb\textsubscript{2}O\textsubscript{5})

Many researcher applied Nb\textsubscript{2}O\textsubscript{5} as photo-electrode in photovoltaic cells as nano-particles [63-67], nanobelts [68], and as TiO\textsubscript{2}–Nb\textsubscript{2}O\textsubscript{5} bilayers [69-70] and also as blocking layers which check the electrons backside move[71-72]. Nb\textsubscript{2}O\textsubscript{5} has wide band gap i.e. 3.49 eV [73]. DSSCs made-up with Nb\textsubscript{2}O\textsubscript{5} as photoelectrode and N3 dye reported higher \( \text{V}_{oc} \) than that obtained using anatase. Hoshikawa et al. carried the comparative analysis of the impedance characteristics of photovoltaic cells applying the Nb\textsubscript{2}O\textsubscript{5} as photoelectrode with TiO\textsubscript{2} [64]. Sayama et al. used porous semiconductor films of TiO\textsubscript{2}, Nb\textsubscript{2}O\textsubscript{5}, ZnO, SnO\textsubscript{2}, In\textsubscript{2}O\textsubscript{3}, WO\textsubscript{3},
Ta$_2$O$_5$, and ZrO$_2$ in DSSC using N3 dye [74-75]. More research is still needed for the development of mesoporous-Nb$_2$O$_5$ with one dimensional nanostructure. The higher conduction band energy and high chemical stability of Nb$_2$O$_5$ made it as an alternative to TiO$_2$ for the production of high performance DSSC.

1.6.2.4 Ternary Photoelectrode Materials

Ternary metal oxide materials i.e SrTiO$_3$ [65, 76] and Zn$_2$SnO$_4$ [77] have been applied as photoelectrode compounds for the DSSCs. The SrTiO$_3$ and TiO$_2$ are having equivalent band gap of 3.2 eV. Its high dielectric constant made the SrTiO$_3$ to act as electrically mesoporous even with a high particle size ~80 nm [78]. The efficiency analyzed for DSSCs using SrTiO$_3$ is comparatively poor due to the specific surface structure of SrTiO$_3$. The energetically preferred surface of SrTiO$_3$ is (001) face having SrO or TiO$_2$ possible termination. Though the SrO surface is more basic so negatively charged carboxylate group of the sensitizer are poorly absorbed onto the semiconductor.

Two research groups used the Zn$_2$SnO$_4$ as a photo-electrode in DSSC [76-77]. The Zn$_2$SnO$_4$ is having band gap ~3.6 eV and inverse spinel structure. The structure having the octahedral coordinated Sn$^{4+}$ atoms with half of the Zn$^{2+}$ atoms are available in tetrahedral coordination and the other half in octahedral coordination. Mixture of ZnO and SnO$_2$ as working photo-electrode, efficiency gets improved [79]. The Zn$_2$SnO$_4$ based DSSCs obtained the solar efficiency 3.8 that is equivalent to the efficiency obtained from the ZnO based fabricated at the comparable situation (4.1). The Zn$_2$SnO$_4$ when applied with ZnO for fabricating the DSSC then the stability problems can be overcome in acidic medium of dyes. Hence, the Zn$_2$SnO$_4$ is found more suitable than the ZnO or SnO$_2$ for making the DSSC.

1.6.2.5 Other metal oxide

TiO$_2$, SnO$_2$, SrTiO$_3$, Fe$_2$O$_3$, etc were used as photoelectrodes for generationing of photocurrent with the influence of the solar radiation [80-81]. These metal-oxide based DSSCs gave meager efficiency characteristically with $J_{sc}$ of few hundred microamperes with radiation of one sun due to poor absorption coefficient as well as low carrier mobility (~0.01 cm$^2$/Vs). A key basis which controls the $J_{sc}$ is the charge carrier recombination happens in metal-oxides [82-84].

Corma et al. [84] reported the photovoltaic effect in CeO$_2$, mixed ZrO$_2$/La$_2$O$_3$ with CeO$_2$ nanomaterials of ~5 nm by sandwiching between conducting glass plates using iodide/triiodide electrolyte. These solar cells were not sensitized with any dyes. CeO$_2$ is
having band gap of 3.2 eV hence in bulk CeO$_2$ is not suitable for photoactive material. However, nanoparticles of pure CeO$_2$ doped with Zr$^{4+}$ and La$^{3+}$ exhibited the photovoltaic comeback [84] due to presence of significant fraction of Ce atoms which exist on surface which lead to the oxygen vacancies and defects. The observed photoconductivity could be explained in terms of hopping of electron and holes between these surface states.

Chemically stable SnO$_2$ has conduction band edge ($E_{cb}$) ~0.5 eV lower than that of TiO$_2$-anatase. Hence it could be applied as photoelectrode with the combination of dyes with low-lying LUMOs that inject poorly into TiO$_2$, i.e. some perylene sensitizers [85]. The SnO$_2$ based DSSC provided 2.8 with the organic dye D149 while with N719 gave 1.2 in similar condition [86]. Significant improvement in $V_{oc}$ and efficiency of DSSCs can be found by covering mesoporous-SnO$_2$ materials via fine shell of some metal-oxide i.e ZnO/ MgO/ Al$_2$O$_3$ etc [87-90]. The excellent result uptill now obtained using ZnO-coated with SnO$_2$ photoelectrode 6.3 [89]. It is not certain whether a ZnO shell is formed or the formation of a Zn$_2$SnO$_4$ shell occurs. Zn$_2$SnO$_4$ is a chemically stable wide bandgap material through which efficiencies of DSSC was obtained 3.8 [91]. The photo-electrochemical characterization of this material suggests that it has higher conduction band edge energy than TiO$_2$-anatase [92].

1.6.3 Photosensitizers

The design of molecule as sensitizer should have various properties to work effectively in DSSCs. The ideal sensitizer should have the following properties:

(i) The sensitizer should be able to absorb the radiation in whole visible and near infrared (NIR) region.

(ii) Sensitizer should have one of the -COOH, -H$_2$PO$_3$, -SO$_3$H etc. group for the anchoring on the semiconductor surface.

(iii) LUMO of the sensitizer should be complement to the edge of the conduction band of the semiconductor to reduce the energy potential losses in the electron transfer process.

(iv) HOMO of the sensitizer should be adequately lower to take electrons from a redox electrolyte.

(v) Sensitizer should be resistant to degradation by photon, electrochemical reaction and thermally stable.

Based on these requirements, many different photosensitizers including metal complexes, synthetic organic and natural dyes have been designed and applied to DSSCs in the past decades.
1.6.3.1 Metal complexes as sensitizers

Metal complex sensitizers as sensitizer consist of two ancillary and anchoring ligands. Anchoring ligands play an important role to bind the complex to the semiconductor layer while ancillary ligand has ability to absorb radiation from sunlight. Photovoltaic properties investigated in terms of efficiency and stability. To achieve maximum efficiency and stability large numbers of metal complexes were synthesized and characterized. For effective sensitizer, The metal complex should have structure i.e. ML₂(X)₂, where M can be one of the Ru, Re, Pt or Os and L is 2,2'-bipyridyl-4,4’-dicarboxylic acid and X presents a cyanide, halide, acetyl acetonate, thiocyanate, thiacarbamate or water substituent group [93].

1.6.3.1.1 Ruthenium complexes as sensitizers

Among all the Polypyridyl complexes, Ru-complexes dyes are the most proficient. These metal complexes may be categorized as phosphonate ruthenium dyes, carboxylate polypyridyl ruthenium dyes and polynuclear bipyridyl ruthenium complex [94]. cis-[Ru(dcbH₂)₂(NCS)₂] (also known as N3) dye has been the most capable as photosensitizer in DSSCs reported by Grätzel in 1993. Other Ru-complexes also have been investigated i.e. N719, N749 and Z907. N3 complex consist of two NCS ligands and absorption of radiation at 800 nm whereas N749 (also known as Black dye) shows maxima in absorption spectrum at 860 nm making it better in terms of performance. However other factors like low absorption coefficients turns out to be a limitation for N749 [94-95]. There have been research carried out on near IR dyes as sensitizer for DSSC which include ruthenium complexes containing biquinoline or 1,8-naphthyridyl moieties, cyclometallated ruthenium complexes, osmium polypyridyl complexes, and phthalocyanine and perylene dyes.

A new Ru(II) polypyridyl complex was prepared with 2,6-bis(quinolin-2-yl) pyridine derivatives exhibit excellent performance [96-97]. A Ru-complex (RC730) having crown-ether entity on 4,4’ positions of the bipyridine ligand was prepared and characterized shows efficiency of 2 at 530 nm [98].
Ru-complex of the type [Ru(bpin)(dcbpyH₂)Cl]Cl where dcbpyH₂ is 4,4-dicarboxy-2,2-bipyridine and bpin is 2,6-bis(pyrazol-1-yl)isonicotinic acid was prepared and characterized for fine tuning the LUMO level of the ruthenium sensitizer to attain superior stability in the excited state which keeps the excess energy to maintain high driving force for electron injection. The photovoltaic properties of these molecules as photosensitizer in a nano-TiO₂ based DSCC was investigated and its efficiency was obtained 1.9 [99]. Another heteroleptic sensitizer, Ru((4,4-dicarboxylic acid-2,2¢-bipyridine)(4,4¢-bis(p-hexyloxystyryl)-2,2-bipyridine)(NCS)₂, gave efficiency of 7.1 in conjunction with binary ionic liquid redox electrolyte and good stability when absorb under light at 60°C [100]. The synthetic routes are now available making Ru(II)bipyridine analogous complex coordinating by 1-(2,4,6-trimethylbenzyl)-2-(20-pyridyl)benzimidazole ligand. DSSC with CS23 exhibits 3.4 efficiency which is similar with reference ruthenium complex (Z-907) under the same conditions [101].

1.6.3.1.2 Osmium complexes as sensitizer

The photo-stability of osmium complexes as sensitzers is much higher than other metal complexes. The synthesis and characterization of [Os(II)(H₃tcterpy)(CN)₃]− where H₃tcterpy = 4,4′,4″-tricarboxy- 2,2′:6′,2″-terpyridine and osmium sensitizer containing 2,2′-bipyridine-4,4′-bisphosphonic acid ligand were shown to have good efficiency and absorption above 900 nm. The complex in methanol solvent shows a reversible Os(II)→Os(III) oxidation process that increases the absorption spectrum on TiO₂ layer [94,102-103].
1.6.3.1.3 Platinum complexes as sensitizers
Pt(II) based complexes having 4,4′-dicarboxy-2,2′-bipyridine and quinoxaline-2,3-dithiolate ligands achieve proficient sensitization of nano-TiO$_2$ DSSC over a broad range in visible spectrum, generating $J_{sc}$ 6.14 mA/cm$^2$ and $V_{oc}$ 600 mV under simulated AM 1.5 solar irradiation, exhibit efficiency of 2.6 [94,104].

1.6.3.1.4 Rhenium complexes as sensitizers
Rhenium (I) complexes of benzothiazole derivatives have been investigated that showed efficiency in range 1.43-1.76. Chlorotricarbonyl rhenium (I) complex [94,105] is shown in Figure 1.11.
1.6.3.1.5 Iridium complexes as sensitizers

A novel type of iridium (III) complexes with carboxyl pyridine ligands were prepared and fabricated device showed 2.16 efficiency. The efficiency can be enhanced by overlapping the spectrum of Ir (III) complex and the solar radiation. Cyclometalated Ir(III) complexes have high stability due to chelate ring formation and excited-state lifetime of cyclometalated Ir(III) complex is longer than that of N3 that increases efficiency of devices [106].

![Figure 1.12: Structure of Ir-complex](image)

1.6.3.1.6 Other Metal Complexes complexes as sensitizers

Other metal complexes that have been researched are with Cu and Fe. While Cu (I) complexes has shown surprisingly higher efficiency in range of 1.9 to 2.3, Fe (II) complexes show excellent photo-stability with lower efficiency [94,107-108]. Metal complexes of ruthenium having a 2-quinolinecarboxylate ligand were synthesized for the same purpose. The sensitizers absorb radiation in visible region as well as near infra red region show efficiency nearly 8.2 [109]. A overall efficiency of 7.2 has been obtained in DSSC based on Mordant dye as sensitizers. A group of 6 best proeficient mordant dyes were analyzed and found that these produce $J_{sc} > 0.2$ mA which is comparable to the N3 dye. One of the mordant dyes [110] has been shown in Figure 1.13.

![Figure 1.13. Structure of Mordant Black 5 (bis–azo)](image)
1.6.3.2 Synthetic organic dyes as sensitizers

Dyes are colored organic compounds having the property of imparting their colors to another substance such as paper, leather, fur, hair, food, drug, cosmetics, waxes, plastics, and coir and textile materials. For a compound to be called a dye it must have (a) suitable color, (b) fixing tendency on a fabric that is impregnated with their solution and (c) the characteristics of being fast when fixed, it must be able to resist the action of light, water, soap solutions, detergent, etc. [111]. Dyes have chromophore, auxochromes, \( \pi \)-conjugated double bonds, delocalized electron systems and electron withdrawing or electron donating groups that cause or intensify the color of the dyes. Examples for chromophores are \(-\text{C} = \text{C}-\), \(-\text{C} = \text{N}-\), \(-\text{C} = \text{O}-\), \(-\text{N} = \text{N}-\), \(-\text{NO}_2\) and quinoid rings and that for auxochromes are \(-\text{NH}_3\), \(-\text{COOH}\), \(-\text{SO}_3\text{H}\) and \(-\text{OH}\) [112-113]. Dyes absorb radiation in visible region, i.e. 350 to 700 nm and the relationship between light absorption and color is shown in Table 1.2. The absorption of UV-Visible radiation by dye molecule is associated with transition of electron between molecular orbital.

Table 1.2 Relationship between light absorption and color

<table>
<thead>
<tr>
<th>Color</th>
<th>Color absorbed</th>
<th>Absorbed radiation (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Violet</td>
<td>Yellow-green</td>
<td>350-435</td>
</tr>
<tr>
<td>Blue</td>
<td>Yellow</td>
<td>435-480</td>
</tr>
<tr>
<td>Green-blue</td>
<td>Orange</td>
<td>480-490</td>
</tr>
<tr>
<td>Blue-green</td>
<td>Red</td>
<td>490-500</td>
</tr>
<tr>
<td>Green</td>
<td>Purple</td>
<td>500-560</td>
</tr>
<tr>
<td>Yellow-green</td>
<td>Violet</td>
<td>560-580</td>
</tr>
<tr>
<td>Yellow</td>
<td>Blue</td>
<td>580-595</td>
</tr>
<tr>
<td>Orange</td>
<td>Green-blue</td>
<td>595-605</td>
</tr>
<tr>
<td>Red</td>
<td>Blue-green</td>
<td>605-750</td>
</tr>
</tbody>
</table>

Organic dyes show better advantages over Ru-complexes as sensitizers:

- Organic dyes are easy to design and synthesize as per requirement of sensitizer.
- Organic dyes are economical, eco-friendly as compared to metal complexes.
- The molar extinction coefficients of organic dyes are much higher than Metal based complexes which make them attractive for DSSCs.
Generally, donor-π-bridge-acceptor (D-π-A) occurs between dye and sensitizer (Figure 1.14). In the designing of new sensitizer some parameters should be kept in mind i.e. absorption spectrum of sensitizers, HOMO and LUMO energy of which carried out charge transfer. In DSSC, the excited sensitizer should be able to inject electron to conduction band of semiconductor. Lots of efforts have been made to improve the dyes to optimize DSSC properties. Today, many organic dyes [114-115], including coumarin dyes [116-122], indoline dyes [123-129], tetrahydroquinoline dyes [130-132], triarylamino dyes [133-140], heteroanthracene dyes [141-143], carbazole dyes [144-145], N,N-dialkylaniline dyes [146-148], hemicyanine dyes [149-152], merocyanine dyes [153-155], perylene dyes [156-159], anthraquinone dyes [160], boradiazain-dacene (BODIPY) dyes [161-162], oligothiophene dyes [163-164] and polymeric dyes [165-167] are used as sensitizers.

1.6.3.2.1 Coumarin dyes as sensitizers

Coumarin dyes with cyanoacrylic acid and substituted group like thienyl, vinylene and isophorone were used as sensitizers in fabrication of DSSCs by Arakawa, Hara, Wang, and co-workers [116-122]. The coumarin part considered as electron donor while cyanoacrylic acid behave as electron acceptor due to the intensive electron withdrawing capability of CN and COOH groups. CMD-I dye showed efficient properties in electron injection process when used as sensitizer in DSSC [168]. The absorption range in visible spectrum of CMD-I is limited, so its efficiency is much lower than Ru-complex based DSSCs. The incorporation of vinylene (–CH=CH–) group shifted absorption spectrum towards longer wavelength (red-shifts). CMD-II, CMD-III and CMD-IV showed extensive absorption spectra that enhanced efficiencies of devices. The changes in absorption spectra of these dyes are endorsed to alter the energy of HOMOs rather than reduce the energy of LUMOs. The increase in molecular size of dye with vinylene group also improve aggregation on semiconductor layer thereby decrease in rate of electron injection. The use of co-adsorbent with these dyes reduces the aggregation [117,120]. The efficiency of CMD-III based DSSCs was found 6.0 in optimized conditions [117].

Figure 1.14: Schematic drawing of D-π-A organic dyes
CMD-V dye exhibits elevated photovoltaic properties having 7.6 efficiency with volatile redox electrolyte and high photostability under visible illumination exhibit 6.0 efficiency with non-volatile electrolyte for 1000 h [121-122]. Recently, Katoh et al. comparatively studied these dyes through irradiation of dyes soaked onto TiO$_2$ layer and pointed that dyes having oligothiophene unit illustrate elevated stability [169].

1.6.3.2.2 Indoline dyes as sensitizers

Horiuchi, Uchida and co-workers investigated indoline dyes with easy synthesis method and economical cost. IDD-I exhibits good 6.1 efficiency in fabricated DSSCs [124]. To enhance the photovoltaic properties, substitution of rhodanine in chemical structure of IDD-I to extend the absorption in visible region which provides a class of indoline dyes [125]. IDD-II dye
exhibits as high as 8.0 efficiency [123-129]. Gra¨tzel et. al. achieved 9.0 efficiency with IDD-II under optimized TiO$_2$ layer thickness [126]. Schmidt-Mende et al. applied IDD-I dye to make solid-state DSSCs and reported efficiency over 4.0, which was better to N719-based DSSCs [127]. Ito et al. reported an efficient IDD-III dye with rhodanine unit and n-octyl to suppress the sensitizer π-stacked aggregation on TiO$_2$ layer and found 9.5 efficiency [123]. These dyes show one of the best efficiencies for DSSCs.

Figure 1.16: chemical structure of Indoline dyes

1.6.3.2.3 Tetrahydroquinoline dye as sensitizers

Sun, Yang, and co-workers reported Tetrahydroquinoline dye as sensitizer in DSSCs [130-132]. These dyes have been studied systematically for the relationship between chemical structures and photovoltaic properties of devices. These dyes showed low efficiency due to presence of –C= C- that show twisting leading to possible cis-trans photoisomerism [131]. The reports recommended that dyes with rigid structures are supportive for good photovoltaic properties in DSSCs. The dye having more thiophene group could easily raise the recombination process of electrons in the TiO$_2$ and I$_3^-$ in the electrolyte leading to a lower $V_{oc}$ [132]. TQH-I dye based DSSCs exhibits 4.5 efficiency while N3 dye shows 6.2 efficiency under similar conditions. The dithieno[3,2-b;2′,3′-d]thienyl (DTT) unit was incorporated into
dye i.e. TQH-II. The introduction to a new class of dyes for DSSCs, in which anchoring group was separated from the acceptor groups of the dye, was effectively obtained giving a new series of D-π-A dyes as sensitizers in near infra red region [131]. TQH-III dye based DSSC exhibit 3.7 efficiency at 660 nm.

Figure 1.17: chemical structure of Tetrahydroquinoline dyes

1.6.3.2.4 Triarylamine dyes as sensitizers

Triarylamine dyes have important electron-donating capability and hole transport properties due to which these are extensively used as sensitizers in DSSCs. Till date, a huge number of triarylamine dyes have been applied as sensitizer and mainly shows good efficiencies in DSSCs [133-140]. Yanagida et. al reported the photovoltaic properties of TAA-I and TAA-II dye exhibit 3.3 and 5.3 efficiencies respectively [133]. Sun et. al. reported a new class of triphenylene dyes as sensitizers in DSSCs [134-135]. TAA-III dye has simple structure and exhibits over 5.1 efficiency while N719 has 6.0 efficiency in similar condition [134].

Lin and co-workers reported a class of these dyes as sensitizer in DSSCs [134-135]. TAA-IV dye showed good 3.8 efficiency due to presence of benzoseniadiazole and benzothiadiazole non-planar which hindered charge recombination. They also investigated a fluorene-based TAA-V dye that exhibits 5.2 efficiency while N3 dyes shows 5.5 efficiency. Lin and co-workers substituted the thiophene group of TAA-I with furan and achieved an efficient TAA-VI dye to give 7.4 efficiency. TAA-III dye show 6.1 efficiency under similar conditions.
Chen and co-workers analysed sensitizing properties of a class of triphenylamine dyes having high electron density on donor unit to enhance the photovoltaic properties [136]. TAA-VII dye showed 4.3 efficiency [136]. The photovoltaic properties of these dyes can be enhanced by adding electron acceptor group or extension of π-conjugated system. Recently the incorporation of diphenylvinyl unit as electron donor groups in TAA-VIII showed 6.3 efficiency with good stability.

Wang and co-workers improved the photovoltaic properties of triarylamine dyes based DSSCs [137]. TAA-IX dye showed a wide absorption band at 525 nm and good molar extinction coefficient, $44.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. The fabricated of DSSCs using TAA-IX dye as sensitizer show 8.0 efficiency with liquid electrolyte. The lower 7.0 efficiency was found with solvent free ionic redox electrolyte. The replacement of DTT group with thienothiophene (TT) produced TAA-X dye, which had excellent 4.8 efficiency in solid state DSSCs [138]. Later, the addition of a 3,4-ethylenedioxythiophene (EDOT) π-bridge, that enhanced the photovoltaic properties as compared to thiophene and bithiophene [139].

TAA-XI dye having biEDOT group gave improved 8.3 efficiency, as compared to bithiophene counterpart TAA-XII dye. The enhanced performance of TAA-XI dye due to good solar spectral match with the solar radiation spectrum by incorporating biEDOT group. By introducing alkoxy group in these dyes further obtained a new class i.e. TAA-XIII, TAA-XIV, TAA-XV, TAA-XVI and TAA-XVII [137-139]. TAA-XVII having both TT and EDOT π-bridges exhibited absorption peak at 552 nm. The TAA-XVII shows efficiency 9.8 with liquid electrolyte and 8.1 with solvent free ionic electrolyte under similar condition.

Yang et al. investigated few tailormade triarylamine dyes [140], dyes TAA-XVIII and TAA-XIX dyes have N,N,N',N'-tetraphenylbenzidine (TPD) entity as donor to give 5.6 and 4.3 efficiencies, respectively [140].
TAA-I: (E)-2-cyano-3-(4-(diphenylamino)phenyl)acrylic acid
TAA-II: (2E,4E)-2-cyano-5-(4-(diphenylamino)phenyl)penta-2,4-dienoic acid
TAA-III: (Z)-2-cyano-3-(5-(E)-4-(diphenylamino)styryl)thiophen-2-yl)acrylic acid
TAA-IV: (Z)-2-cyano-3-(5-(7-(4-(diphenylamino)phenyl)benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)acrylic acid
TAA-V: (Z)-2-cyano-3-(5-(9,9-diethyl-7-(naphthalen-2-yl)(phenyl)amino)-4,9-dihydro-3H-fluoren-2-yl)thiophen-2-yl)acrylic acid
TAA-VI: (Z)-2-cyano-3-(5-(E)-4-(diphenylamino)styryl)furan-2-yl)acrylic acid
TAA-VII: (E)-2-(5-(4-(diphenylamino)benzylidene)-4-oxo-2-thioxothiazolidin-3-yl)acetic acid
TAA-VIII: (E)-2-(5-(4-(2,2-diarylvinyl)phenyl)(phenyl)amino)benzylidene)-4-oxo-2-thioxothiazolidin-3-yl)acetic acid
TAA-IX: (E)-2-cyano-3-(6-(4-(9,9-dimethyl-9H-fluoren-2-yl)(9,9-dimethyl-9H-fluoren-3-yl)amino)phenyl)dithieno[3,2-b:2',3'-d]thiophen-2-yl)acrylic acid
TAA-X: (Z)-2-cyano-3-(5-(4-(9,9-dimethyl-9H-fluoren-2-yl)(9,9-dimethyl-9H-fluoren-3-yl)amino)phenyl)thieno[3,2-b][thiophen-3-yl]acrylic acid
TAA-XI: (E)-2-cyano-3(7-(4-(9,9-dimethyl-9H-fluoren-2-yl)(9,9-dimethyl-9H-fluoren-3-yl)amino)phenyl)-2,2',3,3'-tetrahydro-[5,5'-bithieno[3,4-b][1,4]dioxin]-7-yl)acrylic acid
TAA-XII: (Z)-3-(5-(4-(bis9,9-dimethyl-9H-fluoren-2-yl)(phenyl)thiophen-2-yl)-2-cyanoacrylic acid
TAA-XIII: (Z)-3-(5'-(E)-1-(4-(4-methoxyphenyl)amino)phenyl)prop-1-en-2-yl]-[2,2'-bithiophen]-5-yl-2-cyanoacrylic acid
TAA-XIV: (Z)-3-(5'-(4-(bis(hexyloxy)phenyl)amino)phenyl)-[2,2'-biseilenophen]-5-yl)-2-cyanoacrylic acid
TAA-XV: (Z)-3-(5-(4-(bis(hexyloxy)phenyl)amino)phenyl)thieno[3,2-b][thiophen-2-yl]-2-cyanoacrylic acid
TAA-XVI: (E)-3-(5'-(4-(bis(hexyloxy)phenyl)amino)phenyl)-[2,2'-bithieno[3,2-b][thiophen]-5-yl]-2-cyanoacrylic acid
TAA-XVII: (E)-3-(5'-(4-(bis(hexyloxy)phenyl)amino)phenyl)-[2,2'-bithieno[3,2-b][thiophen]-5-yl]-2-cyanoacrylic acid
TAA-XVIII: (Z)-2-cyano-3-(5-(E)-4-((2,4-dimethylphenyl)(4'-(2,4-dimethylphenyl)(phenyl)amino)-[1,1'-biphenyl]-4-yl)amino)styryl)thiophen-2-yl)acrylic acid
TAA-XIX: (E)-2-cyano-3-(4-(E)-4-((2,4-dimethylphenyl)(4'-(2,4-dimethylphenyl)(phenyl)amino)-[1,1'-biphenyl]-4-yl)amino)styryl)phenyl)acrylic acid

Figure 1.18 Chemical structure of triarylamine dyes

1.6.3.2.5 Heteroanthracene dyes as sensitzers

Heteroanthracene dyes developed for DSSCs incorporate phenoxazine, xanthenes and phenothiazine. Xanthenes dyes have economical cost e.g. eosin Y, mercuro-chrome and fluorescein were applied as photosensitzers in DSSCs [141-143]. This series of dyes exhibited moderately low efficiency due to narrow visible light absorbance spectrum and low stability. Recently, Yang, Sun and co-workers investigated a class of proficient phenoxazine and phenothiazine dyes as sensitzers [141-142]. Phenoxazine and phenothiazine entity have intense electron donating capability and are used as photosensitzers. HAD-I phenothiazine dye have 5.5 efficiency in liquid state electrolyte [141]. The incorporation of rhodanine and phenylene vinyl in this class i.e. HAD-II, HAD-II and HAD-IV enhanced efficiency of DSSCs. HAD-V dye has co-rhodanine as electron acceptor and thienyl π-bridge system that
decreased aggregation and increased solubility [142]. HAD-V has been investigated for DSSCs and showed 3.0 efficiency. Mu¨llen et. al. reported phenothiazine based dyes with pentaphenylene π-bridge exhibiting 1.8 efficiency [143].

Figure 1.19 Chemical structure of Heteroanthracene dyes

1.6.3.2.6 Carbazole dyes as sensitizers
Wang et al. investigated sensitizing properties of carbazole dyes and its derivative with π-conjugated system of n-hexyl substituted oligothiophenes [144]. Open circuit voltage ($V_{oc}$) and efficiency of DSSCs enhanced by adding n-hexyl group and thiophene entity e.g. $V_{oc}$ (0.69-0.75) for DSSCs based on CBD-I and CBD-II dye (Figure 1.2) that consist of alkyl; group, were higher than CBD-III (0.63-0.67). CBD-II dye as sensitizer with n-hexyl and thiophene exhibited 8.3 efficiency [144]. Kim et. al. synthesized few dyes having N-aryl carbazole entity i.e. CBD-IV dye exhibited good conversion 5.2 efficiency while DSSC based on N719 show 7.8 efficiency under similar condition [145].
1.6.3.2.7 \textit{N,N-Dialkylaniline dyes as sensitizers}

Hara et al developed N, N-dialkyl-aniline entity act as electron donating group, cyanoacrylic acid as electron acceptor and thieryl as π-bridge to introduce new class of dyes i.e. NDA-I, NDA-II, NDA-III, NDA-IV and NDA-V (Figure 1.21) \cite{146-148}. The incorporation of π-conjugated system to N, N-dialkylaniline entity shifted the absorption spectra towards longer wavelength (red shift) in NDA-II, NDA-III and NDA-IV dyes. The maximum 6.8 efficiency was obtained in NDA-III dye \cite{147}. Li et. al. introduced two new dyes NDA-V and NDA-VI containing thiophene segment, that also have rhodamine as electron acceptor and π-conjugation systems \cite{148}. Both dyes exhibited good photovoltaic properties. NDA-VI showed good conversion efficiency of 6.2. Overall, these dyes are good as sensitizers in fabrication of DSSCs.

\textit{Figure 1.20 Chemical structure of Carbazole dyes}
Figure 1.21 Chemical structure of N, N-dialkylaniline dyes

1.6.3.2.8 Hemicyanines as sensitizers
Hemicyanine dyes have p-dialkylaniline entity as electron donor and cationic unit as electron acceptor connected with methine (-CH=CH-) as π-bridge [149-152]. Huang et. al. made many efforts to use these dyes as efficient sensitizers in DSSCs [149-152]. They investigated HCD-I dye (Figure 1.22) consisting benzothiazolium propyl sulfonate group as anchoring and electron acceptor in DSSCs [150]. The study of these dyes showed some effective sensitizers i.e. HCD-II, HCD-III and HCD-IV) (Figure 1.22) [151-152]. HCD-IV showed excellent 6.3 efficiency illumination of white light [152].

![Figure 1.22 Chemical structures of Hemicyanine dyes](image)

### 1.6.3.2.9 Merocyanines as sensitizers

Arakawa et al introduced a class of benzothiazole merocyanine dyes as sensitizers in DSSCs. These dyes have various substituted alkyl, methylene group lengths between the COOH group and the electron donating group [153-155]. MCD-I dye (Figure 1.23) has long alkyl group and showed high efficiency in DSSCs. It was observed in these dyes that increasing the length of alkyl group facilitated the aggregates and enhanced the photovoltaic properties. However, increasing the length of methylene group affected the photovoltaic performance. MCD-II based DSSCs exhibited maximum 4.5 efficiency [155].
1.6.3.2.10 Perylene dyes as sensitizers

Perylene have been used conventionally as pigment or dye for the coloring of several objects. Perylene dyes and its derivatives have excellent photo-stability, resistant to oxidation, fastness properties and show high molar extinction coefficients ($\sim 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) in the visible region [156]. The color of these dyes can be tuned using several substituents on perylene entity [156-159]. Various efforts have been made to improve the photovoltaic properties of perylene dyes [157-158]. Li et al. [159] designed an effective sensitizer PLD (Figure 1.24) which has two thiophenol groups at the 1 and 6 positions. PLD exhibited two absorption bands at 620 and 462 nm with high molar extinction coefficient. DSSCs were fabricated using PLD dye that showed 6.8 and 1.8 efficiencies in liquid and solid-state devices, respectively.

**PLD**: 8-(bis(4-(2,4,4-trimethylpentan-2-yl)phenyl)amino)-5,12-bis(phenylthio)benzo[5,10]anthra[2,1,9-def]isochromene-1,3-dione

*Figure 1.24 Chemical structure of perylene dyes*
1.6.3.2.11 Other organic dyes as sensitizers

Besides the series of dyes described above, some more dyes have been used as sensitizers in DSSCs. Yang et al. introduced few anthraquinone dyes with distinct absorption spectra for DSSCs [160]. However, anthraquinone dyes exhibited low efficiencies. For example, AQD dye based DSSCs exhibited best 0.13 efficiency. Akkaya et al. developed boradiazain dacene (BODIPY) (Figure 1.25) dyes as sensitizers in DSSCs [161]. These dye showed good absorption spectrum in visible region and near infra red (NIR) region. Later, Thummel, Ziessel and others [162] also synthesized and characterized BODIPY dyes. The photovoltaic properties and stability can be enhanced by replacing the fluorine atom on boron. The BODIPY-II (Figure 1.25) dye showed excellent absorption spectrum in visible region.

![Chemical structures of other organic dyes](image)

*Figure 1.25 Chemical structures of other organic dyes*
Zhai et. al investigated the photovoltaic properties of oligothio-phene dyes [163]. The efficiency with OTP dye was found 3.4. Harima, Otsubo and other [164] investigated the oligothio-phene dye sensitizers by improving the structure by substitution of various group i.e. thiophens and alkyl chain. However, the improvement in oligothio-phene structure did not show enhancement in photovoltaic properties.

1.6.3.2.12 Conducting polymers as sensitizers

Many conducting polymeric materials are also reported as sensitizers in DSSCs e.g. polypyrroles (PPY), polyaniline (PANI), poly(p-phenylene ethynylene) (PPV) and poly-thiophenes (PT) [165-167]. Ramakrishna, Liu and other investigated the photovoltaic properties of PMD-I (Figure 1.26) polymer as sensitizer in DSSCs. The efficiency of PMD-I was found 1.4 with high stability [166]. Harima, Ohshita, and other [167] developed few polymeric sensitizes based on disilanylene-oligothienylene entity. PMD-II polymer formed Ti-O-Si bond on the surface of semiconductor layer. The efficiency of PMD-II was found to be 0.12 with good photo stability. These materials have good prospects for the future due to high photo-stability.

Figure 1.26 Chemical structure of polymeric sensitizer

1.6.3.3 Natural dyes complexes as sensitizer

Naturally available fruits, flowers, leave, bacteria etc. shows several colors and contain various pigments which can be simply extracted and applied in fabrication of DSSCs [170]. Advantages of employing these natural dyes as photosensitizers in DSSC are due to their large absorption coefficients in visible region, relative abundance and environmental friendliness [171-172]. Most importantly, the synthesis route for natural dye based DSSC is cost effective as it does not involve noble metals like ruthenium as these were used earlier [173]. These plant pigments exhibit electronic structure that interact with sunlight and alter the wavelengths which are either reflected or transmitted by the plant tissues. This process leads to the occurrence of plant pigmentation and each pigment is described from the wavelength of absorbance maxima ($\lambda_{\text{max}}$) and the color professed by eyes [174]. Pigments for
natural dyes include chlorophyll, carotenoid, flavonoid and anthocyanin that are relatively easy to extract from natural products when compared to synthetic dyes [175]. Figure 1.27 shows the flow chart diagram of different classification of pigments present in plants. The plant pigments are classically defined into four different types as shown in flow chart.

![Plant Pigments](image)

**Figure 1.27 Classification of plant pigment**

1.6.3.3.1 Chlorophyll as sensitizers

Chlorophyll is a green pigment that is found essentially in the leaves of mainly green bacteria, algae and plants. Chlorophylls belong to natural photosynthetic pigments [176-177] which give plants green color. Efficient harvesting of solar power and conversion of energy used for photosynthesis process are the primary functions of chlorophyll and are mainly achieved by their spectral properties. As many as, six different types of chlorophyll pigment have been found and the main form is chlorophyll α. The molecular structure includes a porphyrin ring with Mg center, along with different side chains and a hydrocarbon trail, depending on the chlorophyll type (Figure 1.28). Chlorophyll pigment absorbs radiation in violet, blue and red region of solar spectrum and reflects green color.

![Figure 1.28 Chemical structure of chlorophyll ‘a’ and chlorophyll ‘b’](image)

Chlorophyll is the main pigment in natural photosynthetic systems [178-179]. Its function include harvesting sunlight, converting solar energy (to chemical energy) and transferring electrons. Chlorophyll includes a group of more than 50 tetapyrrolic pigments [180].
Chlorophyll and their derivatives can be applied into DSSC as dye sensitizers because of their beneficial light absorption tendency modes; the most efficient of which is chlorophyll α chlorophyll derivative-methyl trans-3'-carboxy-pyropheophorbide α. Xiao et al. reported that chlorophyll has capability to link titanium oxide (TiO₂) and Zinc oxide (ZnO) layer through various modes [181]. Chlorophyll acts as excellent photosensitizers because of its absorption maxima at 670 nm in the visible radiance region. Amao and Komor reported that the chlorine-e₆ (Chl-e₆) created by Chlorophyll hydrolysis contains three carboxylate groups in a molecule. Furthermore, Chlorophyll does not have any transition metal ion, so is appropriate photosensitizers from the green environment point of view. The absorption spectrum of Chlorophyll-e₆ is similar to that of Chl. The most efficient is the derivative of chlorophyll a (methyl trans-32-carboxy-pyropeophorbid) [174]. The J_sc, V_oc, and FF of the solar energy cell using Chlorophyll-e₆ adsorbed on TiO₂ film electrode are 0.305 mAcm⁻², 426 mV, and 0.45, respectively [182].

1.6.3.3.2 Flavonoids as sensitizers

Flavonoids are the most widespread and important natural constituents that are contributing color to flowers [183-184]. The term "flavonoid" was first applied by Geissman and Hinreiner [185] to wrap up all the compounds whose structure is based on flavones having a basic C₆–C₃–C₆ skeleton. Flavone consist of two benzene rings, joined together by a γ ring that distinguishes one flavonoid compound from the other. Despite these similarities in chemical structures, a few flavonoids have the capability to absorb radiation in the visible spectrum [174]. Fig. 1.29 shows the basic chemical structure of commonly occurring flavonoids.

![Figure 1.29 Chemical structure of commonly occurring flavonoid](image)

There are limited numbers of flavonoid structures that occur in nature, which differ in their oxidation state commencing flavan-3-ol to flavonols and anthocyanins. Flavonoids also include flavanones, flavan-3,4-diols and flavanonols [186]. Also there are as many as five classes of compounds such as dihydrochalcones or 3-phenylpropiophenones, isoflavones,
chalcones or 3-phenyl chromones, or 4-phenyl coumarins and 2-benzylidine-3-coumaranones. The individual compounds in each class are distinguished mainly by the number and orientation of hydroxy and methoxy groups in these two benzene rings [187]. In case of flavonoids, the charge transfer transitions in flavonoides from HOMO to LUMO require lesser energy. Thereby energizing the pigment molecules by visible light, presenting a broad absorption band in the visible region [188]. These natural pigments can be classified into three types, depending on the linkage position of the phenyl ring to the benzopyran moiety: i.e. (a) flavonoids (2-phenylbenzopyrans), (b) isoflavonoids (3-benzopyrans) and (c) neoflavonoids (4-benzopyrans). Flavonoid molecules comparatively have loose electrons; thus, the energy required for electron excitation to LUMO is lower, allow pigment molecules to take energy from the visible radiation. The various flavonoids pigment colors are determined by the property absorbance of wavelengths in visible spectrum and reflected to eyes.

The adsorption of flavonoids to the mesoporous TiO$_2$ layer is excellent presenting an hydroxy (OH) group counter ion from the Ti sites to combine with a proton donated by the flavonoid structure [189]. Flavonoid color is dependent on its primary and secondary structures and are affected by pH consisting intermolecular and intramolecular interactions [190]. The flavonoids dye extracted from Botuje (Jathopha curcas Linn) had been used as a DSSC sensitizer. This solar cell is sensitized to achieve up to $J_{sc}$ 0.69 mAcm$^{-2}$, $V_{oc}$ 0.054 V, and FF 0.87 with a cell conversion efficiency ($\eta$) of 0.12 [191].

### 1.6.3.3 Anthocyanins as sensitizer

Anthocyanins are naturally occurring pigments which reflects colors in the visible region. These compounds are substituted glycosides salts of phenyl-2-benzopyrilium based on a C$_{15}$ frame with chromane ring containing a second substituted phenyl group in position 2 (C$_6$–C$_3$–C$_6$) [192-193]. Basic chemical structure of anthocyanin is shown in Figure 1.30. As many as, 17 structures of anthocyanins have been reported [194] and are classified as per the number of sugar molecules.

Anthocyanins are liable for existence of eye-catching colors, from crimson to blue color of leaves, flower and fruits etc. and are also identified in mosses and ferns [195]. Anthocyanins are also capable to influence the quality and quantity of radiations which incident on the chloroplasts [196]. The type of anthocyanins present in plants is so variable that ornamental plants like dianthus and petunia present one main type of anthocyanin, whereas verbena, tulipa, and rosa have mixtures. Alternatively, several fruits are also sources of anthocyanin pigments. All types of anthocyanins are found in grapes. Whereas, cyanidin is present in
peach, cherry and apple; delphinidin is present in pomegranate. Both cyanidin and peonidin are present in cherry sweet and cranberry. Flowers contain anthocyanins pigment present mostly in epidermal cells and intermittently present in mesophyll [192].

Figure 1.30. Basic chemical structure of anthocyanin pigment in which ‘R’ could be replaced with H, OH or OCH$_3$ based on the pigment. The number can be substituted with hydroxyl group from Table 1.3

Anthocyanin molecules have carbonyl(C=O) and hydroxyl (-OH) functional groups bound to the TiO$_2$ semiconductor layer, which helps in excitation and electrons injection from anthocyanin molecules to the conduction band of porous TiO$_2$ layer [196]. The anthocyanins comprise main flavonoids that are liable for colors range from violet to dark blue, pink through red of mainly leaves, flowers and fruits of angiosperms. These are also present in some other parts of plants i.e. stems, roots and tubers [197]. Commonly anthocyanidins present in flowers are malvidin (blue-red), petunidin (blue-red), delphinidin (blue-red), cyaniding (orange-red) and pelagonidin (orange) [198].

Table 1.3 summarizes characteristic hydroxyl groups that are substituted in various positions in the basic anthocyanin structure. Anthocyanidins occurs in nature have different position of hydroxyl group

<table>
<thead>
<tr>
<th>Name</th>
<th>Position of substitution</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apigenininidin</td>
<td>5,7,4’</td>
<td>Orange</td>
</tr>
<tr>
<td>Aurantinidin</td>
<td>3,5,6,7,4’</td>
<td>Orange</td>
</tr>
<tr>
<td>Cyanidin</td>
<td>3,5,7,3’4’</td>
<td>Magenta and crimson</td>
</tr>
<tr>
<td>Delphinidin</td>
<td>3,5,7,3’4’,5’</td>
<td>Purple, mauve and blue</td>
</tr>
<tr>
<td>6-Hydroxycyanidin</td>
<td>3,5,6,7,3’4’</td>
<td>Red</td>
</tr>
<tr>
<td>Luteolinidin</td>
<td>5,7,3’4’</td>
<td>Orange</td>
</tr>
<tr>
<td>Pelargonidin</td>
<td>3,5,7,4’</td>
<td>Orange, salmon</td>
</tr>
<tr>
<td>Triacetidin</td>
<td>5,7,3’,4’,5’</td>
<td>Red</td>
</tr>
</tbody>
</table>
Anthocyanins extracted from several plants present different photosensitizing properties [199]. These are generally in solution from inside the vacuole, though occasionally available in vesicles called ‘anthocyanoplasts’ [200]. These contain some phenolic groups which are liable to color of several vegetables, flowers and fruits (berries). These are derivatives of glycosylated poly-hydroxyl or poly-methoxy and 2-phenylbenzopyrylium or flavylium salts that are composed of three six-member rings as shown in Figure 1.31.

Figure 1.31(a) Chemical structure of abundant anthocyanidins, (b) anthocyanidins in acidic and basic medium, (c) Chelation mechanism of anthocyanidins with TiO$_2$ layer.

Anthocyanins extracted from different plants present diverse various sensitizing performances [201]. Polo et al. used the extracts of blue violet anthocyanin from Jaboticaba and Calafate as sensitizers and reported to achieve up to $J_{sc}=9.0$ mA cm$^{-2}$, $V_{oc}=0.59$ V, $P_{max}=1.9$ mW cm$^{-2}$ and FF=0.54, whereas Calafate extracts presented up to $J_{sc}=6.2$ mA cm$^{-2}$, $V_{oc}=0.47$ V, $P_{max}=1.1$ mW cm$^{-2}$ and FF=0.36 [202]. Nishantha et al. constructed a solar cell with an anthocyanin pigment, obtained from the barks of Kopsia flavida fruit. The functional group present in these pigments attached to the semiconductor oxide layer which showed $J_{sc}=1.2$ mA cm$^{-2}$, $V_{oc}=520$ mV and FF=0.62 [203]. Khwanchit et al. extracted anthocyanin natural dyes from the flowers of rosella (Hibiscus sabdariffa L.) and blue pea (Clitoria ternatea) as sensitizer of DSSC. They investigated the performance of the DSSC using mixed blue pea–rosella dye and hypothesized that two anthocyanin dyes having various absorption
spectra provided even more synergistic effect than the mixed chlorophyll–anthocyanin dye [204-205]. This result is due to the advantages of anthocyanin over the chlorophyll dye as a DSSC sensitizer [206-207]. Li et al. studied the sensitizing properties of fabricated DSSC with anthocyanin extracted from red cabbage to improve photovoltaic properties [208].

1.6.3.3.4 Carotenoids as sensitizer

Carotenoids are a large group of isoprenoids responsible for providing which provide color (yellow, orange and red) to several flowers and fruits. Carotenoids are distinguished by the presence of C₄₀ hydrocarbon backbone which induces structural and oxygenic modifications. Figure 1.32(a–c) shows the chemical structure of an isoprene unit, xanthophyll and carotene, respectively. The most abundant end group is the β-ionone ring of β-carotene or its derivatives that serve as precursors for vitamins. Other end groups are the ε-ring, which are commonly present in plants and the unusual cyclopentane ring of capsanthin which develop red color in peppers [174]. All carotenoids can be considered as lycopene (C₄₀H₅₆) derivatives which may be converted into different chemical compounds with many chemical reactions [209-210].

They are also classified by their chemical structure as:

1. Carotenes constituting C and H,
2. Oxycarotenoids/ xanthophylls containing C, H and O.

Carotenoids are also categorized as primary and secondary. Primary are essential for plants for their process of photosynthesis. However, secondary are available in flowers and fruits. β-cryptoxanthin, lutein, α- and β-carotene etc. are present in chloroplast of plants [211]. Most of carotenoids synthesized are aliphatic, but some carotenoids have aromatic or β-rings in chlorobiaceae and chloroflexaceae [212]. Carotenoids play two significant roles in photosynthesis process,

(i) light harvesting pigment,
(ii) photo-protectors against oxidative damages.

Figure 1.32  (a) Basic structure of an isoprene unit  (b) Chemical structure of xanthophyll  
(c) Chemical structure of carotene
One of the major structural characteristics of carotenoids is the ability to absorb light that is established with the help of chlorophyll pigments. The light absorption is achieved by a photo induced transformation of ‘p’ delocalized electrons of carotenoid molecules. This in turn transfers the absorbed energy to the chlorophyll molecules to form a singlet chlorophyll state with a slightly higher energy. This transfer of energy from carotenoids to chlorophyll molecules is facilitated by physical structure of chlorophyll [192]. Hemalatha et al. reported that the conversion efficiency of the Kerria japonica carotenoid dye is 0.22 [213]. Carotinoids are compounds consisting of eight isoprenoid units that are widespread in nature, and have great potential as energy harvesters and sensitizers for DSSCs [214].

Theoretical achievements of the chemical and physical properties of natural dye as sensitizers are important in detecting the relationship between the performance, structure properties of dyes and synthesis of sensitizers [215-216]. Koyama et al. reported that the main factor for the increased cell performance is the reduced interface with excited state of sensitizers. A set of retinoic acid and carotenoic acid sensitizers have π-conjugated double bonds [217]. Yamazaki et al. studied natural carotenoids, crocetin, and crocin as DSSC sensitizers. The conversion efficiency of crocetin-sensitized DSCs (0.56) is three times, or higher than crocin (0.16), because of the presence of carboxylic groups in the crocetin molecule [218].

A DSSC was fabricated using anthocyanin, flavonoids pigment, obtained from blackberries was reported by Cherepy et al. [219]. Only the anthocyanin pigment; a mixture of cyanin-3-glycoside and cyanin-3-rutinoside was used as a sensitizer for TiO₂. The photo electrochemical cell was established to show efficiency of 0.56 under full sun. The V_{oc} of 0.4–0.5 V and J_{sc} of 1.5–2.2 mA/cm² were observed suggesting the possibility of efficient charge carrier injection. The value of efficiency was predictable from the electron injection and charge recombination rate. The electrons bring back by the redox electrolytic medium and radiation screening mechanisms were found to edge the efficiency of device.

Usage of blackberry extract to sensitize TiO₂ has been reported by Olea et al. [220]. The black berry extract sensitized TiO₂ was reported to exhibit an increased photocurrent response attributing to excess generation of photoelectrons due to light absorption by the extract. The maximum current, the maximum voltage and overall efficiency of DSSC with 4 cm² active area cell were reported to be 4 mA, 300 mV, and 1, respectively. Garcia et al. [221] reported the use of colorant extracted from mulberry, cabbage palm fruit and chaste tree fruit as TiO₂ photoanode in DSSC. These natural dyes resulted in a short circuit current and open circuit voltage values similar to that of traditional synthesized dyes. The short-
circuit current obtained from 0.5 cm² of DSSC using the extraction of mulberry, cabbage palm fruit and chaste tree fruit as sensitizers were 1.06, 0.86 and 0.37 mA, respectively and the open-circuit voltage for these sensitizers were 390, 422 and 442 mV, respectively.

Hao et al. [222] fabricated DSSC using extraction from rosa xanthina, black rice, kelp, capsicum and erythrina variegata flower. The short circuit current values was found to vary from 1.142 mA to 0.225 mA, the open-circuit voltage from 0.551 V to 0.412 V, the fill factor from 0.52 to 0.63, and the maximum power from 58 μW to 327 μW. Among all these sensitizers, black rice was reported to have the best photosensitization effect. This was attributed to the enhanced interface between carbonyl (C=O) and hydroxyl (O-H) groups of anthocyanin molecule present in the black rice extraction with the layer of TiO₂.

Fernando et al. analised the sensitizing properties of tropical flowers extraction using TiO₂ [223]. J_sc was found in range 1.1 to 5.4 mA/cm² with V_oc ranging from 390 to 410 mV. The efficiency and fill factor of DSSCs obtained was found to vary from 0.2 to 1.1 and 0.53 to 0.64, respectively. Wongcharee et al. [224] constructed DSSC’s with natural colorant extracted from blue pea, rosella flowers as well as combination of these extracts. The team was reported that the mixed extraction adsorbed on TiO₂ did not exhibit synergetic light absorption and sensitization as compared to the entity extracts. The efficiency of DSSC with colorant extracted from rosella, blue pea flowers and combined of these extracts was reported to be 0.37, 0.05 and 0.15, respectively. pH value had an effective on temperature of rosella dye, it was found that the efficiency improved from 0.37 to 0.70 for the DSSC utilizing rosella extract at low pH.

Calogero et al. [225] characterized DSSC based on purple wild prickly pear fruit, bougainvillea flowers, red turnip fruit. The fabrication of DSSC with red turnip extract was reported to be the best performance resulting in a notable J_sc of 9.5 mA/cm² and efficiency of 1.70. The purple colorant of the wild prickly pear fruit exhibited good performances, with a current density of 9.4 mA/cm², with a conversion efficiency of 1.26. The ball-shaped roots of red turnip contain a high concentration of betaxantins (betalain pigments) which was reported to be the reason for the high efficiency of DSSC using red turnip extract. The presence of carboxylic groups in the betalains may be a reason to increase the anchoring of this sensitizer on the surface of TiO₂.

Bazargan et al. [226] investigated the photovoltaic properties of DSSC fabricated with pomegranate extract and found the efficiency1.50. The pomegranate juice contains flavylium (cyanin derivative) at neutral pH which was responsible for good bonding between the dye
and the TiO₂. Flavylium is red in color and has strong bond with Ti⁴⁺ via emanating H₂O molecule which is also responsible for the increase in the efficiency.

Pigments of shisho plants, a well-known vegetable in Japan were employed as sensitizer. Two anthocyanin pigments of shiso plant, referred as shisonin and malonylshisonin were used in DSSC. A promising efficiency of 1.30 with Jₘₑₙ of 4.80 mA/cm² and Vₜₒₙ of 0.53 was reported by Kumara et al. [227]. The pigment shisonin was also separately examined by the authors and reported to have an efficiency of 1.01.

Zhou et al. [228] extracted natural dyes from various parts of plants of traditional Chinese medicines and then used as sensitizers for the fabrication of DSSC. The open circuit voltage obtained was found to vary from 0.38 to 0.69 V and the current density was found to vary from 0.14 to 2.69 mA/cm². Specifically, a high open circuit voltage of 0.69 V was reported for the colorant extracted from mangosteen pericarp.

Kazmerski et al. [229] reported the extraction of several natural colorants containing anthocyanins from tropical flowers. Flavonol glycosides from Sesbania grandiflora and Hibiscus rosasinesis were obtained to produce a promising efficiency of 1.02. The extraction of delphinidin contains flavonol and anthocyanins glycosides in magenta-colored Hibiscus surattensis, which was also extracted to report the results with Vₜₒₙ value ranging from 0.39 to 0.41 V, short circuit current ranging from 1.1 to 5.4 mA/cm², fill factor varying from 0.53 to 0.64 with overall efficiency ranging from 0.20 to 1.14.

Blue–violet pigment extracted from jaboticaba and calafate were applied on TiO₂ sensitizers by Polo et al. [230]. DSSC sensitized by jaboticaba extracts was reported to exhibit a Jₘₑₙ of 9.0 mA/cm², Vₜₒₙ of 0.59 V, maximum power of 1.9 mW/cm² and a fill factor of 0.54. On the other hand, the calafate sensitized cells revealed Jₘₑₙ of 6.2 mA/cm², Vₜₒₙ of 0.47 V, maximum power of 1.1 mW/cm² and fill factor of 0.36. Photochemical stability of tannins made them an interesting and important class of natural dyes.

Tannin pigments were obtained from red sicilian orange juice and were investigated by Calogero et al. [231]. DSSC using tannins and other polyphenols extracted from Ceylon black tea was found to exhibit photocurrents of up to 8 mA/cm² with a conversion efficiency of 0.66. Dyes of curcumin obtained from Curcuma longa L. by Kim et al. [232] were used as sensitizer in DSSC. The Jₘₑₙ, Vₜₒₙ and FF were reported to be 1.6544 mA/cm², 0.5511 V and 0.6646 respectively resulting in a conversion efficiency of 0.60. Natural dyes from the pigments of rhoeo spathacea stearn were used as sensitizers in water based DSSC by Lai et al. [233]. Gold nanoparticles were used as a schottky barrier on a TiO₂ electrode that adsorbs
the dye on it. Such water based DSSC was reported to have reached the efficiency of 1.49 with the aqueous electrolyte of Ce⁴⁺/Ce³⁺ system.

So far, various natural dyes have been utilized as sensitizers in DSSC and it is found that the DSSC with different pigments can produce varied photosensitizing effects, mitigating that only preferred pigments convert solar energy into electricity. The excellent performance was found for betalain pigment due to the better interaction between betalain and TiO₂ [234]. From the investigation it can be seen that, a highest efficiency of 1.86 is achieved in the year 2012 for punica grantum peel consisting anthocyanins [235]. As a next step, red turnip having betalin pigment was identified as a best candidate to exhibit an efficiency of 1.7 in the year 2010 [225]. An efficiency of 1.50 was obtained in the year 2009 and 2014 from the pomegranate juice consisting of flavylium as an important pigment [226]. Likewise, in the year 2013, Rhuc/sumas fruits with anthocyanin pigments were studied and an efficiency of 1.50 was achieved. Natural dyes from the pigments of rhoeo spathacea stearn yielded a conversion efficiency of 1.49 which was reported in the year 2008 [233]. The next highest efficiency of 1.3 was obtained for shisho leaf pigments in the year 2006 [227]. In 2005, chlorophyll derived pigments were used as sensitizers to yield an efficiency of 0.8 [176]. Recently, shiahkooti fruit containing anthocyanin pigment was found to yield an efficiency of 0.73 [236]. In 2011, Huizhi et al. [228] studied on 20 different natural dyes and reported an efficiency of 1.17 as the highest for fructus lycii fruit containing anthocyanin pigment. Extract of rosella flower containing anthocyanin pigment yielded a conversion efficiency of 0.7 in the year 2007 [224]. Though research on natural sensitizers gained attention from the year 2004, anthocyanin pigment containing natural dye based DSSC was successfully fabricated and studied by two research groups in the year 1997 [220,229]. An efficiency of about 1.02 was achieved by them by employing the extracts of blackberries, sesbania grandiflora and hibiscus rosasinesis flowers to fabricate DSSCs.

1.6.4. Electrolytes

The electrolyte plays one of the most relevant roles in the process of light-to-electricity conversion, since it works as an electron transfer mediator with the function of regenerating the dye sensitizer from the oxidized state. The requirements that must be met for any electrolyte employed in a Dye-sensitized Solar Cell are listed here below:
a) The electrolyte must have long-term stability, including chemical, thermal, optical and electrochemical stability and must be able to prevent the degradation of the dye from the oxide surface.

b) The electrolyte must be able to transport efficiently the carriers between the working electrode and the back electrode. After the injection of the electrons into the conduction band of the oxide material, the oxidized dye must be regenerated and reported to its ground state. That is why the electrolyte must be chosen in a proper way in order to take into account the redox potential and the recombination properties of the dye.

c) The electrolyte must ensure the fast diffusion of the charge carriers into the device and produce good contact with the porous nanocrystalline oxide layer and the counter electrode. For liquid electrolytes it is necessary to prevent the loss of the solution by leakage or evaporation.

d) The electrolyte should not exhibit a significant absorption in the range of visible light. For electrolytes containing I-/I$_3^-$ couple, since I$_3^-$ has its own color and reduces the visible light absorption by the dye, and I$_3^-$ ions can react with the injected electrons, the dark current should be increased; that is why the concentration of I$^-$/I$_3^-$ must be optimized.

Electrolytes for DSSCs can be classified as liquid, quasi-solid, or solid, depending on their viscosity. The most common class of electrolytes used in DSSCs are the liquid organic solvent-based materials. They are usually constituted by a redox couple dissolved in a high dielectric constant organic solvent; however some additives can be added to increase the device performances [237-238].

1.6.4.1 Liquid electrolytes

The iodide/triiodide (I$^-$/I$_3^-$) is the most prominent liquid redox electrolyte used in DSSCs due to its kinetics [239]. The electron injection into the semiconductor (TiO$_2$) conduction band occurs in the femto-second range of time that is very rapid to recombination of electron with I$_3^-$, and the oxidized molecule combined with I$^-$ than combining with the injected electrons. The highly employed redox couple is iodide/triiodide (I$^-$/I$_3^-$), mainly because of the slow recombination reaction; electrolytes based on this couple are commonly prepared by dissolving iodide salts with different cations (Li$^+$, Na$^+$, Mg$^{2+}$) in a solvent. The corrosive properties of iodine have however led to the investigation of alternative redox couples, like Br$^-$/Br$_3^-$ [240], SCN$^-$/SCN$_3^-$ [241] and SeCN$^-$/SeCN$_3^-$ [242], which have promising
electrochemical and noncorrosive properties, these electrochemicals lack in chemical instability [238]. However, some coordination compounds such as copper and cobalt complexes can act as redox mediators [243-244]. Currently, Co complexes are the most promising redox couples, since they are noncorrosive, nonvolatile, and relatively transparent to the visible light. Moreover, it has been recently shown that Co(II/III)tris(bipyridyl)-based redox electrolyte exceeds 12 efficiency [245].

Concerning the solvent, it must have low volatility in the operating DSSC temperature range, low viscosity in order to allow the fast diffusion of charges, and a high dielectric value to make the redox couple dissolution easier[238]. Amongst all the solvents used in DSSC, acetonitrile is regarded as the most performing, due to its excellent stability, low viscosity and capability to dissolve a lot of salts and organic molecules. Unfortunately boiling point of acetonitrile is low (78 °C), so for long-term stability tests of the DSSCs the preferred choice falls on 3-methoxypropionitrile (MPN), characterized by 164 °C boiling point and low toxicity: an efficiency of 7.6 after 1000 h of continuous irradiance has been achieved using MPN as solvent [246].

1.6.4.2 Solid state electrolytes

A solid-sate electrolyte exhibits good mechanical stability and easy fabrication method as compared to liquid electrolyte. These can overcome the drawbacks of liquid electrolyte i.e. evaporation of solvent and leakage of in devices. However, the main disadvantage of solid electrolyte is the poor contact interface between semiconductor and electrolyte.

Tennakone et al. [247] and O'Regan and Schwartz [248] first reported the solid-sate electrolyte i.e combination of CuSCN and CuI. The efficiency of DSSCs was found less than 1 due to formation of unfilled voids on semiconductor interface. Kumara et al. [249] investigated triethylaminehydrothiocyanate (THT) that inhibit the crystal growth to enhance efficiency up to 3.75. Heng et al. [250] reported an efficient electrode TiO$_2$/CuI/Cu which exhibit 4.73 efficiency. Bach et al. [251] investigated p-type semiconductor, spiro-OMeTAD (2,2’,7,7’-tetranis-(N,N-di-p-methoxyphenyl-amine)9,9-spirobiﬂuorene) exhibiting excellent efficiency nearly 5.

Solid state electrolytes are represented by conductive polymers, hole-conducting molecular solids or organic p-type conductors, like polypyrrole [252], poly(3,4-ethylenedioxythiophene) (PEDOT) [253], poly(3-hexylthiophene) (P3HT) [254], polyaniline (PANI) [255] and
2,2',7,7'-tetranis-(N,N-di-p-methoxyphenyl-amine)9,9-spirobifluorene(spiro-OMeTAD) [256]. However, the photovoltaic performances of DSSCs based on all these alternative electrolytes are currently lower with respect to the liquid solvent-based ones, so further research is required.

1.6.4.3 Quasi-solid electrolyte

The maximum efficiency of solid state electrolyte DSSCs is less than 5 due to poor contact at interface of semiconductor and electrolyte which decrease the conductivity of device [257]. To solve this problem an attempt was made in which properties of both liquid and solid electrolyte can be combined to form a gel electrolyte or quasi-solid electrolyte. These electrolytes have various advantages over solid state electrolytes i.e. higher ionic conductivity, good stability and remarkable interface contact between semiconductor and electrolyte. Wang et al. [258] investigated PVDF-HFP polymer with MPN liquid electrolyte exhibit efficiency more than 6. Later, Semi-solid ionic electrolyte by adding nano-SiO₂ to form ionic quasi-solid-liquid state electrolyte was presented which exhibited efficiency nearly 7 [259].

1.6.5 Counter Electrodes

1.6.5.1 Platinized Conducting Glass

Counter electrodes in DSSCs are formed by applying Pt layer as catalyst on the substrate. Substrate act as poor counter electrode due to high resistance in standard I/I₃ solution [260]. Electrodeposition, sputtering, spray and chemical vapor deposition methods can be used for making counter electrode. Best stability and photovoltaic properties has been shown by nano-platinum layer formed by thermal decomposition of PtCl₄. The counter electrode still remains transparent because a very low amount of platinum (5µ/cm²) is needed. The low resistance (1Ω cm²) of counter electrode was achieved by electrodeposition [261] and chemical vapour deposition (CVD) [262] on the substrate.

1.6.5.2 Carbon Materials

Carbon materials are considered to be suitable as catalysts for the reduction of I₃⁻. Kay and Gra`tzel analysed a counter electrode from a combination of carbon black and graphite with the monolithic cell geometry in DSSCs [263]. Pettersson et al. investigated the properties of the counter electrodes by using two carbon layers: one layer to increase the adhesion to the substrate and another layer for improving catalytic properties (doped with Pt) as well as
conductivity [264]. The layer deposited on the substrates from carbon powders having particle sizes in the range of 30 nm (carbon black) showed a low resistance (1 Ω cm$^2$) with a thickness of layer up to 20 µm[265-266]. High conductivity and good catalytic properties were observed to the reduced I$_3^-$ by applying layer single wall carbon nanotubes [268].

### 1.6.5.3 Conducting Polymers

Conducting polymers have also been used in making of counter electrode due to their high stability and conductivity. Poly(3,4-ethylenedioxythiophene) (PEDOT) doped with toluenesulfonate anions exhibit good catalytic properties for the reduction of triiodide DSSCs [269-271]. The layer prepared on substrates showed less than 1 Ω cm$^2$ resistivity with 1 µm thickness. Other conducting polymers (i.e. polyaniline, polypyrrole) can be used in making of counter electrode [269].

### 1.7 Aim of the present work

Despite of lesser relative efficiency, dye sensitized solar cells have many advantage over silicon cells. The main advantages of these cells over silicon cells are very low cost, ease of making and constructing from abundantly available dye materials. Several dyes can absorb entire region of the solar energy that can be exchanged to electric energy. Of course, a vast number of synthetic dyes and naturally occurring pigments/colorants are available, our aim is to select a few potential synthetic dyes and some commonly available colorant present in local flowers and fruits and then to characterize them for their potential use for harvesting solar energy through radiation excited or ‘photo-generated’ electrons. Several synthetic dyes that have been aimed as photosensitizers are as follows:

1. Azo dyes
   1. Solochrome black T
   2. Methyl orange
   3. Amido black 10B
   4. 4-(2-Pyridylazo) resorcinol

2. Triarylmethanes
   1. Patent blue V
   2. Rosaniline hydrochloride
   3. Solochrome cyanine R
   4. New fuchsine
3. Xanthenes dye
   (i) Rhodamine B
   (ii) Rhodamine 6G

4. Other dyes
   (i) Alizarin
   (ii) Safranine

Several colorants have been extracted from the naturally occurring flowers and fruits and have been explored from their higher harvesting characteristic and these were:

   (i) Rosaceae (Red rose)
   (ii) Hibiscus rosa-sinensis (China rose)
   (iii) Callistemon viminalis (Bottle brush)
   (iv) Delonix regia (Flame Tree)
   (v) Papaver somniferum (Moth Poppy)
   (vi) Tagetes erecta (Marigold yellow)
   (vii) Tagetes patula (Marigold orange)
   (viii) Bombax ceiba (Cottan tree)
   (ix) Pentas lanceolata (Star cluster)
   (x) Syzygium (Blackberry)
   (xi) Punica granatum (Pomegranate)
   (xii) Solanum nigrum (Nightshade)

Another part of the research aim is to utilize several combinations of electrolyte solutions, which serve as internal pathway for negatively charged ions to carry electron from cathode to anode, Thereby completing the electrical circuit. The following combination of electrolytes have been investigated:

   (i) Potassium iodide (KI) with iodine (I$_2$)
   (ii) Tetramethylquaternaryammonium iodide [(CH$_3$)$_4$NI] with iodine (I$_2$)
   (iii) Tetraethylquaternaryammonium iodide [(CH$_3$CH$_2$)$_4$NI] with iodine (I$_2$)
   (iv) Tetrapropylquaternaryammonium iodide [(CH$_3$CH$_2$CH$_2$)$_4$NI] with iodine (I$_2$)

The efforts carried out for our research work has been subsequently presented in the following chapters.
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