Introduction, theoretical background and brief literature survey of the research topic are given in the chapter. In the beginning, the general introduction of energy sources, solar radiations and solar energy is given. In next section different generations of solar cells, dye sensitized solar cells, their merits, working principle and processes are given. In the next section, the different functional components of DSSCs are explained in detail along with their role in DSSC, present status and opportunities. Further, in the ensuing section, a brief survey of data reported in literature in terms of photovoltaic parameters and different combination of DSSC components are tabulated. In the last section, the aims and objectives of present research work along with the orientation of thesis are defined.
1.1: Introduction

To fulfill almost all day to day essential needs of human beings on earth, energy particularly, electric energy with sufficient supply is an essential component. The energy needs of the world are increasing super linearly with increase in population as an effect of globalization. At present, most of energy needs are met from the fossil fuels. Fossil fuels are rapidly declining and also are cause of environmental pollution. In view of the above, there is an urgent need to search for an alternative energy source to solve the problem of limited capacity of fossil fuels and related environmental issues [1, 2]. Also the source must be abundant and economic all over the world. Some natural sources such as geothermal, biomass, wind, hydrothermal and solar radiations are the emerging alternatives. Out of all these renewable energy sources, the solar energy is one of the most attractive alternatives due to its clean and abundant availability over the surface of earth. The magnitude of solar power incident on the earth’s surface is about 4.3x10^{20} J per hour, which is higher than all the energy consumed by the whole of humanity in one year (4.1x10^{20} J)[2-4].

1.2: Solar radiation

Sunlight comes in many waves with different frequencies, combining photons of low (~1.1 eV, infrared) to high (~3.5 eV, ultraviolet) energy. Fig. 1.1 shows the extraterrestrial and terrestrial spectrum of sunlight with respect to planet earth directly facing the sun. The radiant energy falling within the visible spectrum, with wavelengths between 0.4 µm and 0.75 µm, is about 46% of the total spectrum, 47% constitutes infrared region and only 7% of it is in the ultraviolet region. The actual amount of solar energy reaching the earth surface after passing though atmosphere varies with time, latitude and weather conditions and is known as insolation (incident solar radiation). When the Sun is directly overhead i.e. perpendicular to earth surface, the insolation is typically 1000 Watts per square meter (W/m^2). Due to rotation of earth round the sun, insolation is below this value most of the time. This causes the change in path length of solar radiations. The ratio between the actual path length of the solar radiation through the atmosphere and the vertical path length through the atmosphere is known as Air Mass (AM).
As shown in Fig. 1.2, with the sun overhead, the radiations passes straight away directly to the earth surface, known as 1 AM radiation. However, if the solar radiations are not reaching perpendicular to the Earth, the path length through the atmosphere will be longer. This results in either gain or loss of the solar energy.
absorption by a factor of $1/\cos \phi$, where, $\phi$ is the deviation of solar radiation from perpendicular of the radiation and is also called the zenith angle. The atmospheric path for any zenith angle is simply described relative to the overhead air mass [4-6].

International Electrotechnical Committee (IEC) has defined standard test condition (STC) for efficiency measurements of solar cells as 1000 W/m$^2$ irradiance with 1.5 AM and 25$^\circ$C temperature, giving $\phi = 42^\circ$ [4-6].

### 1.3: Solar power conversion

In order to utilize the solar energy, the radiation needs to be converted into an electric energy. This phenomenon is known as photovoltaic effect. The device which is able to convert the solar radiations directly into electric energy is known as solar cell. Photovoltaic effects were first observed about 150 years ago. In 1839, Becquerel detected a photo voltage when sunlight was incident on one of the two electrodes placed in an electrolyte solution [7]. Incident photon flux causes generation of electron hole pairs at the electrode. As electrons and holes move in opposite directions from one another, a small current is established that can drive a load. Various semiconducting materials are used for this purpose. The interaction of photons of sufficient energy in the variety of a p-n junction of a semiconductor through absorption results in the release of electron hole pairs. These charge carriers are driven by the junction field to their n and p regions, respectively giving rise to some voltage with drives the external load resulting in current. Though the photovoltaic effect first observed by Bacquerel, the first modern solar cell was patented by Russel ohl in 1946[8]. In 1954, researchers at the Bell Telephone Laboratories demonstrated the first practical conversion of solar radiation into electricity via use of a p-n junction type solar cell with 6% efficiency. During the 1960’s and 1970’s silicon cell technology emerged as a useful source for alternative energy. To increase the utility of this abundant resource, increases in production by the decrease in cost besides attaining maximum photoconversion efficiency are the challenges before the researcher in this field. Since the emergence of this alternative as a reasonable and clean technology, for energy production, there have been three generations in to which it is classified[2,9,10].
1.4: Generations of solar cells

1.4-1: First generation

First generation solar cells are known as the silicon based solar cell. This is because, the cells were based almost solely on silicon technology, specifically single-crystal silicon and operate on the basis of a p-n junction type semi-conducting system. They usually consist of crystalline silicon which is doped with inorganic solid-state materials. Si has a low band gap 1.11 eV, which provides broad spectral absorption range. The laboratory scale solar cells have already achieved 25% efficiency, but it is expensive and energy intensive manufacturing technology, which increases the generated power cost. It is estimated that material contributes to 70% of the total cost of 1st generation and has little room for a decrease in production costs or increases in solar conversion efficiency beyond 18%. Also, for this type of device the theoretical limit (Shockley-Queisser limit) is 31%. This led to the advancement in photovoltaic technology with less expensive thin film materials. The device based on such a class of material falls under second generation [2, 9, 11].

1.4.2: Second generation [12-14]

The second generation contains types of solar cells based on less requirement and cheaper materials, like amorphous silicon (a-Si), polycrystalline silicon (p-Si) and polycrystalline CdS, InSe, Copper Indium Gallium Selenide (CIGS), copper indium gallium diselenide (CuInSe₂) and cadmium telluride (CdTe). The absorber layer CuInSe₂, CdTe coupled with n-type CdS is used to create pn-hetero junction. Due to the large band gap of CdS (2.4 eV), it is utilized as a window to the p-n junctions. For direct band gap semiconductors, only a thin film (~5 μm) is required for complete light absorption, unlike to first generation silicon cells (~100μm). One of the major advantage of this technology is, it requires very less material to prepare thin films, which contributes greatly to reduced costs for thin film solar cells. Several second generation technologies/semiconductor materials are currently under investigation for mass production. The major disadvantage of a-Si panels is that they are much less efficient (~ 10%) and are generally not suitable for roof installations. Long term stability of amorphous silicon cells is also a matter of concern. p-Si consists, solely of crystalline silicon grains (1mm), separated by grain boundaries and has low band
gap ~ 1.1 eV. Charge carrier mobility in p-Si is one order of magnitude higher than a-Si, and shows greater stability under electric field and light-induced stress. Maximum efficiency of p-Si cells is ~ 20%. However, p-Si cells are fragile and the cost is still high for widespread use. On the other hand, CdTe has an excellent solar matching absorption spectrum with a band gap of 1.5 eV and is relatively easy to handle as a thin film. With CdTe as a absorber layer, the laboratory scale efficiency of about ~ 20.4% has already been achieved (Feb 2014) by First Solar, USA. However, due to large differences in work functions with the metals used for contacting, there are problems in creating low resistance ohmic contacts. In addition to this, toxicity of these materials has been an environmental concern. Another material namely CIGS is a compound semiconductor, solar cell made of which shows efficiency ~ 20.8%. It is worth noting that CIGS based cells have a complex hetero-junction model and are difficult to prepare. In addition to this, because they are ternary compounds, their preparation entails complex manufacturing techniques. In view of the above demerits, a new generation of solar cells evolved and is known as third generations of solar cell [15-17]

1.4-3: Efficiency limits in 1st and 2nd generation solar cell

In 1961, William Shockley and Hans Queisser reported the maximum theoretical photo conversion efficiency of an ideal solar cell using a p-n junction mechanism, known as the Shockley Queisser (SQ) Limit. The modern SQ Limit calculation is a maximum efficiency of 33% for any type of single junction solar cell. The original calculation by Shockley and Queisser was 31% for a single junction silicon based solar cell [2, 9, 11, 13]. Till date solar cells from both these generations could not exceed the SQ limit.

1.4-4: Third generation

The third generation solar cell differs from conventional solar cell not only in their structure but also in working mechanism. It is an approach to provide low cost, easy fabrication photovoltaic technology and to overcome the 31% SQ limit on photo conversion efficiency [3]. Most of the technologies in this generation are not yet commercialized. The photovoltaic research and development, however is looking towards it as a suitable and affordable alternative to conventional one. Hence, lot of
research is going on in this area. The solar cells developed under this generation are of two types viz. the organic hetero-junctions and dye-sensitized solar cells (DSSCs).

In organic heterojunction solar cells, the charge separation occurs at the junction of organic polymers. In general it comprises the pair of electron donor and acceptor polymers. Organic heterojunctions have two different structures, the bilayer and the bulk heterojunctions. The bilayer is similar to the p-n heterojunction, while the bulk heterojunction is the p-n interfaces by interlinking. The maximum reported efficiency with this system is around 7%, but it has a vast potential due to availability of limitless organic polymers and their tailored properties [18-22].

However, DSSC received great attention because of being eco-friendly and their cost effective technology for solar energy conversion. [3, 23-27].

1.5: DSSCs as a promising alternative to the present photovoltaic technology

DSSC is a promising alternative to conventional semiconductor solar cell because of its less cost and easy fabrication technique. In 1991, O'Regan and Gratzel published first report on DSSC working device with a photo conversion efficiency of 7%. Since then DSSC drew great attention of research community as an inexpensive alternative. DSSCs can be easily fabricated using abundant environment friendly metal oxide nanoparticles and metal complexes or organic dyes without using any expensive vacuum technology or high temperatures processing required for conventional Si based or thin film photovoltaic device production [3, 23, 24].

1.5-1: Schematic of DSSC

DSSC comprises four different components: mesoporous semiconductor electrode with a high surface area, light harvesting dye molecules, hole transfer mediator redox electrolyte couple and counter electrode. The schematic of DSSC structure is shown in Fig. 1.3.

It is basically composed of two transparent conducting substrates (mostly, FTO) onto which a few micrometers thick film of wide band gap metal oxide semiconductor nanoparticles has been deposited. This will provide a high surface area for adsorption of dye molecules and nanoparticle network for the diffusion of injected electron. The dye is regenerated by a redox couple in the electrolyte. Another remaining conducting substrate is act as counter electrode [24, 28].
The dye adsorbed metal oxide semiconductor film acts as a light harvesting electrode. Redox couple is used for regeneration of the oxidized dye molecules after electron injection. The conducting substrate coated with thin catalytic layer of platinum or carbon act as counter electrode for regeneration of redox species. The device is illuminated from the light harvesting electrode side [24, 28-32].

**1.5-2: Merits of DSSC over conventional p-n junction solar cells**

DSSC has potential to become an effective alternative to conventional photovoltaic technology based on the following merits:

- Maximum surface area of the photoanode facilitates greater quantities of dye adsorption leading to better light harvesting efficiency.
- Have a capability to exceed SQ limit.
- Manufacturing depends on cheaper and abundant oxide nanoparticles and coordination complexes or organic dyes without processing in vacuum or high temperatures. This makes DSSC cost effective.
- Fabrication on flexible substrate with aesthetic designs and colors is also possible.
- Light in weight
- Short energy payback time (<1 year)
- Works better in diffused light hence explore its applications in indoor conditions.
- Independent of angle of incident solar radiation.
1.5-3: Operating mechanism of DSSCs

The operating mechanism of the DSSCs is shown in Fig. 1.4. The current generation process under illumination happens throughout the following five processes at different interfaces in the devices [28-33].

1.5-3(i): Charge generation and collection processes

Process 1: photon absorption ($P_1$):

Under illumination, dye molecules absorbs the photon flux, causes electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The LUMO must have energy level above the conduction band edge of the semiconductor metal oxide.

Process 2: electron injection ($P_2$):

The electrons are injected from dye molecule to conduction band of metal oxide. The difference in energy, density of states and the complex conjugate orbits between dye molecule and semiconducting metal oxide surface are responsible for electron injection.

Process 3: electron percolation ($P_3$):

The injected electron is forced to move towards conducting electrode via trapping and de-trapping events in the material nanoparticle network. These electrons move through the external circuit towards the counter electrode.

Process 4: dye regeneration ($P_4$):

The oxidized dye species is reduced back by means of redox couple before it recaptures the conduction band electron. This process allows the dye molecule to absorb the photon striking it next.

Process 5: redox species regeneration ($P_5$):

With the help of catalytic activity at the counter electrode, the oxidized species of redox electrolyte is reduced to its original state before recombination of CB electrons occurs. Therefore the maximum photo voltage with DSSCs is given by the difference between the semiconductor conduction band edge and the redox potential of electrolyte. Thus, as long as there is incidence of light over the
photoanode, the electric power is generated without permanent chemical transformation.

![Diagram of DSSC operating mechanism](image)

**Fig. 1.4: The operating mechanism of the DSSCs**

If the above process does not happen ideally, as stated, the device operation undergo certain unwanted processes and which further contribute to the rate limiting factor for the performance of DSSCs.

**1.5-3(ii): Performance limiting factors [30-36]**

There are also several factors, which affects the performance of DSSCs, during electron transfer. **Fig. 1.5** shows the schematic of performance limiting factors.

**Performance Limiting Process (LP₁):**

The rate of electron injection must be faster than the decay of the oxidized dye. It is also possible that the dye may decay without injection of electron.

**Performance Limiting Process (LP₂):**

The injected electron may undergo recombination with the oxidized redox species itself before regeneration of dye.
**Performance Limiting Process (LP₃):**

If the redox species is able to regenerate the oxidized dye molecules in a stipulated time, then this will prevent the electron from recombination, which happens due to LP₂. But the oxidized redox species, which is created during dye regeneration process, provides new chance for electron recombination. The CB electron may recombine with the oxidized redox species; this is known as back electron transfer.

**Performance Limiting Process (LP₄):**

The Conduction band electron may also recombine with oxidized dye molecule.

**1.6: Functions, required properties of each component of DSSC and commonly used materials**

**1.6-1: Conducting substrate**

The substrate is the base support layer of DSSC. It must have high transparency in visible spectral region to pass the photon flux. It must also have good
conductivity with low sheet resistance. The material which falls under such category is known as transparent conducting oxide (TCO). The preferred TCO in DSSCs are indium doped tin oxide (ITO) [37], fluorine or antimony doped tin oxide (FTO, ATO) and indium doped zinc oxide [37const, 38]. TCOs generally are prepared on a glass substrate by sputtering, electron beam evaporation, chemical vapor deposition and oxygen ion beam assisted deposition methods. A cost effective spray pyrolysis techniques is also adopted for this purpose [39]. Of all these, fluorine doped tin oxide (FTO) is mostly used due to its better thermal stability, low sheet resistance, good transparency to the visible light as compared to others. It is observed [40] that the resistivity of ITO increases considerably after heat treatment to the metal oxide semiconductor layer deposited on it. This further contributes to the increase in series resistance of DSSC. Such a performance limiting process is not observed in case of FTO [33, 41]. In SnO₂, fluorine substitutes O²⁻ ions, and therefore acts as an electron donor, resulting in increase in conductivity while maintaining transparency. Now a days FTO and ITO based TCOs are commercially available with surface resistivity of about (7 Ω /Sq.) for FTO, (70-100 Ω /Sq.) for ITO and optical transparency near about 90 % [40].

1.6-2: Metal oxide semiconductor as a photoanode

The assembly of metal oxide deposited on TCO is known as photoanode. It has to carry out two major functions in DSSC. First, it has to act as a support for anchored dye molecules and provide a path for fast transport of photo-induced electron towards the conducting substrate before recombination. Large surface area with good amount of porosity, structure and suitable morphology of the semiconductor materials are important features for better performance of DSSC [23, 24, 42, 43].

In addition to this the favorable band energies between the semiconductor and the light harvesting dye is highly indispensible. To have an energetically favorable electron injection, the CB position must be lower as compared to LUMO of the dye with respect to the reference of vacuum level. Since the semiconductor has a wide band gap, it will not absorb the visible light, and not many electron-hole pairs are created. Sensitization of metal oxide semiconductor surface with light harvesting molecules extends their absorption into the visible wavelength region for photo conversion.
As possible candidates for photo anode in DSSC, the metal oxides should not undergo decomposition under illumination [24, 42, 43].

For conduction of photo-induced electrons, it must be of n-type, although there is the possibility, that quenching of the sensitizer can occur through energy transfer from the presence of conduction band electrons [44]. The sensitizing property can be improved through the use of metal oxide nanoparticle layer of optimal thickness and porosity, both of which increase surface activity of the layer significantly [45]. The nanostructured mesoporous material will offer maximum surface area as compared to a flat surface of photoelectrode, which will be beneficial for increased uptake of a sensitizer loading to enhanced light harvesting [46].

There are several metal oxide films which are suitable for this application viz, TiO$_2$, ZnO, SnO$_2$, SrTiO$_3$, CdO, Nb$_2$O$_5$ and WO$_3$ [24, 47-49]. At present, TiO$_2$ has been the most widely used semiconducting surface for DSSCs, due to its high abundance, relatively low cost, non-toxicity, ease of production and chemical inertness [23,45]. The anatase form of TiO$_2$ is a wide band-gap (3.2eV) indirect semiconductor [45]. The TiO$_2$ semiconducting surface thus allows the low energy visible light photon flux to pass through it.

For TiO$_2$ films, mostly the colloidal suspension of commercially available TiO$_2$ nano powder, (P25, Degussa AG) has been used in this research. It consists of TiO$_2$ nanocrystalline particles with particle sizes averaging around 25 nanometers. A mixture of organic binder, surfactant and nanoparticles in suitable solvent is used for the preparation of paste. The films are made by doctor blade and screen painting method at large scale. The organic binders are used to have a mesoporous structure of the layer, while the surfactant helped to get a better suspension of nano particles in order to form network like structure. The sintering process after drying burns out the organic binders and also sinters the nano particles together to form adherent film on TCO. However, the literatures do not show any particular optimized process for the fabrication of photo electrode. The process varies depending on need, particle size, material and availability of the organic binders.

Other than TiO$_2$, research on different metal oxides also showed considerable performances. In particular, the extensive research is still going on DSSCs with the photo electrode of ZnO, Nb$_2$O$_5$ and SnO$_2$, but still they exhibited lower performance in comparison to DSSCs prepared with TiO$_2$ [50-52]. The nature of band structure also
influences the electron density and electron injection, even though the semiconductors have large band gaps. For instance, the band structure of Nb$_2$O$_5$ has the same band gap energy as TiO$_2$ (3.2 eV). But its conduction band is located 0.2-0.3 eV more negative with respect to vacuum. Such a CB position is not favorable for injection of electrons from LUMO of the dye. Another attractive photo electrode is ZnO. It is a wide band gap semiconductor with better carrier mobility as compared to TiO$_2$ [48]. Its conduction band position is also at same position as that in TiO$_2$. But, the performance of DSSCs based on ZnO is not as effective as TiO$_2$. The limiting factor in ZnO based DSSCs is mainly due to two reasons; one lies with the surface chemistry of ZnO film, which restrict sufficient dye adsorption and another is lack of variable valence of the metal ion. For example, Ti is variable as Ti$^{3+}$, Ti$^{4+}$, but Zn is always in the state of Zn$^{2+}$.

1.6-2(i): SnO$_2$ as a suitable material for photo anode in DSSC

Promising optical and electrical properties of SnO$_2$, drew the attention of researchers as an alternative photo anode for DSSCs. SnO$_2$ is a wide band-gap n-type semiconductor (E$_g$= 3.6 eV at 300 K) with suitable optical and electrical properties for its use in DSSC [53]. Its large band gap as compared to other metal oxides, makes it possible to avoid generation of holes in the valence band through direct photon absorption. The wide band gap SnO$_2$ can also withstand UV illumination without degradation. It also possesses high electron mobility (upto 240 cm$^2$ V$^{-1}$ s$^{-1}$) than TiO$_2$ and ZnO which is beneficial for charge diffusion in SnO$_2$ based DSSCs. The energy conversion efficiency of DSSCs based on SnO$_2$ is still low as compared to that based on TiO$_2$ due to interfacial charge recombination losses [49, 54].

Under normal conditions, electron concentration and mobility, estimated from Hall Effect measurements for SnO$_2$ mono crystals is 10$^{16}$ cm$^{-3}$ and 200-400 cm$^2$ V$^{-1}$s$^{-1}$, respectively [55-57]. Tin dioxide is also chemically inert compound similar to many other oxides.

The position of the conduction band of SnO$_2$ (vs. Normal Hydrogen Electrode, NHE), is almost 0.4 - 0.5 V lower than that of TiO$_2$, which favors the fast electron injection from dye into its conduction band [58]. Studies performed on SnO$_2$ based DSSCs using N3 and N719 dye have reported photo conversion efficiency up to
around 4% [49, 54, 58-62]. However, the performance of SnO$_2$ photo anode based DSSCs are lower as compared to those based TiO$_2$ or ZnO [59, 60].

Figure 1.6: Band positions of different metal oxide semiconductors with respect vacuum and NHE.
(Source: http://www.nature.com/nature/journal/v414/n6861/fig_tab/414338a0_F2.html, [3])

The poor device performance has been attributed mostly to the faster electron recombination in the SnO$_2$ layers as well as the weak adsorption of dyes [62, 63].

**Fig. 1.6** shows the band energies of different metal oxides with respect to vacuum as well as normal hydrogen electrode (NHE). It is observed from figure that, SnO$_2$ has the conduction band edge minimum more positive as compared to ZnO and TiO$_2$ (at -0.5 volt Vs NHE) [3, 64].

**1.6-2(ii): Physical properties of SnO$_2$**

Tin dioxide has a tetragonal rutile crystalline structure known in its mineral form as cassiterite with space group $P4_2/mnm$, No. 136. Its crystalline structure consists of Sn and O atoms in octahedral and planar coordination, respectively. Unit cell parameters are: $a = b = 4.7437$ Å, $c = 3.186$ Å and cell volume is about 71.5 Å. The ionic radius for Sn$^{4+}$ at six fold coordination was found to be 0.69 Å. In spite of the
high enthalpy of Sn–O bond formation ($\Delta H_{298}^{\circ} = -286 \text{ kJ/mol}$ [57] the bond is not completely ionized [53, 55].

![Structure of SnO$_2$ unit cell](image)

**Fig. 1.7: Structure of SnO$_2$ unit cell** [adopted from [56]]

The intrinsic defects due to surface oxygen vacancies in crystallite structure and “partial” ionization makes SnO$_2$ behave like an $n$-type semiconductor material [53]. The atomic orbital configuration of Sn and O atoms is $5s^2 \ 5p^2$ and $2s^2 \ 2p^4$. The band model shows that valence band is made up of O 2p states, while conduction band is made up of Sn 5s states. Conduction band with s orbital becomes one of the reasons for transparency of SnO$_2$ with good conductivity [57].

The cost reduction in the manufacturing process of the device involves several easy fabrication methods. These are already adopted for the synthesis of metal oxide semiconductor layer at lab scale as well as in industries. These technique includes doctor blade method, screen printing, ink-jet printing, low temperature sintering [65, 66] and hydrothermal growth [67, 68].

**1.6.3: Dye molecules as light harvester**

This is one of the functional components of DSSC also known as photosensitizer. For efficient light harvesting, the sensitizer should have intense absorption in the visible region and strong adsorption onto the semiconductor surface. With this, it should also have following essential characteristics [69, 40].

The molecular structure of the dye should be able to absorb the maximum visible region and near-infrared (NIR) region, where the intensity of sunlight is strong. It should have high molar absorptivity over a broad spectral range. The light
harvesting efficiency (LHE) and observed photocurrent of the device should have strong dependency on light absorptivity of the dye.

1. The dye must have energy levels at proper position. The energy of LUMO should be at higher level than the conduction band minimum of metal oxide photoelectrode, so that, an efficient electron transfer process between the excited dye and CB of the semiconductor can take place.

2. For dye regeneration after injection of electron in CB, the oxidized state energy level of the dye must be more positive than the redox potential of electrolyte.

3. The dye should have anchoring groups to bind strongly to the oxide surface.

4. The dye molecules should have thermal as well as chemical stability for long term device performance.

1.6-3(i): Anchoring of dye molecules on the metal oxide surface

The dye must adhere to the semiconductor surface through linkages on the dye molecule. Without this, the dye would not be able to inject electrons into the conduction band of the semiconductor efficiently. The current is dependent on the number of adsorbed dye molecules on the semiconductor surface, and the voltage is dependent on the redox potential of the electrolyte and the Fermi level of the semiconductor [70].

The dye molecule can adsorb on metal oxide surface by numerous ways, which includes [71, 72, 73].

- **Covalent linkage:** This is a direct link between the complex and the metal oxide through covalent attachment.

- **Electrostatic interactions:** the interactions due to ion exchange, ion-pairing or donor-acceptor interactions.

- **Hydrogen bonding.

- **Hydrophobic interactions.** van der Waals’ forces due to physisorption of dye molecules on metal oxide solid surface. This leads to ester like linkages, leading to self-assembly of long chain fatty acid derivatives.

- **Physical entrapment:** physical entrapment inside the pores or cavities of hosts such as cyclodextrins, micelles, etc.

The adsorption modes of dyes on semiconductor surfaces are found to be very important for the DSC efficiency [74].
To form the complex linkages, the dye must have an anchoring group, which rejoins with the hydroxyl groups of the metal oxide surface to form strong chemical bonds. Recently, the most widely used covalent linker is a carboxylic acid (-COOH). This is because, it is easy to synthesize and comparatively cheaper. The derivatives of -COOH, such as carboxylate salt, amide, ester have also have been used. Moreover, sulfonate (-SO$_3^-$) and silane (-SiX$_3$ or -Si(OX)$_3$) have also been well studied to enhance the performance of DSSCs [75, 76].

1.6-3(ii): Popular dye molecules as a photo sensitizer in DSSC

The dyes used in dye sensitized solar cell are divided into two types: the organic and inorganic dyes according to their constitution.

Inorganic dyes includes metal complexes such as polypyridyl complexes of ruthenium and osmium, metal porphyrin, phthalocyanine and inorganic quantum dots, while organic dyes includes natural, organic and synthetic organic dyes [38, 44].

Among these, the most efficient sensitizers in DSSC are based on ruthenium(II) polypyridyl complexes because of their broad absorption in visible region, suitable energy band positions and relatively long excited-state lifetime. Several Ru complexes used in DSSCs have shown more than 11% solar cell efficiency under standard measurement conditions. During excitation of dye, there is transfer of electrons from the metal d orbitals to the ligand π* orbital, this process in known as metal-to-ligand charge transfer (MLCT). These excited electrons are then injected in to a CB of metal oxide semiconductor due to difference in energy [77].

In 1991, O'Regan and Gratzel achieved a maximum of 7.9% photoconversion efficiency using a trinuclear Ru complex [23, 78] anchored on mesoporous TiO$_2$ electrode. Again in 1993, Nazeeruddin, Gratzel and co-workers [79] synthesized mononuclear Ru complexes, cis- (X)$_2$bis(2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium(II), where X are Cl, Br, I, CN, and SCN. The thiocyanato derivative, cis-(SCN)$_2$bis (2, 2'-bipyridyl-4, 4'-dicarboxylate)ruthenium( II), known as N3 (dye 2). Nazeeruddin et al. [70] investigated the effect of proton content of the N3 dye on the performance of DSCs. The doubly protonated form, (Bu4N)$_2$[Ru(dcbpyH)$_2$(NCS)$_2$],
named N719, exhibited an improved power conversion efficiency. Among these sensitizers, cis-bis(isothiocyanato)-bis(2,2’-bipyridyl-4,4’-dicarboxylato)-ruthenium(II), which is usually referred to as ‘N3’, or in its partially deprotonated form (a di-tetra-butyl ammonium salt) known as ‘N719’. The Ru complex dye structures (N3 and N719 dye) are shown in Fig. 1.8.

![Fig. 1.8: Structure of Commercially available N3 and N719 dye](69)

The maximum absorption of N3 and N719 dyes are in the range of wavelengths, 300-700 nm. Also their extinction coefficients are respectively, \(1.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}\) and \(1.33 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}\) [68, 70, 75].

So far, N3 dye has emerged as the standard dye to compare and other sensitizers for DSSC, because of its high photo- and chemical-stability [75, 80-82]. So far, the best performance of a DSSC was achieved with a mesoporous TiO2 film sensitized with the ruthenium complex cis-dithiocyanato bis(2,2’-bipyridyl-4,4’-dicarboxylate) Ru(II), (N3 dye). This has achieved an efficiency of 11.2\% [83].

One of the drawbacks of ruthenium complexes is the limited absorption in the near-infrared region of the solar spectrum. Porphyrin and phthalocyanine systems exhibit intense spectral response bands in the near-IR region and possess good chemical, photo, and thermal stability. These are good potential candidates for photovoltaic applications [84-86].
Organic dyes are an alternative to the noble Ru complexes sensitizers and have the following advantages [87, 88]:

1. The molecular structures of organic dyes are in diverse form and can be easily designed and synthesized.

2. With respect to the cost and environmental issues, organic dyes are superior Ru complex based dyes.

3. The molar extinction coefficients of organic dyes are usually higher than those of Ru complexes, making them attractive for thin film and solid-state DSSCs.

4. At present, organic dyes exhibit higher efficiencies compared with that of Ru complexes in p-type DSCs. Generally, donor-π-bridge-acceptor (D-π-A) structure is the common character of these organic dyes.

With this construction, it is easy to design new dye structures, extend the absorption spectra, adjust the HOMO and LUMO levels and complete the intramolecular charge separation. When a dye absorbs light, intramolecular charge transfer occurs from subunit A to D through the π-bridge. For n-type DSCs, the excited dye injects the electron into the conduction band of the semiconductor via the electron acceptor group, A.

Many efforts have been made to change the different parts of organic dyes to optimize DSC performance.

In recent years, several organic dyes with broad absorption spectrum in visible region and with more molar extinction coefficient have been discovered. These include, coumarin dyes [87-90], perylene dyes [91-93], indoline dyes [94, 95], xanthene dyes [96, 97] and carbazole dyes [98, 99]. Also, the squaraine dyes [100, 101] and natural dyes [102, 103] have been used to act as sensitizers for DSSCs.

Organic dyes such as Eosin Y and Rose Bengal are xanthene class of dye, used as photosensitizers for DSSCs in early studies [48, 63, 104-106]. The Eosin Y and Rose Bengal dye structures are shown in Fig. 1.9. Although, earlier studies on DSSC, with an organic dye as a sensitizer, showed comparatively poor performance, but till date they are widely being used. This is because of its moderate oxidation/reduction
ability and several other advantages including low cost, high absorption coefficient, and easy handling, as compared with metal complexes. Besides being a low cost dye, it is also suitable as sensitizer by virtue of the energy difference between the lower unoccupied molecular orbital (LUMO) of the dye and CB position of SnO$_2$ [35, 104, 105]. Such band energetics between the dye and the metal oxide facilitate efficient electron injection into the CB of SnO$_2$ through the separation of exciton formed in dye molecule after light absorption by dye molecules. Sensitizers like Rose Bengal have a carboxyl group, which can be easily adsorbed on the SnO$_2$ surface through the interaction between carboxyl group of dye molecules and valence-unfilled Sn (IV) of SnO$_2$ surface.

The most commonly used method for the adsorption of the dye onto the semiconductor is by immersion of the semiconductor substrate into a solution of the dye. The substrate is left in the solution for several hours in the dark. Subsequently it is washed with ethanol and air dried, before being assembled into a DSSC.

![Eosin Y dye](http://en.chembase.cn/molecule-104968.html#)

![Rose Bengal dye](http://en.chembase.cn/molecule-134126.html#)

**Fig.1.9: Structure of low cost Rose Bengal and Eosin Y dye**

**1.6-4: Electrolyte**

It is also known as hole transporting medium. Its properties influence prominently the photo conversion efficiency and stability of DSSC. The electrolyte used in DSSC comprises redox couple, organic solvent and suitable additives.
Redox couples must satisfy both energetic and kinetic requirements in order to effectively function in DSSCs. These requirements are:

1. Its redox potential should be more negative than the position of energy level of HOMO of the dye for its regeneration.
2. It must facilitate the fast regeneration of oxidized dye molecule than the recombination of CB electron with the dye.
3. The back electron transfer i.e. recombination of CB electron with oxidized redox species after dye regeneration must be slow as compared to electron percolation process to TCO.
4. It must have low viscosity and fast ion diffusion.
5. Its synthesis, design should be simple and must have capability to percolate easily into the nano particle network of photo electrode.
6. It must be soluble in a variety of organic solvents.
7. Its oxidized and reduced species must be stable.

Organic solvent based electrolytes have been widely used in DSSCs due to their appropriate redox potential, low viscosity and fast ion diffusion [107-110]. The Organic solvent used in organic liquid electrolyte includes acetonitrile, valeronitrile, ethylene carbonate, propylene carbonate and ethanol [111].

Typically, ionic liquid of iodine/ tri-iodide(I⁻/I₅⁻)redox couple in acetonitrile solvent is used as electrolyte for DSSCs [41]. It is of particular interest, since first report by O’rgan and Gratzel in 1991, because, its redox potential closely matches the HOMO level of the Ru based dye. Also the dye regeneration by I⁻ is much faster than recombination loss of CB electron with oxidized dye [112, 113]. The oxidized redox species I₅⁻ diffuses towards the counter electrode is much faster than the recombination of CB electron with the oxidized species I₅⁻ occurs on time scales of tens of milliseconds [29, 114].

According to Nogueira and co-workers, the I⁻/I₅⁻ redox couple have negatively charged carrier, and hence it reduces the probability of recombination with CB electrons [115]. Although the kinetic processes of the I⁻/I₅⁻ redox couple are favorable with almost all dyes used in DSSCs, the redox potential and the energetic processes are not favored [33, 115]. The redox potential of I⁻/I₅⁻ redox couple is 0.55V (Vs. SHE) [44, 69] which is much higher than the most of the dyes. Such a
difference in the HOMO and redox potential causes reduction in the open circuit voltage of DSSC. Also the multi-electron transition processes of $I^-/I_3^-$ redox couple during dye regeneration is one of the limiting factor in DSSCs [29]. Furthermore, it is also corrosive to many metals and semiconductor sensitzers. Thus, replacement of $I^-/I_3^-$ redox couple with single step electron transfer could help increase the photovoltage.

Few efforts have been made to overcome the limitations and problems associated with $I^-/I_3^-$. Colbalt II (Co(II)), Colbalt III (Co(III)), Br-/Br$_3^-$ were considered as an alternative to $I^-/I_3^-$ redox couple [116, 117], but their performance was not as comparable as that of $I^-/I_3^- electrolyte$.

The DSSCs with cobalt complexes as an electrolyte shows efficiencies of about 7.9%, when exposed under low light intensity However, the performance of the same device decreases with reduction in photo conversion efficiency to about 3.9% under 1 sun condition. Such a decrease in performance is attributed to slow kinetic processes and mass transport limitations [118]. Moreover, several other groups have shown photo conversion efficiency of about 12% under 1 sun condition for DSSC with organic dyes as a sensitizer and cobalt complexes as an electrolyte [117, 119, 120]. Maximum efficiency of about 12.3% for DSSC has been reported using cobalt(II/III) tris-bipyridyl redox couple and co-sensitization with two donor-p-acceptor dyes [120].

The Br-/Br$_3^-$ is another alternative. This has more positive potential (0.5V, SHE) as compared to $I^-/I_3^-$, and therefore should result in improvement in photo voltage ($V_{oc}$). It has been observed that, more positive potential do not result in improved $V_{oc}$, even though redox potential of this electrolyte matched well with HOMO of N3/N719 dyes, because of poor kinetic processes. On the other hand, DSSC with Eosin-Y dye as a sensitizer and Br-/Br$_3^-$ as a redox couple show $V_{oc}$ of about 0.81V as compared to 0.45V for $I^-/I_3^-$ [121]. The solid and gel electrolytes have also been used as an alternative using polymeric or gel materials [122, 123]. In spite of this, $I^-/I_3^-$ is still the campaigner, because of its fast dye regeneration, slow recombination, high solubility and fast ion diffusion.
1.6-5: Counter electrode

Counter electrode (CE) is also known as cathode in DSSC. It must ensure the reduction of oxidized species of the electrolyte [124]. To perform this action it should meet following important characteristics [125].

1. It must have efficient electro-catalytic activity for better device performance.
2. Chemically stable
3. Must able to perform long lasting catalytic activity

At present, DSSCs with platinum coated FTO (Pt-FTO) CE shows best device performance, because of its high catalytic activity and stability against iodine in the electrolyte [109, 110, 126]. Without platinum, FTO substrate has a very high charge transfer resistance in a standard iodide/ tri-iodide electrolyte, hence its direct use is not suitable for catalytic activity [127].

The sputter deposition or thermal deposition methods are commonly used to fabricate platinum counter electrode [109, 110].

In order to enhance the catalytic activity, CEs with electrochemically prepared Pt-FTO is also considered. It shows photo conversion efficiency of DSSCs to about 7.6% as compared to CEs fabricated with conventional methods (6.4%) [128]. Electrochemical deposition of CEs increases the catalytic activity due to increase in surface area and decrease in sheet resistance of the film. For the same enhancement, Kim et al. prepared platinum-nickel oxide (Pt-NiO) based CE by RF magnetron sputtering on FTO substrate. It is observed, that this not only provides the maximum active surface area but also increase the adhesion on the substrate. The decrease in series resistance in Pt-NiO CE also reflects in enhancement of short circuit current density and photo conversion efficiency from 0.44 to 0.61 mA/cm² and 3.2 to 4.3%, respectively [129]. However, the high cost of Platinum material and its limited availability restricts the low cost fabrication of DSSCs in large scale [46]. However, the replacement of Pt-FTO based CEs must ensure a low charge transfer resistance and high catalytic activity.

In recent years, carbon-based materials such as carbon black, activated carbon and carbon nanotube are also applied as the material for counter electrode but the efficiencies are found to be lower [130, 131]. They are considered as suitable alternative because they are inexpensive and also have a good catalytic activity [132].
Kay and Gratzel have used a composite of carbon black and graphite for CE in DSSC. The carbon black helps to enhance catalytic activity of graphite, which possess very good electronic conductivity. Single wall carbon nanotubes have also been used as CE and showed good conductivity and catalytic properties with iodide electrolyte [46].

Recently, conductive polymers are emerging as a best suitable alternative for conventional CEs. One of the major characteristics is that, they can be fabricated on flexible substrate [133]. The Poly (3, 4-ethylenedioxythiophene) (PEDOT) polyaniline and polypyrrole are some of the popular conducting polymers for CEs [134]. Metal plates such as Titanium, steel and nickel could also be used as CEs, but because of corrosive nature of $I^-/I_3^-$ redox couple, it is difficult to use them as electrode in DSSCs [135, 136].

1.7: Summary of literature review

Many researchers have reported enhanced performance of DSSC with the optimal combinations of photo anode film, dye, electrolyte and counter electrode. These combinations have also shown a better alternative to most of the popular materials and high cost fabrication techniques. The obtained device performance in term of photovoltaic parameters with various combinations of components of DSSCs is summarized in Table 1.1.

Table 1.1: Comparison of photovoltaic parameters of DSSC based on photoanodes of different metal oxide.

<table>
<thead>
<tr>
<th>Photoanode</th>
<th>Substrate</th>
<th>Dye</th>
<th>Electrolyte</th>
<th>CE</th>
<th>$V_{oc}$ (volt)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$\eta$ %</th>
<th>Year/Ref.</th>
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</thead>
<tbody>
<tr>
<td>TiO$_2$, (anatase)</td>
<td>FTO</td>
<td>black dye</td>
<td>$I^-/I_3^-$</td>
<td>Pt-FTO</td>
<td>0.721</td>
<td>20.53</td>
<td>10.4</td>
<td>1999 [137]</td>
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<td>TiO$_2$, ITO</td>
<td>Eosin Y</td>
<td>I$^-$/I$_3^-$</td>
<td>Pt-ITO</td>
<td>0.57</td>
<td>0.87 (Isc, mA)</td>
<td>2.6</td>
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<td>2003 [138]</td>
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<td>TiO$_2$ (P25)</td>
<td>ITO</td>
<td>N3 dye</td>
<td>$I^-$/I$_3^-$</td>
<td>Pt-FTO</td>
<td>0.72</td>
<td>18.1</td>
<td>8.43</td>
<td>2005 [139]</td>
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<tr>
<td>TiO$_2$ FTO</td>
<td>N719</td>
<td>$I^-$/I$_3^-$</td>
<td>Pt-TCO</td>
<td>0.554</td>
<td>15.67</td>
<td>5.50</td>
<td></td>
<td>2005 [121]</td>
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<td>TiO2 FTO</td>
<td>N719</td>
<td>Br$^-$/Br$_3^-$</td>
<td>Pt-TCO</td>
<td>0.556</td>
<td>3.51</td>
<td>1.05</td>
<td></td>
<td>2005 [121]</td>
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<tr>
<td>Photoanode</td>
<td>Substrate</td>
<td>Dye</td>
<td>Electrolyte</td>
<td>CE</td>
<td>$V_{oc}$ (volt)</td>
<td>$J_{sc}$ (mA/cm²)</td>
<td>$\eta$ %</td>
<td>Year/Ref.</td>
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<tr>
<td>TiO₂</td>
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<td>Eosin Y</td>
<td>$I^-/I_3^-$</td>
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<td>5.15</td>
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<td>TiO₂</td>
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<td>Coumarin 343</td>
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<td>Pt-TCO</td>
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<td>3.25</td>
<td>0.54</td>
<td>2005 [121]</td>
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<td>TiO₂</td>
<td>FTO</td>
<td>Coumarin 343</td>
<td>Br⁻/Br₃⁻</td>
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<td>3.83</td>
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<td>FTO</td>
<td>D149</td>
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<td>16.13</td>
<td>6.67</td>
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<td>TiO₂ nanotube</td>
<td>FTO</td>
<td>Ruthenium-535</td>
<td>$I^-/I_5^-$</td>
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<td>0.829</td>
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<td>Pt-FTO</td>
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<td>2.2</td>
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<td>TiO₂</td>
<td>FTO</td>
<td>Rose Bengal</td>
<td>$I^-/I_3^-$</td>
<td>PEDOT-PSS graphite-FTO</td>
<td>0.890</td>
<td>3.22</td>
<td>2.09</td>
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<td>N719</td>
<td>$I^-/I_3^-$</td>
<td>Pt-ITO</td>
<td>0.82</td>
<td>6.8</td>
<td>3.6</td>
<td>2009 [144]</td>
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<td>TiO₂−MWCNT nanocomposites</td>
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<td>$I^-/I_5^-$</td>
<td>Pt-FTO</td>
<td>0.70</td>
<td>21.9</td>
<td>7.37</td>
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<td>N719</td>
<td>$I^-/I_5^-$</td>
<td>Pt-FTO</td>
<td>0.599</td>
<td>14.7</td>
<td>4.82</td>
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<td>Electrolyte</td>
<td>CE</td>
<td>( V_{oc} ) (volt)</td>
<td>( J_{sc} ) (mA/cm(^2))</td>
<td>( \eta ) %</td>
<td>Year/Ref.</td>
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<td>Mesoporous TiO(_2)</td>
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<td>N719</td>
<td>( I^-/I_3^- )</td>
<td>Pt-FTO</td>
<td>0.562</td>
<td>12.4</td>
<td>4.38</td>
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<td>Mg(^{2+}) coated TiO(_2)</td>
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<td>N719</td>
<td>( I^-/I_3^- )</td>
<td>Pt-FTO</td>
<td>0.588</td>
<td>17.3</td>
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<td>TiO(_2) Substrate</td>
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<td>N719</td>
<td>( I^-/I_3^- )</td>
<td>Pt-FTO</td>
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<td>7.94</td>
<td>3.76</td>
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<td>TiO(_2) treated with Mg(OH)(_2)</td>
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<td>N719</td>
<td>( I^-/I_3^- )</td>
<td>Pt-FTO</td>
<td>0.847</td>
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<td>4.01</td>
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<td>10.7</td>
<td>5.6</td>
<td>2011 [150]</td>
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<td>TiO(_2) nano leaves + TiO(_2) Degussa P25</td>
<td>FTO</td>
<td>N719</td>
<td>( I^-/I_3^- )</td>
<td>Pt-FTO</td>
<td>0.74</td>
<td>13.7</td>
<td>6.5</td>
<td>2011 [150]</td>
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<td>ALD TiO(_2) coated ZnO aggregates</td>
<td>FTO</td>
<td>N719</td>
<td>( I^-/I_3^- )</td>
<td>Pt-silicon wafer</td>
<td>0.706</td>
<td>11.8</td>
<td>4.6</td>
<td>2011 [151]</td>
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<td>TiO(_2), P25</td>
<td>plastic PEN-ITO</td>
<td>D149</td>
<td>( I^-/I_3^- )</td>
<td>Pt PEN-ITO</td>
<td>0.811</td>
<td>11.10</td>
<td>5.76</td>
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<td>Rutile TiO(_2) Nanorod</td>
<td>FTO</td>
<td>Organo-lead iodide, CH(_3)NH(_3) PbI(_3)</td>
<td>spiro-MeOTA D</td>
<td>Au-thermal evaporation</td>
<td>0.955</td>
<td>15.6</td>
<td>9.4</td>
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</table>
### Dye Sensitized Solar Cell: An Introduction

**Ph.D. Thesis:** Sandeep A. Arote

<table>
<thead>
<tr>
<th>Photoanode</th>
<th>Substrate</th>
<th>Dye Description</th>
<th>Electrolyte</th>
<th>CE</th>
<th>( V_{oc} ) (volt)</th>
<th>( J_{sc} ) (mA/cm(^2))</th>
<th>( \eta ) %</th>
<th>Year/Ref.</th>
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<td>FTO</td>
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<td>Co(^{3+/2+}) complex</td>
<td>Not mentioned</td>
<td>1.036</td>
<td>15.6</td>
<td>12.5</td>
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<td>FTO</td>
<td>Porphyridin dye with 4-dimethylamino phenyl group</td>
<td>( I^−/I_3^− )</td>
<td>Pt-FTO</td>
<td>0.72</td>
<td>18.82</td>
<td>10.03</td>
<td>2014 [155]</td>
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<td>FTO</td>
<td>Organo-lead iodide, CH(_3)NH(_3) Pb(_3) Perovskite</td>
<td>Spiro-MeOTA D</td>
<td>Gold back contact</td>
<td>1.110</td>
<td>17.41</td>
<td>13.03</td>
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<td>FTO</td>
<td>Carbazole-based organic dyes</td>
<td>Li(^+)/( I^−/I_3^− )</td>
<td>Pt-FTO</td>
<td>0.73</td>
<td>10.3</td>
<td>5.6</td>
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### ZnO

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<th>Dye</th>
<th>Electrolyte</th>
<th>CE</th>
<th>( V_{oc} ) (volt)</th>
<th>( J_{sc} ) (mA/cm(^2))</th>
<th>( \eta ) %</th>
<th>Year/Ref.</th>
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<td>ITO</td>
<td>Eosin Y</td>
<td>( I^−/I_3^− )</td>
<td>Pt-ITO</td>
<td>0.64</td>
<td>0.96 (Isc, mA)</td>
<td>4.4</td>
<td>2003 [138]</td>
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<tr>
<td>ZnO</td>
<td>FTO</td>
<td>Eosin Y</td>
<td>( I^−/I_3^− )</td>
<td>Pt-FTO</td>
<td>--</td>
<td>--</td>
<td>2.4</td>
<td>2004 [158]</td>
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<td>ZnO nanowire</td>
<td>FTO</td>
<td>N719</td>
<td>( I^−/I_3^− )</td>
<td>Pt-FTO</td>
<td>0.54</td>
<td>6.79</td>
<td>1.7</td>
<td>2007 [159]</td>
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<tr>
<td>ZnO nanowire arrays</td>
<td>ITO</td>
<td>Rose Bengal</td>
<td>( I^−/I_3^− )</td>
<td>Pt-ITO</td>
<td>0.55</td>
<td>49 ( \mu ) A/cm(^2)</td>
<td>0.7</td>
<td>2007 [105] (*( 2mW/cm^2, 570) nm)</td>
</tr>
</tbody>
</table>
## Chapter - 1

**Dye Sensitized Solar Cell: An Introduction**

<table>
<thead>
<tr>
<th>Photoanode</th>
<th>Substrate</th>
<th>Dye</th>
<th>Electrolyte</th>
<th>CE</th>
<th>$V_{oc}$ (volt)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>η %</th>
<th>Year/Ref.</th>
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<td>ZnO nanowire</td>
<td>FTO</td>
<td>N719</td>
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<td>Pt-FTO</td>
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<td>ALD TiO$_2$ coated ZnO aggregates</td>
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<td>0.706</td>
<td>11.8</td>
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<td>ZnO</td>
<td>ITO</td>
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### SnO$_2$

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### Dye Sensitized Solar Cell: An Introduction

#### Ph.D. Thesis: Sandeep A. Arote

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<th>CE</th>
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<td>SnO$_2$ nanoparticle</td>
<td>FTO</td>
<td>N719</td>
<td>$I^-/I_3^-$</td>
<td>Pt-FTO</td>
<td>0.414</td>
<td>1.97</td>
<td>0.414</td>
<td>2014 [178]</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>FTO</td>
<td>Eosin-Y</td>
<td>$I^-/I_3^-$</td>
<td>carbon coated FTO</td>
<td>0.363</td>
<td>0.131</td>
<td>0.31</td>
<td>2014 [63]</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>FTO</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.65</td>
<td>12.87</td>
<td>4.63</td>
<td>2014 [179]</td>
</tr>
<tr>
<td>TiO$_2$ – SnO$_2$</td>
<td>FTO</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.73</td>
<td>13.47</td>
<td>6.17</td>
<td>2014 [179]</td>
</tr>
<tr>
<td>Urchin-like SnO$_2$ Microsphere</td>
<td>FTO</td>
<td>Dyesol N-719</td>
<td>$I^-/I_3^-$</td>
<td>Pt-FTO</td>
<td>0.38</td>
<td>7.62</td>
<td>1.43</td>
<td>2014 [180]</td>
</tr>
<tr>
<td>TiO$_2$/SnO$_2$ Microsphere</td>
<td>FTO</td>
<td>N-719</td>
<td>$I^-/I_3^-$</td>
<td>Pt-FTO</td>
<td>0.74</td>
<td>14.70</td>
<td>6.05</td>
<td>2014 [180]</td>
</tr>
</tbody>
</table>

#### 1.8: Orientation of the present research work

##### 1.8-1: Aim of Present Research Work

The review of literature, brings out the fact that, although, TiO$_2$ is providing a very promising role of photoanode in DSSC, but still there are many questions that have remained to be answered. These are with regards to charge transfer, charge collection and stability of DSSC. SnO$_2$ is best suitable alternative to overcome these problems up to certain level. It was therefore thought worthwhile to undertake investigation on factors influencing the performance of tin oxide based dye sensitized solar cell. It was expected that this experimental investigation would answer some of the above mentioned questions.
In the light of the above, as a primary goal, a wide band gap SnO\textsubscript{2} as photo electrode material in DSSC, was proposed here to replace the most popular TiO\textsubscript{2}, because of its promising electrical and optical properties. However, the DSSC with SnO\textsubscript{2} shows poor performance. This is closely related to the various factors related to fabrication of DSSC. Therefore, the main objective of the present research work has been to explore various key factors that affect the performance of SnO\textsubscript{2} based DSSC. This in turn, is expected to explain the role of each key factor in general and their optimization to enhance the performance of SnO\textsubscript{2} based DSSC in particular.

1.8.2: Research Objectives

The objectives set for present research work were:

1. To synthesize the tin oxide (SnO\textsubscript{2}) nanostructures using chemical methods and fabrication of their photo electrode films on conducting substrates.
2. To characterize these films by different techniques like XRD, UV-spectrophotometer, SEM, EDX, etc.
3. Sensitization of porous SnO\textsubscript{2} films with low cost organic dye and their characterization.
4. To Fabricate and study the photovoltaic performance of SnO\textsubscript{2} based DSSCs.
5. To optimize the processing / deposition parameters.
6. To study the influence of dye residence time on the performance of porous SnO\textsubscript{2} photo anodes in dye sensitized solar cells
7. To study the influence of geometrical thickness of compact/porous SnO\textsubscript{2} photo anode films on the performance of dye sensitized solar cells
8. To study the effect of morphology of SnO\textsubscript{2} on the performance of dye sensitized solar cells
9. To study surface passivation of SnO\textsubscript{2} photo anode films through MgO coating and its influence on the performance of dye sensitized solar cells

It is expected that, by optimization of various key factors, the performances of SnO\textsubscript{2} based DSSC can be enhanced.
1.8.3: Organization of Thesis

The thesis is subdivided into seven different chapters. Chapter-1 gives the introduction to energy resources, solar energy, various generations of solar cells, efficiency limit, introduction to DSSCs, structure of DSSCs, its operating principle, literature survey and research objectives. Chapter- 2 presents a brief theoretical background of various material synthesis and characterization techniques. Chapter-3 describes on how the dye residence time influences photovoltaic performance of DSSC based on Eosin-Y and Rose Bengal dye sensitized SnO₂ photo anodes. Chapter- 4 describes as to how incorporation of compact layer between porous layer and FTO while making DSSC assemblies affect their photovoltaic performance. The effect of geometrical thickness of porous and compact layer on photovoltaic performance of DSSC based on EY sensitized SnO₂ photoanode has also been studied. Chapter- 5 describes the investigation into the role of surface morphology of SnO₂ into determining the pathway for electron transfer, and hence performance of DSSC. Chapter- 6 deals with surface passivation treatment to porous SnO₂ and hydrothermally synthesized SnO₂ photo electrodes by means of MgO coating and its effect on DSSC performance. Finally, Chapter- 7, presents the summary of investigations into how all these key factors viz. dye residence time, compact layer, geometrical thickness of compact and porous layer, surface morphology and surface passivation treatment affect the DSSC performance.
References:

Chapter 1

Dye Sensitized Solar Cell: An Introduction


