

Chapter I - INTRODUCTION

This Chapter deals with the current energy scenario and the renewable energy potential of India. An overview of different generations of solar cells has been presented. The third generation solar cell especially, the construction of Dye Sensitized Solar Cells (DSSCs) their working principle and applications are explained in detail. Improvisations employed in recent years in dye sensitized solar cells are being discussed along with relevant literature support. Finally, novelty and outcome of the proposed work and its objectives are presented in this Chapter.

1.1 Current Energy Scenario

One of the most fundamental and driving forces of the universe is Energy. Energy is called the engine of economic development as a country's development and economic growth strongly depends on the availability of energy sources [1]. Given the incredible advancements in technology and the elevated style of living, demand for energy is increasing at a rapid pace. India is the fourth largest energy consumer in the world after the United States, China, and Russia [2]. India, home to 18% of the world's population, uses only 6% of the world's primary energy. As on March 2013, the per capita total electricity consumption in India was 917.2 kWh [3]. Electricity consumption in India is expected to rise to around 2280 BkWh by 2021–22 and around 4500 BkWh by 2031–32 [4]. India's energy consumption has been increasing at a comparatively fast rate due to increase in population and living standard as well. Since 2000, India's energy utilization has nearly doubled and the potential for further rapid growth is enormous.

India became the world's third largest producer of electricity in the year 2013 with 4.8% global share in electricity generation surpassing Japan and Russia but is still a power deficit country. As the economy grows in coming years, the electricity demand will further rise as there is a strong correlation between rise in energy consumption and economic growth [5]. Most of the commercial energy demand in India is met largely by imported fossil fuels. In 2016, India

was the 4th biggest consumer and net importer of crude and petroleum products in the world. As the country is essentially dependent on energy import, any shortfall due to unforeseen geopolitical situations may cause acute energy scarcities which will consecutively impede the industrial growth and economic progress. In order to achieve energy independence, the dependency on imported oil has to be reduced by developing alternate energy sources [6]. India's major electricity supply is generated from fossil fuels: coal, oil and natural gas. These traditional sources of energy face the challenges of rising price, growing environmental pollution, global warming, climate change risk, etc. It is predicted these natural resources from fossil fuels will be depleted within this century based on today's energy consumption rate [7].

India's Energy Consumption for Electricity Generation

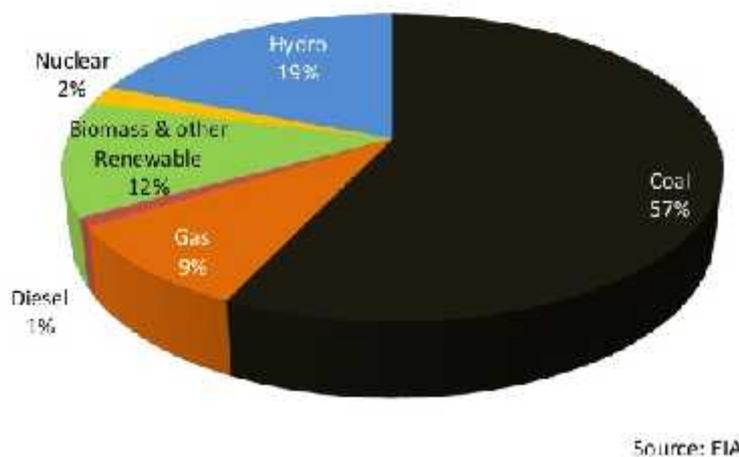


Fig. 1.1 Energy Consumption in India

In addition, the over-dependence on fossil fuels leaves us exposed to air pollutants, namely CO, NO_x and SO_x and their related health risks. As a result, there is an increasing support from the Government, businesses and consumers in the development of alternative energy sources and new technologies for electricity generation. The potential of renewable energy sources (energies which can be tapped from sun, wind, ocean, hydropower, biomass, geothermal resources, biofuels and hydrogen) is also huge and they can meet our future energy demands [8]. The energy policy of India is largely defined by the country's expanding energy deficit and increased focus on developing alternative sources of energy, particularly nuclear, solar and wind energy [9]. Renewable energy is thus seen as one of the promising ways to supplement conventional power generation and meet energy demands especially in the rural and remote areas.

1.2 Energy Sources

There are two different forms of energy sources: (i) Renewable and (ii) Non-renewable energy resources.

a) Renewable sources

Renewable energy is the energy sources which are in constant supply to us by nature and are inexhaustible. The word “renewable energy” stands for obtaining energy from abundant natural resources such as wind, solar, geothermal, hydropower etc. which are self regenerating.

b) Non-renewable sources

They are defined as the sources which cannot be used repeatedly and are exhaustible. Utilization of non-renewable energy sources leads to their depletion. Now, we are in search of technologies which supply renewable energy easily and cheaply because exhaustible energy sources are limited. Renewable energy sources are gaining popularity and have become the most preferred topic for research and therefore many are interested in developing technologies to tap energy from them.

1.2.1 Renewable Energy

Expanding population and their larger consumption have led to increasing reliability on sustainable energy supply in order to meet the ever increasing energy demand. For a long time, the energy boom was dependent on supply from fossil fuels. The energy contribution from oil, coal, and natural gas is limited additionally contributing to major pollution and environmental concerns [10]. Renewable energy sources, which include solar, wind, hydroelectric, biomass and geothermal, have emerged as potential alternatives as they provide unlimited availability. India was the first country in the world to set up a ministry of non-conventional energy resources, in the early 1980s. As of September 30, 2016, India's cumulative grid interactive or grid tied renewable energy capacity (excluding large hydro) reached about 44.24 GW [11, 12]. 65% of the renewable power came from wind, while solar contributed nearly 11%.

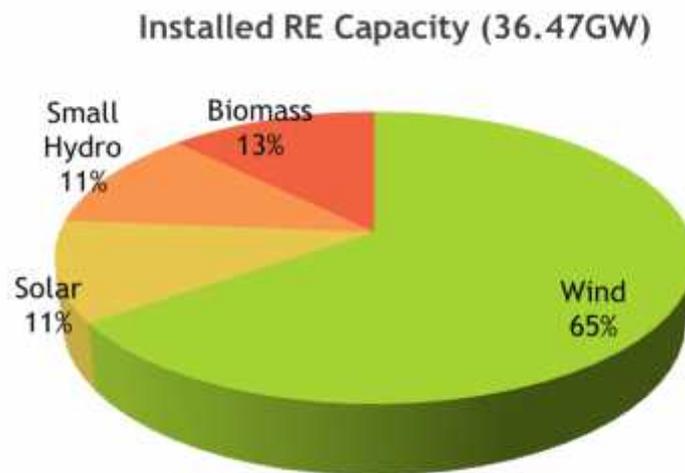


Fig. 1.2 Renewable Potential in India

Among the identified renewable energy sources, solar energy is abundantly available at no cost. It is pollution free, requires minimal maintenance and saves natural resources, electricity bill and foreign exchange in the Indian context [13, 14].

1.2.2 Types of Renewable Energy Sources

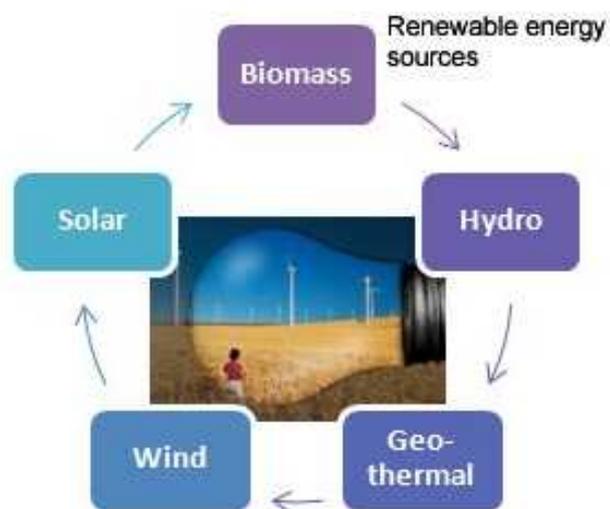


Fig. 1.3 Types of Renewable Energy Sources

1.2.2.1 Wind Energy

Wind energy (or wind power) is one of the oldest and most explored renewable energy sources and describes the process by which wind is used to generate electricity. Wind power, as an alternative to burning fossil fuels, is plentiful, renewable, widely distributed, clean, produces no greenhouse gas emissions during operation, consumes no water. Wind energy can be used to pump water or generate electricity, but requires extensive areal coverage to produce significant amounts of energy [15].

1.2.2.2 Biomass Energy

Biomass is the term for energy derived from plants and living organisms or recently lived organisms. The biomass energy can be derived directly by burning to produce heat or indirectly by converting it to some form of fuel referred as biofuel. Dead trees, dead leaves, wood chips and various types of wastes from plants are also used for energy generation besides wood which is invariably the largest source of biomass energy. Methane generation and production of alcohol for automobile fuel and fueling electric power plants are some modern forms of biomass energy [16, 17]. The major disadvantages involved in utilizing biomass energy are high investment cost and large area requirement.

1.2.2.3 Hydro Power

Hydro-power is the power derived from the energy of falling water and running water, which may be harnessed for useful purposes. Water constantly moves through a vast global cycle, evaporating from lakes and oceans, forming clouds, precipitating as rain or snow, then flowing back down to the ocean. The energy of this water cycle, which is driven by the sun, can be tapped to produce electricity or for mechanical tasks like grinding grain. Because the water cycle is an endless, constantly recharging system, hydropower is considered a renewable energy [18]. The limitations involved in hydropower generation are its environmental impact, High cost of building power plants, Shortage of water supply etc.,

1.2.2.4 Geothermal Energy

Geothermal energy is obtained from the thermal energy generated and stored in the Earth. The constant flow of heat from the earth ensures an inexhaustible and essentially limitless supply of energy for billions of years to come. The heat that is used for geothermal energy can be from deep within the Earth, all the way down to Earth's core – 4,000 miles (6,400 km) down. At the core, temperatures reach over 9,000 °F (5,000 °C) and heat gets conducted from the core to surrounding rocks. Enormously high temperature and pressure make some rocks to melt, which is commonly known as magma which then heats

rock and water in the crust, sometimes up to 700° F (371 °C). From hot springs, geothermal energy has been for space heating since ancient Roman times and been used for bathing since Paleolithic times and, but it is now better known for electricity generation [19, 20].

1.2.2.5 Solar Energy

Solar power is a primary choice in developing a reasonable, feasible, global power source that can replace fossil fuels in all climate zones around the world. Energy received from the sun is unlimited and is free from environmental pollution and noise. The solar radiation striking the earth's surface in one year is providing more than 10,000 times over the yearly needs worldwide [21]. Currently, the energy requirement worldwide is 13 Terawatts (TW) and it is expected to increase by another 10 TW in the next 40 years. The amount of sunlight reaching the earth's surface is 120,000 TW. In other words, the amount of solar radiation reaching the earth over a three-day period is equivalent to the amount of energy stored in all fossil fuel energy sources [22]. It means that 20 minutes of sunlight is sufficient to meet the energy requirement of the 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 their impact on environment and on the 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 third choice of renewable energy based on sun as the source, is very attractive and promising [23].

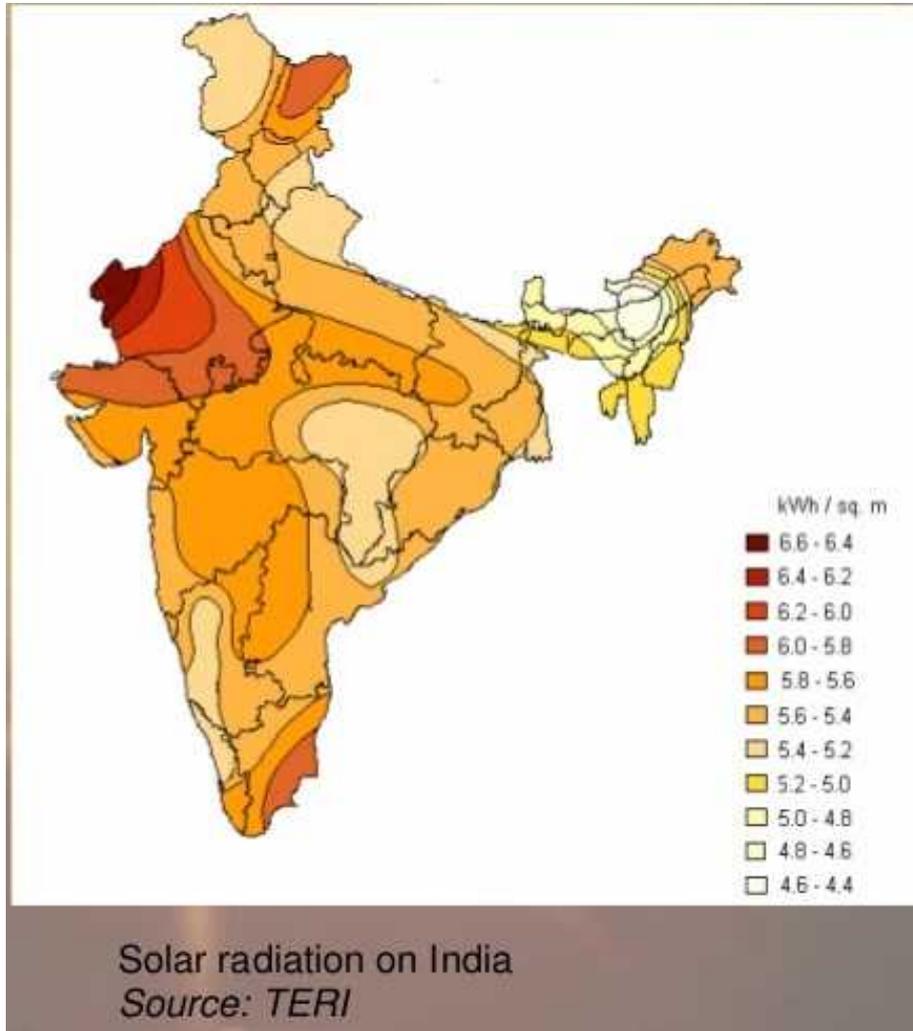


Fig. 1.4 Installed Solar Power Capacity in India

The profusion of this energy reaching the Earth can be successfully utilized in various ways namely [24];

- (i) Concentrating Solar Power;
- (ii) Solar Electricity (Photovoltaics);**
- (iii) Solar Heating Systems;

- (iv) Solar Thermal Electric Power Plants; and
- (v) Solar Fuel systems.

1.3 Photovoltaics

Photovoltaics (PV) is a solar power technology which uses solar cells to convert sunlight directly into electricity. Conversion of light energy to electrical energy is based on a phenomenon called photovoltaic effect. When semiconductor materials are exposed to light, some of the photons of light rays are absorbed by the semiconductor crystal which causes a significant number of free electrons in the crystal. This is the basis for the production of electricity due to photovoltaic effect. **Photovoltaic cell** is the basic unit of the system where photovoltaic effect is utilized to produce electricity from light energy. [25].

The PV effect was discovered in 1954, when scientists at the Bell Telephone discovered that Silicon (an element found in sand) created an electric charge when exposed to sunlight. Soon, solar cells were being used to power space satellites and smaller items like calculators and watches [26]. The basic steps in the operation of a solar cell are:

- the generation of light-generated carriers;
- the collection of the light-generated carriers to generate a current;
- the generation of a large voltage across the solar cell; and

- the dissipation of power in the load.

Silicon is the most widely used semiconductor material for constructing a photovoltaic cell. The other common materials employed in solar cells are cadmium-telluride, copper-indium-gallium-selenide, and copper-indium-gallium-sulfide. On the basis of these materials, the photovoltaic solar cells are classified into various generations (Figure 1.5) as discussed in the sections that follow [27-29].

1.3.1 First Generation Solar Cells

The first generation solar cells are also known as Silicon-wafer based solar cells which were first discovered in 1941 by Russel Ohl. They are further classified into:

- (i) Single/ Mono-crystalline silicon solar cell.
- (ii) Poly/Multi-crystalline silicon solar cell.

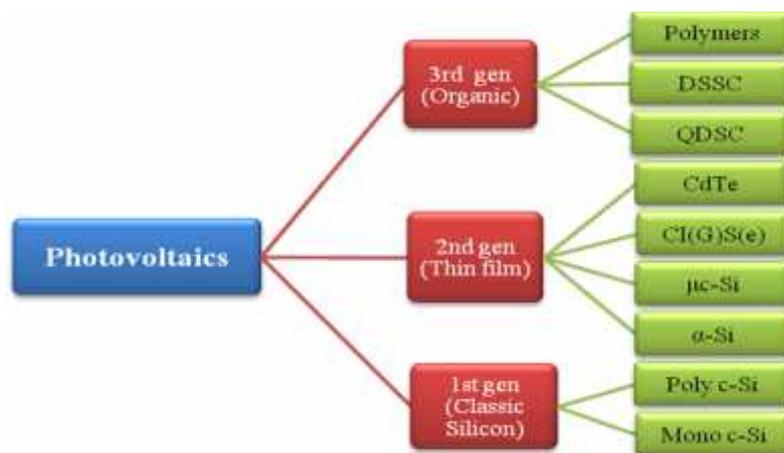


Fig. 1.5 Generations of Photovoltaics

These types of cells were based almost solely on silicon technology, specifically single-crystal silicon and operate on the principle of a p-n junction type semi-conducting system. The boundary between a *p-type* and *n-type* semiconductor sets-up an electric field in the depletion junction and the generated electrons drift towards the *n-type* side and the holes drift towards the *p-type* side. This charge separation results in current flow, and the possibility of the electrons doing work on a connected load. They usually consist of crystalline silicon which is doped with inorganic solid-state materials. Si has a low band gap 1.11 eV, which facilitates broad spectral absorption range. The laboratory scale solar cells have already achieved 25% efficiency, but it is expensive and an energy intensive manufacturing technology, which increases the generated power cost [30-33].

1.3.2 Second Generation Solar Cells

The second generation solar cells are known as thin film solar cells. They are based on cheaper materials, like amorphous silicon (a-Si), polycrystalline silicon (p-Si), Copper Indium Gallium Selenide (CIGS), copper indium gallium diselenide (CuInSe₂) and cadmium telluride (CdTe). The light absorbing layer in the case of silicon wafer cell is 350 μm thick, whereas it is in the order of 1 μm thick in thin film solar cells thereby cutting down on the material requirement.

Amorphous (a-Si) solar cells can be manufactured at a low processing temperature, and it was the first commercialized cell technology permitting the use of various low cost, polymers and other flexible substrates. These substrates require a smaller amount of energy for processing compared to the earlier generation. Cadmium Telluride (CdTe) is one of the leading thin film solar cells for the development of cheaper, economically viable photovoltaic (PV) devices. CdTe possesses high optical absorption coefficient and chemical stability with lower band gap value of ~ 1.5 eV. It is normally constructed by sandwiching semiconducting layer between cadmium sulfide layers to form a *p-n* junction diode. The limited supply of cadmium and environmental hazards associated with its use are the main drawbacks with the CdTe technology. CIGS thin film solar cell comprises of four elements, namely: Copper, Indium, Gallium and Selenium. CIGS holds a higher efficiency $\sim 10\%$ - 12% when compared to the CdTe thin film solar cell. Its prolonged life without considerable degradation is the major advantage in this kind of solar cell which provides an easy solution to enhance efficiency [34-39].

1.3.3 Third Generation Solar Cells

To overcome the disadvantages of first and second generation solar cells, another new generation of solar cells was developed in recent years called third generation solar cells which includes polymer based solar cells, Dye

Sensitized Solar Cells (DSSCs) and Quantum Dot Solar Cells (QDSC). Third generation solar cells are new promising technology devices at the laboratory and are not commercialized extensively.

Polymer solar cells also known as flexible solar cells were first invented by Tang *et al.* They consist of serially connected thin layers coated on polymer foil or substrate and various conjugate/conducting polymers aimed at light absorption. QDSCs (Nano crystal solar cells) generally consist of transition metal groups in the size of nano crystal range of semiconducting materials and have band gaps which can be tuned across a wide range of energy levels by changing the dots' size. This property makes quantum dots more attractive for multi-junction solar cells, where a variety of materials are used to improve efficiency by harvesting multiple portions of the solar spectrum. Dye Sensitized Solar Cell (DSSC) or Grätzel cell is another important third generation solar cell, being relatively simple and cheap to manufacture, eco-friendly and durable with record efficiency of 13% in optimized laboratory conditions has gathered incredible attention in recent times [40-43].

1.4 Dye Sensitized Solar Cells (DSSCs)

Dye Sensitized Solar Cells (DSSCs) are third generation photovoltaic (solar) cells that convert any visible light into electrical energy. This new class of advanced solar cell can be likened to artificial photosynthesis owing to the way in which it mimics nature's absorption of light energy (Photosynthesis).

Dye Sensitized Solar Cells (DSSCs) were invented in 1991 by Professor Michael Grätzel and Dr Brian O'Regan at École Polytechnique Fédérale de Lausanne (EPFL), Switzerland and is often referred to as the Grätzel cell [44]. The history of dye sensitization dates back to the photosensitization phenomenon by organic dyes first reported in 1887. It is an interesting convergence of photography and photo-electrochemistry, both of which rely on photo-induced charge separation at the liquid-solid interface. It is a thin film solar cell based on a semiconductor formed between a photo-sensitized anode and an electrolyte, a photo-electrochemical system. Its price/performance ratio is high enough to compete with fossil fuel electricity generation. DSSC can be produced using low-cost materials and it does not require intricate high-end manufacturing apparatus [45].

1.4.1 Structure of the Dye Sensitized Solar Cell

The cell is composed of four elements, namely, the transparent conducting and counter conducting electrodes, the nanostructured wide band gap semiconducting layer, the dye molecules (sensitizer), and the electrolyte. Typically, dye-sensitized nanocrystalline titania films were used as photoanode, platinized counter electrode, filled with electrolyte solution of I_3^-/I^- in organic solvent, then the sandwiched solar cells are formed [46]. This chemical way of assembling the cell architecture allows simplistic and cost effective processing which makes these cells front runners in view of their basic design and potential for low cost manufacturing.

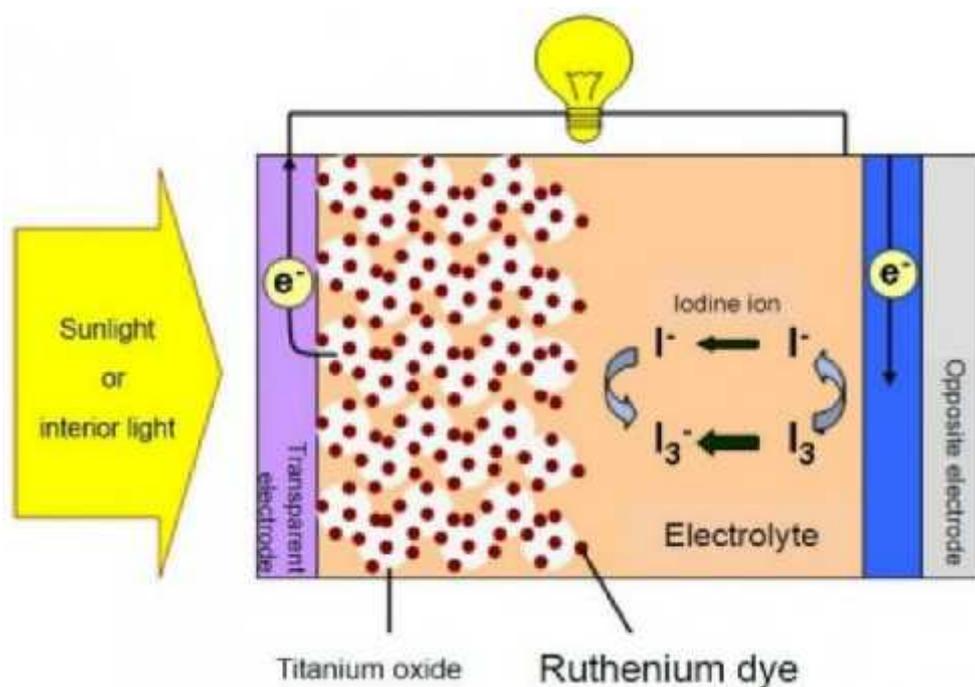


Fig. 1.6 Schematic diagram of a DSSC

In general, DSSCs separate the two basic functions provided by silicon in a traditional cell design. Normally the silicon acts as both the photoelectrons source, as well as providing the electric field to separate the charges and generate a current. In the dye-sensitized solar cell, the bulk of the semiconductor is used solely for charge transport, the photoelectrons are provided from a separate photosensitive dye. Charge separation occurs at the surfaces between the dye, semiconductor and electrolyte [47]. The dye molecules are quite small (nanometer sized), so in order to capture a reasonable amount of the incoming light, the layer of dye molecules needs to be made fairly thick, much thicker than the molecules themselves. To address this problem, a nanomaterial is used as a scaffold to hold large numbers of the

dye molecules in a 3-D matrix, increasing the number of molecules for any given surface area of cell. In existing designs, this scaffolding is provided by the semiconductor material, which serves double-duty [48].

1.4.2 DSSC Components

(i) Transparent Conducting Substrate (TCO)

TCO is base support of DSSC which are required to possess high transparency in the visible region and good conductivity with low sheet resistance. It is a wide band gap *n-type* semiconductor that consists of high concentration of free electrons. The most common ones are Indium doped Tin Oxide (ITO), Fluorine doped Tin Oxide (FTO) and Aluminium doped Zinc Oxide (AZO or Al:ZnO). Transparent conducting oxides - ITO or FTO films are coated on glass, plastic and stainless steel material by sputtering, electron beam evaporation, chemical vapor deposition or oxygen ion beam assisted deposition methods. A cost effective spray pyrolysis technique is also adopted for this purpose [49]. High charge mobility and thermally stable transparent conductive oxides are enhancing the optoelectronic properties. Hence it attracts more attention due to their low cost and simple preparation process. ITO is used as transparent electrode in solar cells due to its high optical transparent properties and good electrical conductivity at visible region. FTO is thermally stable and is reliable even in hydrogen containing environments.

FTO and ITO based TCOs are commercially available nowadays with about 90% optical transparency [50].

(ii) Metal Oxide Semiconductor as Photoanode

A photoanode material is an assembly of metal oxide layer deposited on TCO substrate and is one of the most important factors determining the performance of a DSSC. The two main purposes of a photoanode material is to support anchored dye molecules by providing high internal surface area and to create the path to fast transport of photo-induced electrons towards the conducting substrate before recombination. Hence, the oxide materials have to satisfy several requisites such as high surface area with good porosity in order to load a large amount of dye molecules, conduction band energy level located between the LUMO level of the dye and the redox level of the electrolyte, high electron mobility, chemical stability and suitable morphology of the photoanode materials for better performance of DSSC.

Different metal oxides with semiconducting nature, such as TiO_2 , ZnO , SnO_2 and Nb_2O_5 have been investigated, for use as photo anodes in DSSCs. Amongst them, TiO_2 has been the most widely used semiconductor due to its high abundance, relatively low cost, non-toxicity, ease of production and chemical inertness and high efficiency. The conduction band edge of TiO_2 lies slightly below the excited state energy level of many dyes, which is a

preferred condition for efficient electron injection. The high dielectric constant of TiO₂ facilitates good electrostatic shielding of the injected electrons from the oxidized dye molecule attached to the TiO₂ surface, thus preventing their recombination before reduction of the dye by the redox electrolyte. Hence high performance DSSC is achieved by increased electron injection from the dye and rapid electron transport by the photoanode material [51-53].

Employing Nanostructures as Photoanode

In the earlier generations of photo-electro chemical cells, photoanodes used were made from bulky single or poly crystalline semiconducting materials such as Si, CdS or GaAs. When exposed to light, however the above mentioned photoanodes undergo photocorrosion resulting in poor stability of the photoelectrochemical cell. Also it reported the problem of low light-to-current conversion efficiency essentially owing to inadequate adsorption of dye sensitizer because of limited surface area of the electrode [54]. The possible way to enhance the light harvesting efficiency and hence the light-to-current conversion efficiency is to increase the sensitized photoanode surface area (roughness factor). Nanostructured materials are receiving considerable attention in recent years due to the remarkable changes in their mechanical, electrical, chemical, optical and thermal properties when compared to the corresponding phases in their bulk counterparts [55]. Constructing the

photoelectrode with nanostructures shows improvement in conversion efficiency as they will offer maximum surface area as compared to a flat surface of photoelectrode, which will be highly beneficial for augmented uptake of a sensitizer leading to enhanced light harvesting. Thus, it is possible for nanostructured materials to generate large number of photoelectrons thereby increasing the photo-electron conversion efficiency [56]. Nanoscale regime of the nanostructures affect the electron transport behavior in the perspective of offering a limit to electron mean path, which is otherwise referred as quantum confinement effect [57]. Whereas, on the optical side, nanostructures form photonic band gap for effective light manipulation and management through photonic localization. These unique features of nanostructures have established significant attention and are being widely investigated for applications in photovoltaic, photocatalytic, electronic, sensing and optoelectronic devices [58-62].

Grätzel and his co-workers thus replaced the bulky layer of titanium oxide (TiO_2) with nanoporous TiO_2 layer as photoanode material and reported that the high porosity extended by the nanostructured TiO_2 layer facilitated a facile diffusion of redox mediators within the layer to react with the surface bound sensitizers (Grätzel et al. 1991). Nanostructures can be classified into Zero dimensional (0D), One-dimensional (1D), Two-dimensional (2D) and Three-dimensional structures (3D). Among the different nanostructures, 0D

nanoparticle structures are widely studied as they provide a larger surface area for dye adsorption, contributing to better photon absorption and can be easily fabricated by chemical solution methods [63]. However, the presence of numerous grain boundaries in the nanocrystalline films may increase the interfacial charge recombination between the positive species in electrolyte and photogenerated electrons.

One dimensional nanostructures (1D) such as nanorods, nanotubes, nanowires, nanofibers are preferred over 0D nanoparticles as they provide directional electron transport with a lesser recombination rate. However they lack in sufficient surface area for efficient dye absorption resulting in poor light harvesting capability [64-67]. Three dimensional nanostructures (3D) like nanoflowers and hierarchical microspheres are deeply investigated and considered for their excellent light scattering capability coupled with a faster electron transport rate [68]. Different wide band gap semiconducting materials such as TiO_2 , SnO_2 , ZnO , Nb_2O_5 and WO_3 have been studied as possible candidates for DSSC applications [69-74]. Among them nanostructured TiO_2 reveals better photovoltaic and photocatalytic properties due to its wide band gap nature, versatile structure, high physical and chemical stability, non-toxic nature, environmental compatibility and low cost and hence TiO_2 has been employed as a primary photoanode material in DSSCs [75].

Thus as envisaged from literature, tuning the morphology of photoanode materials has a significant impact on their characteristics which could further reflect on the solar cell performance. Electron transportation and effective dye loading are the two most important parameters in DSSCs and these factors depend upon the surface topography, surface area grain boundaries and porosity of the photoanodes [76]. The above features depend on tailoring the morphology of the photoanode and therefore recent researches are focused immensely on optimizing suitable semiconducting nanostructures for DSSC applications.

(ii) Dye Material

Dye or sensitizer, anchored on the photoanode serves as the light absorbent in DSSCs. It plays an active role in creating electrons and the conversion efficiency. Small band gap energy materials are generally used as dyes for DSSC applications. This is because, the photon's energy cannot be absorbed if it is smaller than the material's band gap energy [77]. The dye molecules should strongly get adhered to the photoanode surface ensuring efficient electron injection into the conduction band of TiO_2 . Moreover, the sensitizer needs to be stable for over 10⁸ times redox reactions for providing a long life-time cell. To ensure efficient electron transfer between the excited dye (S^*) and the conduction band of the semiconductor, the excited level of the dye should be higher than the conduction band level of the semiconductor. For

effective dye regeneration, the oxidized state of the dye should be lower than the redox potential of the electrolyte [78]. The light-harvesting capability of the dye in both the visible and/or near IR regions should be substantial to improve the efficacy of the absorption process [79]. The dyes used in DSSCs are divided into two types based on their structure as Organic dye and Inorganic dye. Inorganic dye includes metal complexes, such as polypyridyl complexes of ruthenium and osmium, metal porphyrin, phthalocyanine and inorganic quantum dots, whereas organic dye includes natural organic dyes and synthetic organic dyes [80].

So far, the highest efficiency of DSSC was achieved with mesoporous titania employing ruthenium complexes [81]. The major drawbacks of ruthenium complexes are high cost and its inability to absorb in the near IR region. On the other hand, organic dyes are an excellent alternative to the noble Ru complex based sensitizers and the advantages are as follows:

- Organic dyes could be easily designed and synthesized as their molecular structures are in diverse form.
- Organic dyes are cost-effective and environmental friendly when compared to superior Ru complex based dyes.
- 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 [82].

In recent years several organic dyes such as coumarin dyes, perylene dyes, indoline dyes, xanthene dyes and carbazole dyes have been investigated for DSSCs.

(iv) Electrolyte

Electrolyte also called as hole transporting medium is the material that is filled between the spaces of the nano porous electrodes. The purpose of electrolyte is to donate electrons to the oxidized sensitizer and to prevent the excited electrons from being recaptured by the sensitizer. It has to be a transparent material that allows the light to go through and, at the same time, has good conductivity and fast redox reaction. Moreover, it needs to have long term stability in many aspects including chemical, optical and especially the interfacial stability that relates to desorption and degradation of dye from oxide film [83]. The electrolyte used in a DSSC is divided into three types: liquid electrolyte, quasi solid-state electrolyte, and solid electrolyte. Liquid electrolyte could be divided into organic solvent electrolyte and ionic liquid electrolyte according to the solvent used [84]. The most commonly used electrolyte is liquid iodide/triiodide redox couple dissolved in organic solvents. Organic solvent electrolytes have been widely investigated in DSSCs owing to their low viscosity, fast ion diffusion, high efficiency, easy design, and high pervasion into the nanocrystalline film electrode [85]. The composition of the electrolytes is given by an organic solvent, redox couple, and additives.

The ideal characteristics of the redox couple for the DSSC electrolyte are:

- The redox potential should be thermodynamically favorable with respect to the redox potential of the dye to maximize cell voltage.
- High solubility to the solvent to ensure high concentration of charge carriers in the electrolyte.
- High diffusion coefficients in the used solvent to enable efficient mass transport.
- Absence of significant spectral characteristics in the visible region to prevent absorption of incident light in the electrolyte.
- High stability of both the reduced and oxidized forms of the couple to enable long operating life [86].

(V) Counter Electrode

Counter electrode, another important component of the DSSC needs to provide high conductivity in order to complete the redox reaction in a very short span of time for ensuring life-time, stability and preventing electron recapture [87]. The most commonly used counter electrode materials are platinum, gold and silver. Currently, platinum based counter electrodes exhibits high efficiency as it has high electron mobility that can regenerate the electrolyte rapidly and has high stability against the electrolyte's corrosive characteristics [88]. Due to the high cost of platinum and scarce availability, researchers are forced to seek for an alternative low cost and efficient counter

electrode. Carbon based counter electrodes with different structures, such as nanotubes and nanofibres, have been widely used and investigated in recent years for DSSCs. Carbon materials are inexpensive and have good conductive and can catalyze the reduction of tri-iodide [89].

1.4.3 The Operating Mechanism of DSSC

The operating mechanism of the DSSC is shown in Figure 1.7. The working principle of DSSCs involves certain important processes such as, absorption of light, separation of charges and charge collection. When DSSCs are exposed to solar irradiation, an incident photon creates a bound electron-hole pair. A broad band component of the solar light generates electron-hole pairs in the dye sensitizer which anchors itself onto the photoanode of wide band gap semiconductor nanoparticles. When the electron-hole pairs are formed in the dye molecules, they are quickly separated at the pico-second scale due to the difference in energy levels. Electrons are then injected from the dye molecules to the conduction band of the photoanode, and are transferred to the transparent conduction oxide film (TCO) that is coated on the glass substrate. In this structure, the maximum output voltage is the difference between Fermi energy of the semiconductor film and the redox potential of the electrolyte [90].

Step (i): Light Absorption

Upon sun-light illumination on the dye surface it will absorb light (photons) and its electron would get excited from the highest occupied molecular orbital

(HOMO) to the lowest unoccupied molecular orbital (LUMO). The LUMO is required to have an energy level above the conduction band edge of the semiconductor metal oxide.

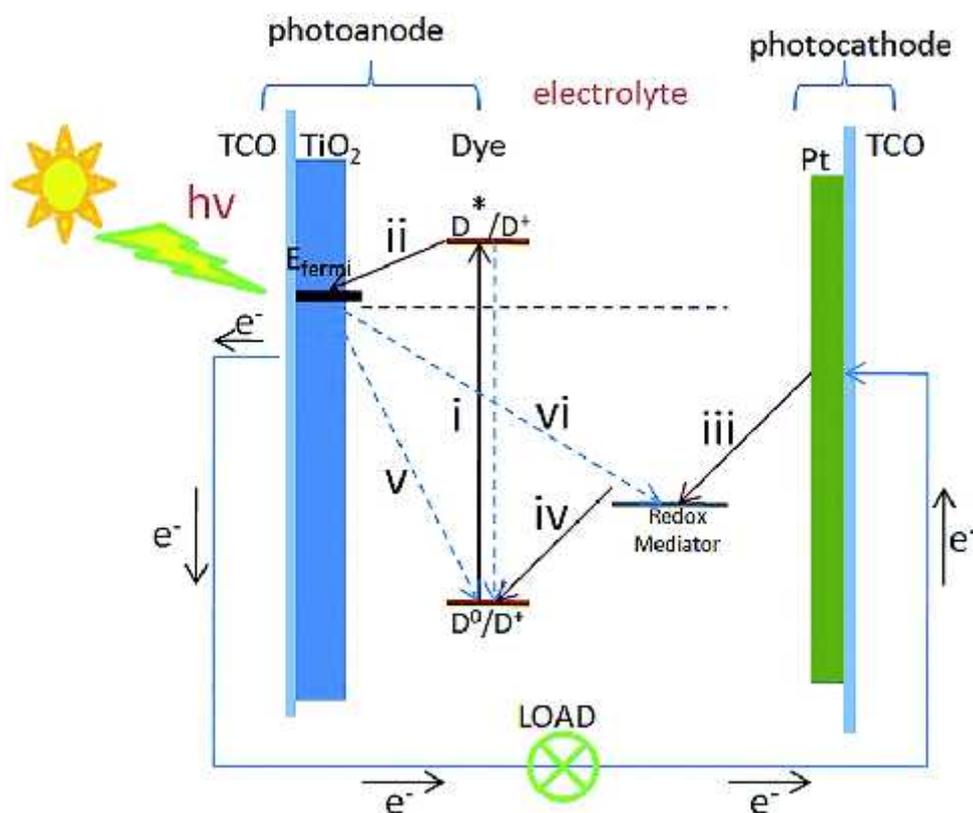


Fig. 1.7 The working principle of DSSC

Step (ii): Charge Injection

The excited dye penetrates electrons in to the conduction band of the working electrode (TiO₂) and consequently the dye becomes oxidized. Charge separation takes place across the semiconductor boundary where an electron is situated in the conduction band of TiO₂ and the hole in the oxidized dye molecule. The difference in energy, density of states and the complex

conjugate orbits between dye molecule and the semiconducting metal oxide surface are responsible for the induced electron injection.

Step (iii): Electron Percolation

The electrons in the conduction band of TiO_2 will then penetrate through the porous network of TiO_2 and reach the conducting surface of the TCO. This electron goes travels to the load to generate electricity in the outer circuit and finally goes back to the counter electrode.

Step (iv): Dye Regeneration

The oxidized dye is reduced by gaining electron from the electrolyte containing I^-/I_3^- before it recaptures the conduction band electron. This process allows the dye molecule to absorb the next photon striking it.

Step (v & vi): Redox Species Regeneration

At the counter electrode I_3^- gets two electrons and generates three iodides and is reduced to its original state before the recombination of conduction band electrons occurs with the help of catalytic activity. Thus the maximum photo voltage within DSSCs is specified by the difference between the semiconductor conduction band edge and the redox potential of electrolyte. In this way, the circuit gets completed by the transfer of electron *via* the external load.

1.4.4 Advantages

Dye sensitized solar cells are considered as the most efficient third-generation

solar technology available and is greatly used in applications like rooftop solar collectors. The power production efficiency is around 11%, as compared to thin-film technology cells which are between 5% and 13%, and traditional commercial silicon panels which operate between 12% and 15%. DSSCs are chosen as a best alternative where Lower-cost High-efficiency cells are required.

- DSSCs are an attractive replacement for current technologies in low density applications, where the light weight and mechanical robustness of the printable cell is a key benefit.
- DSSCs work even in low-light conditions. Hence they are very popular under cloudy weather conditions and non-direct sunlight, where traditional cells would be a failure.
- A traditional solar cell is encased in glass with a metal at its back for increasing its strength. Such a setup may cause a decrease in its efficiency, as the cells heat up internally. However, DSSCs are built up with only a thin layer of conductive plastic on the front side to allow radiation of heat much easily and quickly and therefore operate at low internal temperatures. Also the cell's mechanical structure is such that it indirectly leads to higher efficiencies at higher temperatures [91-93].

Some of the novel applications of DSSCs are shown in Figure 1.8.



Fig. 1.8 Applications of DSSCs

1.5 Literature Review

Dye Sensitized Solar Cells (DSSCs) [94] are one of the most promising solar cells among the third generation PV technologies and are widely acclaimed for their low cost, scalable fabrication techniques and minor environmental impact [95,96]. Typically, DSSCs consist of a sensitized photoanode material on transparent conducting substrate, a redox electrolyte and a platinized counter electrode [97]. The photoanode material in DSSC is a key component which plays a major role in dye loading, electron injection, transportation and collection and thereby it exhibits significant influence on the power conversion efficiency of solar cells [98]. Employing nanostructured semiconductor photo anode materials have attracted much attention as fundamental building blocks for the development of next generation solar

energy conversion devices [99]. Titanium dioxide (TiO_2) has been widely explored as a primary photoelectrode in DSSCs, due to its low cost, non-toxicity, physical stability, wide band gap nature and diverse applications [100, 101]. An ideal photoanode must possess high surface area and porous nature for dye absorption, excellent light scattering ability, less recombination rate for efficient charge separation [102]. Thus efficient operation of DSSC largely relies upon the photoanode and its performance which could be further enhanced by improvisations such as doping [103], forming nanocomposites [104], incorporating plasmons [105], developing nanostructures [106] and introducing blocking or scattering layers [107]. In this regard, we have attempted to improve the properties of TiO_2 based photoanode by forming nanocomposites with the addition of Tin dioxide (SnO_2) which acts as an electron transport layer and also incorporated Copper (Cu) plasmons for boosting its light harvesting ability. SnO_2 is another wide band gap semiconducting material which offers high electron mobility that can be translated into faster transport of electrons for collection [108]. Under UV illumination, it creates less oxidative holes in the valence band to minimize the dye degradation rate and improve the long term stability of DSSCs [109]. Moreover, the conduction bands of SnO_2 act as a sink for photo generated electrons whereas the photo generated holes accumulate in the valence band of TiO_2 , thereby improving charge separation [110]. Thus the photoanode behavior of TiO_2 nanomaterial could be further amplified by coupling SnO_2 ,

hence combining the characteristic features of both materials. Metal nanoparticles have been employed in solar cells to increase light absorption and also to promote light scattering due to their surface plasmon effect [111]. Generally for plasmonization, noble metals such as gold and silver are being explored despite their expensive nature. Herein, we have chosen Cu as the plasmon material as it is more abundant, less expensive than silver and gold and occurs with comparable absorbance in the visible region of the spectrum [112].

As envisaged from literature, tuning the morphology of photoanode materials has a remarkable impact on their characteristics which could further enhance the solar cell performance. Electron transportation and effective dye loading are the two most important parameters in DSSCs and these factors depend upon the surface topography, surface area grain boundaries and porosity of the photoanodes [113]. The above features depend on tailoring the morphology of the photoanode and therefore recent researches are focused immensely on optimizing suitable semiconducting nanostructures for DSSC applications. Though TiO₂ nanoparticle based DSSC has reported the highest efficiency till date, owing to its high surface area, its performance is limited by the surface grain boundaries which results in slow electron transportation [114]. One dimensional nanostructures (1D) such as nanorods, nanotubes, nanowires, nanofibers are considered as a better alternate as they provide dire-

ctional electron transport with lesser recombination rate. However, they lack in desired surface area for efficient dye absorption thereby resulting in poor light harvesting capability [115-118]. Three dimensional nanostructures (3D) like nanoflowers and hierarchical microspheres are deeply investigated and considered for their excellent light scattering capability together with their faster electron transport [119].

Camposeco *et al* have reported the synthesis of TiO₂ nanotubes, nanofibers, nanowires and nanoparticles for photocatalytic applications and found that their photocatalytic activity strongly depends on the nature of TiO₂ nanostructures and the pH medium of the solution [120]. Debabarata Sarkar *et al* have demonstrated the morphology control of rutile TiO₂ hierarchical architectures like 3D microspheres, nanorods with sharp-edge facets, densely packed nanorod arrays, cauliflower like nanostructures on fluorine doped tin oxide substrates (FTO) for field emission properties by varying the volume of HCl [121]. Furthermore, S.S Mali and her co-workers reported the fabrication of nanocorals, nanorods and nanoflowers on FTO substrates with the addition of room temperature ionic liquid [Bronsted Acidic Ionic Liquid] by hydrothermal method for DSSC applications [122]. Hierarchical rutile TiO₂ nanoflower synthesis assisted by various cations via direct hydrothermal growth on FTO glass substrate was studied by Meiden Ye *et al*, who observed an efficiency of about 4% upon TiCl₄ treatment on photoanodes [123]. Also

the studies conducted by Meinan Liu *et al.* and Fang Shao *et al.* showed that a hierarchical TiO₂ nanoarchitecture with microflowers morphology could improve the incident light absorption evidently [124,125]. Hence we were motivated to investigate the morphology based properties of multidimensional TiO₂ nanostructures such as 0D TiO₂ nanoparticles, 1D nanorods and 3D nanoflower architectures and their performance as proficient photoanodes in DSSC applications. Multidimensional photoanode performances were further enhanced by Cu-SnO₂ incorporation and their DSSC efficiencies were tested.

1.6 Objectives of the Present Work

The objectives of the present study are as follows:

- To conduct an extensive literature survey regarding the current status and development of Dye Sensitized Solar Cells, especially the photoanode materials and the means of improving their performance.
- To verify the feasible experimental procedures for synthesis of 0D, 1D and 3D TiO₂ based nanostructured materials under basic laboratory conditions and DSSC fabrication.
- To synthesize 0D TiO₂ nanoparticles using sol-gel method without any additives and to form nanoparticle composites employing plasmon (Cu) activated SnO₂.
- To develop an optimized concentration of plasmon (Cu) on metal oxide (SnO₂) that is to be added to multidimensional TiO₂ nanostructures and to study its impact on solar cell performance.
- To grow 1D TiO₂ nanorods and 3D TiO₂ nanoflowers directly on conducting Indium Tin Oxide (ITO) glass substrates without any surfactants, additives or templates.
- To make a comparative analysis of the multidimensional TiO₂ nanostructures by investigating their structural, textural, surface,

electrical and optical properties and to study the morphological impact on the aforementioned properties.

- To enhance the performance of multidimensional TiO₂ nanostructured photoanode material by the addition of SnO₂/Cu nanocomposite and to examine its characteristics as a potential photoanode material.
- To fabricate prototype Dye Sensitized Solar Cells with Safranine O and Eosin Y organic dyes targeted at achieving good efficiency at low cost.
- To test the I-V characteristics and performance of the as-synthesized photoanode materials under AM 1.5 illumination using Class A Sunlite Solar Simulator.
- To examine and evaluate the role of morphology of multidimensional TiO₂ nanostructures and the incorporation of SnO₂/Cu nanocomposite on the performance of DSSC.

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