Chapter 1

INTRODUCTION

1.1 GENERAL BACKGROUND

With India facing rising fuel prices, threats to energy security, and the need to manage economic growth with pragmatic consideration of climate change, renewable energy offers a critical solution to India's burgeoning energy demand challenges. Further, renewable energy technologies are more labour-intensive than more mechanized fossil fuel technologies, as demonstrated in more mature markets, and can provide a tremendous opportunity to create domestic jobs.

1.2 RENEWABLE ENERGY SOURCES

Renewable energy refers to energy from a source that is continually replenished by natural processes. The following are some examples of renewable resources

i) Wind energy,

ii) Solar thermal energy: using heat from the sun to create electric power,

iii) Photovoltaic energy: a system that directly converts sunlight into electric power,

iv) Biomass: defined as wood or plant material or residue, biological waste, crops grown for use as a resource or landfill gases. Biomass do not include garbage or non vegetation-based industrial, commercial or household waste,
v) Geothermal technology,

vi) Hydroelectric with a capacity of less than 60 megawatts,

vii) Tidal or Wave Action and

viii) Fuel Cell: using a renewable fuel as determined by the Commission.

Most of the Renewable energy sources which are also reliable are expensive. They require huge resources and unless there is a wide scale adoption the cost would not come down.

1.3 SOLAR ENERGY - A RENEWABLE ENERGY RESOURCE

Solar energy is radiant light and heat from the Sun harnessed using a range of ever-evolving technologies such as solar heating, photovoltaic’s, solar thermal energy, solar architecture and artificial photosynthesis. It is an important source of renewable energy and its technologies are broadly characterized as either passive solar or solar depending on the way they capture and distribute solar energy or convert it into solar power. Active solar techniques include the use of photovoltaic systems, concentrated solar power and solar water heating to harness the energy. Passive solar techniques include orienting a building to the Sun, selecting materials with favourable thermal mass or light dispersing properties, and designing spaces that naturally circulate air. The large magnitude of solar energy available makes it a highly appealing source of electricity.

The sun is a natural power source that will keep on shining for an estimated 4 billion years. The spectrum of solar light at the Earth’s surface is mostly spread across the visible and near-infrared ranges with a small part in the near-ultraviolet. The amount of solar energy reaching the surface of the planet is so vast that in one year it is about twice as much as will ever be obtained from all of the Earth’s non-renewable resources of coal, oil, natural gas, and mined uranium combined. Solar power (photovoltaic) systems are a sustainable way to convert the energy of the sun
into electricity. Keeping this in view, scientist concentrates much on the solar energy research.

1.4 MATERIALS FOR SOLAR CELL DEVICES

Solar cell devices are currently emerged as potentially and promising application for solar energy. The newly invented solar cell is more efficient powerful energy-generating device on converting sun’s energy to electrical energy (Askari et al 2015). Conventional solar cells have two main drawbacks: they can only achieve efficiencies around ten percent and their expensive manufacturing cost. The first drawback, inefficiency, is almost unavoidable with silicon cells. This is because the incoming photons, or light, must have the right energy, called the band gap energy, to knock out an electron. If the photon has less energy than the band gap energy then it will pass through. If it has more energy than the band gap, then that extra energy will be wasted as heat. These two effects alone account for the loss of around 70 percent of the radiation energy incident on the cell (Sethi et al 2011) although silicon is the dominant material used in solar cells today; alternative materials are needed to meet long-term clean energy economic goals. Moreover, novel concepts and device ideas can be actually manufactured using present nanotechnology.

Nano particles are motes of matter tens of thousands of times smaller than the width of a human hair. Because they're so small, a large percentage of nano particles' atoms reside on their surfaces rather than in their interiors. This means surface interactions dominate nano particle behaviour. And, for this reason, they often have different characteristics and properties than larger chunks of the same material. Nanotechnology (“nano”) incorporation into the films shows special promise to both enhance efficiency and lower total cost (Escolano et al 2005). Many nanostructured materials are now being investigated for their potential applications in photovoltaic. Nano-structured layers in thin film solar cells offer three important advantages. First, due to multiple reflections, the effective optical path for absorption is much larger than the actual film thickness. Second, light generated electrons and holes need to travel over a much shorter path and thus recombination losses are greatly reduced. As
a result, the absorber layer thickness in nanostructured solar cells can be as thin as 150 nm instead of several micrometers in the traditional thin film solar cells. Third, the energy band gap of various layers can be tailored to the desired design value by varying the size of nano-particles. This allows for more design flexibility in the absorber and window layers in the solar cells (Singha et al 2004)

The first generation photovoltaic devices (PV) are based on single- or multi-crystalline p-n junction silicon cells. They are commercially available for installation with market share of about 85% and deliver power with 15% efficiency, but suffer from high cost of manufacturing and installation. There are high purity requirements for the silicon crystals, high fabrication temperatures and a large amount of material is needed for a wafer-based cell. The second generation PV devices use polycrystalline semiconductor thin films, mostly based on CdTe, having a market share of 15% (Ruhle et al 2010). Thin films of CuInGaSe₂ (CIGS) bring down the cost but their efficiency needs to improve for practical applications. The third generation devices will be based on nanocomposites (nano-structured semiconductors, organic-inorganic hybrid assemblies, and molecular assemblies), aiming to deliver high efficiency at an economically viable cost (Pv 2007). Nanostructure offers spatial quantum confinement for the tailor of the optical properties of semiconductor nanomaterials. The use of multi-components offers a high degree of flexibility for altering and controlling properties and functionalities of nanocomposites.

Scientific base for solar PV electric power generation is solid-state physics of semiconductors. While most PV cells in use today are silicon-based, cells made of other semiconductor materials are expected to surpass silicon PV cells in performance and cost and become viable competitors in the PV marketplace. Despite the unlimited solar energy, harvesting it is a challenged mainly because of the inefficiency of the panels.

Quantum dot solar cell is an alternate device to improve Light harvesting efficiency. A quantum dot solar cell is a solar cell design that uses quantum dots as the absorbing photovoltaic material. It attempts to replace bulk materials such
as silicon, copper indium gallium selenide (CIGS) or CdTe. Quantum dots have band gaps that are tunable across a wide range of energy levels by changing the dots' size. In bulk materials the band gap is fixed by the choice of material(s). This property makes quantum dots attractive for multi-junction solar cells, where a variety of materials are used to improve efficiency by harvesting multiple portions of the solar spectrum.

In the nanometric range, metallic and small band gap semiconducting materials exhibit fascinating quantum phenomena (Alivatas 1996; Gaponenko 2010). Indeed, in the nanometric range, materials may be expected to behave quite differently from both molecular and bulk states since the ratio of the number of surface atoms is quite high. As a consequence of this increased ratio the number of valence unsaturated atoms in the nanoparticle becomes significant. There is thus a curiosity to understand the behavior of materials in the nano length scale and if possible to exploit the new properties exhibited by materials purely as a consequence of the smallness of size.

In nanoparticle systems with a characteristic size comparable to the excitonic Bohr radius, one expects high effective quantum efficiencies for photoluminescence due to quantum confinement. This, however, is usually not realized in the case of bare semiconductor nanoparticles due to the presence of the substantial number of surface electronic states which provide efficient nonradiative decay channels and lead to a degradation of the opto-electronic properties (Parinda et al 2002). In this context, several investigators got interested in considering doped and co-doped semiconductor nanocrystals, two-component nanocomposites, semiconductor- dielectric nanocomposites, semiconductor- polymer nanocomposites, etc (Richard 2002).

Nanocomposites are developed for superior device performance. In solar energy harvest and conversion, nanocomposites are utilized to overcome limits of single materials in solar spectrum response (band gap engineering), transport of electrons or holes (defect engineering), reaction of electrons or holes with chemicals (catalyst engineering), and reduce of costs (economic consideration)
1.5 LITERATURE REVIEW

1.5.1 Nano composites

A composite is a combination of two or more different materials that are mixed in an effort to blend the best properties of both. A nano composite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100nm, or structure having nanoscale repeat distance between the different phases that makes up the material. It consist of one or more discontinuous phases of distributed in one continuous phase. Continuous phase is called matrix whereas discontinuous phase is called reinforcement or “reinforcing material”

The general idea behind the addition of the nanoscale second phase is to create a synergy between the various constituents, such that novel properties capable of meeting or exceeding design expectations can be achieved. The properties of nanocomposites rely on a range of variables, particularly the matrix material, which can exhibit nanoscale dimensions, loading, degree of dispersion, size, shape, and orientation of the nanoscale second phase and interactions between the matrix and the second phase.

The general class of nanocomposite organic/inorganic materials is a fast growing area of research. Significant effort is focused on the ability to obtain control of the nanoscale structures via innovative synthetic approaches. The properties of nano-composite materials depend not only on the properties of their individual parents but also on their morphology and interfacial characteristics. This rapidly expanding field is generating many exciting new materials with novel properties. The latter can derive by combining properties from the parent constituents into a single material. There is also the possibility of new properties which are unknown in the parent constituent materials. Therefore they are reported to be the materials of 21st century in the view of possessing design uniqueness and property combinations that are not found in conventional composites.
1.5.2 Classification of Nano composites

Nano composites are broadly divided into two main classes:

i. Polymer based composites,
ii. Non-polymer based composites.

Broad classification of nanocomposites are shown in Figure 1.1

![Classification of nanocomposites](image)

**Figure 1.1 Classifications of Nanocomposites**

The present study we are focusing on Non-polymer based composites.

1.5.3 History of Solar Nano composites

Nanocomposites have attracted tremendous attention due to their potential applications in biomedical, catalytic, separation, chemical sensing, fuel cell, capacitor, microfabrication, tribological, resonant coupling, high flux gas transport and etc. Nanocomposite materials are complex of nanophase materials and other materials; it optimizes the performance of traditional materials.

The solution to the problem that narrow-band gap semiconductors for efficient absorption of sunlight are unstable against photo-corrosion came in the
separation of optical absorption and charge-generating functions. An electron transfer sensitizer is used to absorb the visible light and inject charge carriers across the semiconductor-electrolyte junction into a substrate with a wide band gap, which is stable. This concept leads to the development of dye sensitized solar cells (DSSC) in 1991 (Reyes 2008; Durr 2006; Tachikawa et al 2007). Matsumura et al. developed ZnO-DSSC in 1976 (Tsubomura et al 1976). In DSSC, the semiconductor is in the mesoscopic state minutely structured with an enormous internal surface area (percolating nanoporous networks). The semiconductor (TiO$_2$, ZnO, SnO$_2$, CdSe etc.) films are made up of arrays of tinny crystals measuring a few nanometers across, which are interconnected to allow electronic conduction to take place. This structure has a much larger surface area (over a thousand times) available for dye chemisorption than a flat, unstructured electrode. The photocurrent in standard sunlight increased 103-104 times when passing from a single crystal to a nano-crystalline electrode. An overall power conversion efficiency of 10.4% has been obtained for DSSC (Wang et al 2010; Green et al 2011). The record efficiency of DSSC is 12% for small cells and about 9% minimodules (Hagfeldt et al 2010). The successful of DSSC has rekindled interest in tandem cells for water splitting by visible light. Tandem cells are needed for two reasons. First, most metal oxide semiconductors (such as WO$_3$, Fe$_2$O$_3$ and TiO$_2$) can only reduce or oxidize water, not both. Secondly, most of the oxide semiconductors only absorb UV light. With DSSC can efficiently utilize the visible light and TiO$_2$ can reduce water, TiO$_2$ DSSC are used as bottom electrode to absorb the visible light and reduce water to hydrogen gas, which is in couple to the top electrode, either crystalline WO$_3$ (Ulmann et al 2001) or Fe$_2$O$_3$ (Khan et al 1999) to absorb the blue part of the sunlight. This configuration is in close analogy to the “Z-scheme” of the photosynthesis of the green plants adsorbing complementary parts of the solar spectrum, where one photo system oxidizes water to oxygen and the other generate the compound NADPH used in fixation of carbon dioxide. At present, the overall conversion efficiency from standard solar light to chemical energy is 4.5%. Further the idea of sensitization, but using quantum dots (QDs) instead of dye to be attached to the semiconductor oxide matrix
as light absorbers, we see the birth of the quantum dots sensitized solar cells (QDSCs) in 1984 (Serpone et al. 1984). Comparing to DSSC, QDSSC has higher absorption, greater stability, wider tunable responsible wavelength range, and importantly the possibility to exploit multiple exciton generation and utilize hot electrons whose energy is higher than the low limit of conduction band (Nozik 2002). The solar efficiency of liquid junction QDSSCs has reach 4.9% at present (Hodes 2008; Zhang et al. 2011). The name of the third generation solar cells are given to devices aim to overcome the Shockley-Queisser limit of single junction or single band gap devices (33.7%), even the limit of an infinite stack of band gaps that perfectly matched to the solar spectrum (68%), and large-scale implementation. In principle, sunlight can be converted to electricity at efficiency close to Carnot limit of 93%. QDSSCs are very promising third generation solar cells due to their potential of achieving competitive cost-efficiency ratio. DSSCs are second generation solar cells with the possibility to become third generation devices if the efficiency can be largely improved.

1.5.4 Mixed Oxides for solar cell Applications

MgO/NiO electrodes have been extensively characterized using physical and electrochemical methods. Dye-sensitized solar cells have been prepared from these films, and the higher concentrations of MgO improved the photovoltage of these devices; however, there was a notable drop in photocurrent with increasing Mg2+. A MgO concentration of 5% was found to strike a balance between the increased photovoltage and decreased photocurrent, possessing a BET surface area of 35 m² g⁻¹ and a large pore volume in both the meso- and macropore range, which lead to a higher overall power conversion efficiency than NiO alone (Marco et al. 2015).

The mixed zirconia/titania electrode can absorb UV light below 380 nm, corresponds to energy band gap (Eg) around 3.27eV, which is higher than that of pure component of titania (Eg = 3.2eV). Due to the conduction band energy (Ec) of ZrO₂ is approximately −1.0eV, which is more negative than −0.3eV of TiO₂, a larger Eg of zirconia/titania electrode could leads more negative value of Ec than that of TiO₂ electrode. This could increase an open-circuit voltage of the cell fabricated from TiO₂-
ZrO$_2$ electrode up to 4%. Both of these increments contributed the improvement on a solar energy conversion efficiency up to 17% (Athapol et al 2005).

The physical properties and photo electrochemical characterization of the spinel ZnFe$_2$O$_4$ have been investigated for the hydrogen production under visible light (Boumaza et al 2010). The forbidden band was found to be 1.92eV and the transition is indirectly allowed. The electrical conduction occurs by small polaron hopping with activation energy of 0.20eV. P-type conductivity is evidenced from positive thermopower and cathodic photocurrent. The flat band potential (-0.33 VNHE) determined from the capacitance measurements is suitably positioned with respect to H+/H$_2$ level. Hence, ZnFe$_2$O$_4$ was found to be an efficient photo catalyst for hydrogen generation under visible light.

Addition of ITO or FTO nanoparticles to the TiO$_2$ nanoparticle film electrode, the overall light conversion efficiency increased.

1.5.5 TiO$_2$ quantum dots

Semiconductors with nanostructures, such as nanowires, nanorods, nanotubes, nanobelts and so on, are well known semiconductor nanostructures which are fascinating due to their novel photoelectrical properties and the unique quantum effects related to the material architectures. Titanium dioxide (TiO$_2$) as one of the most promising photo catalysts which finds applications in the field of optoelectronics, catalysis, medicine, sensor devices, solar cells etc.

TiO$_2$ photo-catalyst has attracted continuously increasing attention of researchers due to its wide range of potential applications in the quantitative destruction of undesirable chemical containments in water and air which gives a reasonable solution to the water and air pollution. The excellent properties of TiO$_2$, such as non-toxicity, strong oxidation power, highest light-conversion efficiency, and high stability towards photo-corrosion makes it more promising material for the photo-catalytic processes (Alex et al 2013; Fujishima et al 2008; Weir et al 2012).
Four naturally occurring titanium dioxide polymorphs exist: rutile, anatase, brookite and titanium dioxide (B) (Banfield & Veblen, 1992). Anatase and rutile are tetragonal, brookite is orthorhombic and titanium dioxide (B) is monoclinic. In all four polymorphs, titanium is coordinated octahedrally by oxygen, but the position of the octahedra differs between polymorphs. The structure of rutile is the most dense and its unit cell is the smallest. Anatase has four formula units per unit cell with \(a = 0.379\) nm and \(c = 0.951\) nm; rutile has two with \(a = 0.459\) nm and \(c = 0.296\) nm; brookite has eight with \(a = 0.917\) nm, \(b = 0.546\) nm and \(c = 0.514\) nm; and titanium dioxide (B) has eight with \(a = 1.216\) nm, \(b = 0.374\) nm, \(c = 0.651\) nm and \(\beta = 107.29^\circ\) (Prasai et al 2012). Only the structures of rutile (titanium dioxide-rutile) and anatase (titanium dioxide-anatase) are reported in commercial products

Titanium dioxide has three different structure types; rutile, anatase, and brookite. All of these crystalline forms of \(\text{TiO}_2\) occur in nature as mineral, but only rutile and anatase have been able to be synthesized in pure form at low temperature until recent days (Zheng et al 2001). Therefore, anatase and rutile phases which belong to the tetragonal crystal system are widely studied on their synthesis, characterizations and photo catalytic properties (Kim et al 1999; Yang et al 2000; Zheng et al 2000). So far anatase phase is known to exhibit higher photo catalytic efficiency compared with rutile phase. Only little efforts have been made on the synthesis, characterization and properties of brookite phase which is belonging to the orthorhombic crystal system (Pottier et al 2001; Zheng et al 2000; Komimani et al 2000). The poor result on brookite phase is due to the difficulty in preparing the pure brookite type \(\text{TiO}_2\) without mixture of rutile or anatase phase. Recently, the method to synthesize pure brookite phase \(\text{TiO}_2\) was reported (Lee et al 2005), which means that versatile studies on the brookite phase can be ignited.
Figure 1.2 Crystal structures of the (a) rutile (b) anatase and (c) brookite phases of TiO$_2$
Table 1.1 Basic Properties of TiO₂

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>TiO₂</td>
</tr>
<tr>
<td>Molar mass</td>
<td>79.866 g/mol</td>
</tr>
<tr>
<td>Appearance</td>
<td>White solid</td>
</tr>
<tr>
<td>Odor</td>
<td>Odorless</td>
</tr>
<tr>
<td>Density</td>
<td>4.23 g/cm³</td>
</tr>
<tr>
<td>Melting point</td>
<td>1843 °C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>2972 °C</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Refractive index (nD)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.488 (anatase)</td>
</tr>
<tr>
<td></td>
<td>2.583 (brookit)</td>
</tr>
<tr>
<td></td>
<td>2.609 (rutile)</td>
</tr>
</tbody>
</table>

Several authors reported the synthesis of TiO₂ nano particles via different techniques like sol-gel synthesis (Selvaraj et al 1992), hydrothermal synthesis (Jae et al 2009), chemical vapour deposition, solvothermal techniques (Djenadic et al 2010; Fei et al 2013) etc. A few publications described the fabrication of TiO₂ nanoparticles via flame method (Yang et al 2013). (Bessekhouad et al 2003) prepared TiO₂ nano particles having size between 8nm and 40nm by emulsification method. Maurya et al prepared rutile phase TiO₂ of 5.6 nm. (Mahshid et al 2000) prepared mixed phase TiO₂ nano particles by sol-gel method of crystallize size between 27nm to 107nm. Optical band gap of TiO₂ nano powder was determined to be 3.17eV, which is in agreement with bulk TiO₂.

(Wu et al 2004) reported the one step synthesis of N- and F-codoped mesoporous TiO₂ photo catalysts via a reproducible, rapid and single-step combustion method. The photo catalytic activity of the synthesized N- and F-codoped mesoporous TiO₂ through the decomposition of acetic acid, showing that the N- and F-codoped mesoporous TiO₂ catalyst fabricated in this study exhibits superb photo catalytic activity and visible light response.

The main drawback of TiO₂ as a photo catalyst for practical applications is its high band gap energy (3.2eV for anatase; 3.0eV for rutile), limiting its use of the visible portion of the solar light (which accounts for about 45% of total solar energy;
ultraviolet light accounts for ~5%. The lowering of the band gap energy is the challenge for developing the future generation of TiO$_2$-based photo catalysts. In order to shift the absorption edge of TiO$_2$ to visible light, much effort has been devoted towards the modification of the electronic structure of TiO$_2$-based materials, for instance, doping with transition metals such as Ag, Fe, Cr or Mo (Morikawa et al 2006; Ohno et al 1999; Behar et al 2006).

However, transition-metal-doped materials suffer from thermal instability, increase of carrier-recombination centers or the requirement of an expensive facility (e.g. ion implantation). Another approach to narrowing the band gap of TiO$_2$ is non metal element doping. This approach can be achieved by substituting lattice oxygen with anionic elements such as C, N, S, F, Br, Cl or I (Kesong yang et al 2012; Adriana Zaleska 2008; Yating Gua et al 2015; Borras et al 2007; Takeshi okato 2005). Thus, research has increasingly focused on the development of non metal doping TiO$_2$ systems; non metal-doped TiO$_2$ nanostructures also have high thermal stability and low carrier-recombination centers (Khan et al 2008).

Ru doped TiO$_2$ particles have been synthesized by a combination of a sol-gel and hydrothermal process. Nanosized Ru doped TiO$_2$ particles were obtained in the temperature range of 170°C-210°C for 6 h (Hyun et al 2009). The average size of the synthesized particles increased when reaction temperature increased. The crystalline phase of the synthesized Ru doped TiO$_2$ particles shows the coexistence of anatase and rutile reaction at the temperature range of 170°C to 210°C for 6 h.

Mwabora et al investigated TiO$_2$–xNx film prepared by sputtering and found an improvement over pure TiO2 under visible light in both optical absorption and photo catalytic activity (Julius et al 2004).

The influence of calcinations temperature on crystallite size, morphology, band gap and luminescence properties of mixed phase TiO$_2$ was investigated by (Gupta et al 2011). The band gap decreases with increases in temperature.
Anpo and co-workers (Lina et al 2006) reported particles of rutile and anatase titania with size (expressed as $2R$, where $R$, is the particle radius) in the range 5.5-200 nm (rutile) and 3.8-53 nm (anatase). Apparently, these crystallites displayed distinct size quantization effects even at such relatively large sizes. For a 12 nm rutile particle the band gap increased by -0.067eV relative to the bulk band gap (3.03eV); for anatase particles the band gap increased by about 0.156eV relative to the bulk value of 3.18eV.

Kormann and co-workers (Sarode et al 2011) indicated that the small particles of TiO$_2$, prepared using the arrested hydrolysis of either titanium tetrachloride or tetraisopropoide, show size quantization when $2R$ = 2.0-4.0 nm. The particles exhibited a 0.15-0.17eV blue shift of the optical absorption edge under anaerobic illumination. They assigned the shift to exciton confinement in these otherwise very small particles.

Nanocrystals of TiO$_2$ photo catalyst have been synthesized by solvothermal method. The photo catalysts were characterized by XRD, UV–Vis spectroscopy and photo catalytic study. The analysis from X-ray diffraction revealed that the annealed product at 1000°C shows crystal phase of rutile.

The optical properties of nanocrystalline TiO$_2$ have been tentatively studied in recent years and many interesting results have been obtained (Dewhurst et al 1996; Wang et al 2010; Matthew et al 2013). Time-resolved photoluminescence spectroscopy studies by (Xiuli Wang et.al 2009) gives an insight into the distribution of trap states and their effect on carrier dynamics in TiO$_2$. The emission studies carried out by Mathew et al (Tang et al 1994 ) show four peaks, which are found to be generated from excitonic as well as surface state transitions. It is found that the emission wavelengths of these colloidal nanoparticles and annealed nanoparticles show two category of surface state emission in addition to the excitonic emission.

More recently, the simultaneous doping of two kinds of atoms intoTiO$_2$ has attracted considerable interest, since it could result in a higher photo catalytic activity
and peculiar characteristics compared with single element doping. Some studies on co
doped TiO$_2$ with atoms such as C and N, S and N, F and N, B and N, C and S, and N
and a variety of metal ions have been reported, and in some cases authors realized the
synergistic effect of co doping.

(Wu et al 2009) reported enhanced visible-light photo activity of
dopant-modified nitrogen-doped TiO$_2$. They reported the formation of PdO nano
particles on a PdO/TiON thin film that can be reduced to metallic palladium under
visible light illumination, which may reduce the electron hole recombination rate
during photo catalysis and enhance the visible light photo activity.

The recent interest in anatase was motivated by its key role in the injection
process in a photo-chemical solar cell with a high conversion efficiency. Forro et al.
investigated the transport properties and revealed a very shallow donor level and a
high n-type mobility in anatase crystals. (Chau- vet et al 2008) studied the magnetic
properties and confirmed the existence of the shallow donors. Tang et al. have stud-
ied photoluminescence in the same anatase crystals. Luminescence due to the
recombination of self-trapped excitons is observed in anatase crystals, but not in t-
utile crystals.

(Tachikawa et al 2008) Eu$^{3+}$-doped TiO$_2$ (TiO$_2$:Eu$^{3+}$) nanocrystals by Ar/O$_2$
radio-frequency thermal plasma oxidation and observed bright red emission either by
exciting the TiO$_2$ host with UV light of shorter wavelength than 405 nm or by directly
exciting Eu$^{3+}$ at a wavelength beyond the absorption edge (405 nm, 3.06eV) of TiO$_2$.
Green, broad band emission has been observed in TiO$_2$ thin films, and has been
assigned to emission of localized excitons (Wu et al 2011). Band-gap excitation of
TiO$_2$ anatase crystals results in Stokes-shifted, visible broad band luminescence which
is interpreted as the emission of self-trapped excitons localized on TiO$_6$ octahedra.
anatase structure and rutile structure appear to host two distinct excitonic states,
namely, self- trapped excitons in anatase, free excitons in rutile (Tang et al 1993).
The band gap value of TiO$_2$ thin films increases with the increasing Au nanoparticles concentrations. The widening of the band gap can be explained by the Burstein-Moss (BM) effect.

(Rocha et al 2001) suggested that change in the crystalline structure of TiO$_2$ are responsible for the decrease in PL intensity in Eu doped TiO$_2$. Merino et al reported that PL intensity becomes weaker after annealing Eu doped TiO$_2$ thin films at 450oC due to thickness reduction of TiO$_2$ film. Jia et al reported the decrease of luminescence intensity for 614nm emission in Eu doped TiO$_2$. Recently Li et al reported that Eu doped TiO$_2$ and Eu$_2$Ti$_2$O$_7$ samples prepared via RF thermal plasma oxidation show the bright red luminescence at 614nm.

TiO$_2$ is a good candidate to be used as the host material of Rare earth in order to excite RE ions (Sm, Er, Eu and Tb) have previously been incorporated into sol-gel prepared TiO$_2$ and their optical properties have been studied.

Pure TiO$_2$ and Eu$^{3+}$ nanocrystallites along with titanium dioxide are prepared by sol-gel route. The dielectric response and the AC electrical conductivity studies of the samples with the Eu$^{3+}$content are performed for a frequency range of 100Hz-2MHz. The presence of Eu$^{3+}$ reduced the dielectric constant and AC Conductivity and shifted the dielectric constant and AC conductivity to a higher frequency region.

Nanocrystalline TiO$_2$ particles doped with different concentrations of Cerium (Ce, 1–10%) have been synthesized using sol-gel method. The a.c. analysis shows that the dielectric constant $\varepsilon$ and dielectric loss tan $\delta$ decrease with the increase in frequency. The dielectric property decreases with the increase in dopant concentration. It is also observed that the impedance increases with an increase in dopant concentration.

The electrical analysis of pure and Pt (1-6%) doped TiO$_2$ showed that the dielectric constant ($\varepsilon^\prime$) and dielectric loss tangent (tan $\delta$) had decrement trend with
increase in frequency. The dielectric property was found to decrease with increase in dopant concentration. Under simulated solar illumination, the amount of dye absorption was found to increase with the increase in optimum content of Pt, resulting in the gradual increase in photovoltaic current, this could be contributed to the improvement in the cell efficiency from 6.45 to 7.62% (Velappan Kandavelu et al 2009).

Pure and doped TiO\textsubscript{2} nano particles are prepared using acid tailored novel sol - gel method using different doping concentration of metal Aluminium and successfully used for making modified photo anode by doctor blade method in dye sensitized solar cells. Ruthenium dye as photo sensitizer along with electrolyte enhanced the performance of DSSCs with the tuned actions of oxidation and reduction reactions (Kirfi Sahu et al 2015).

1.5.6 SnO\textsubscript{2}

Tin oxide (SnO\textsubscript{2}), as one of the most important semiconductor oxides, has been used as photo catalyst for photo degradation of organic compounds. The research on tin oxide semiconductor has been growing due to the wide range of applications, especially as gas sensors. Also, it has been widely used as electrode materials (Yasuhiro Shimizu et al 1991), photovoltaic devices (Ganesh et al 2011), photosensors (Nehru et al 2012), catalysts (Gnanam et al 2010) and antistatic coating (Krishnakumar et al 2008). Tin oxide semiconductor has tetragonal rutile structure, its unit cell parameters and space group are $a = 4.737$ Å, $c = 3.185$ Å and P42/mmm (Paraguay et al 2005) respectively. Tin oxide (SnO\textsubscript{2}) is one of the most intriguing materials to be investigated today, this is because tin dioxide is a well-known n-type semiconductor with a wide band gap of 3.6-3.8eV.

1.5.7 Phase Transition of SnO\textsubscript{2}

The phase transitions in SnO\textsubscript{2} attract special attention because SnO\textsubscript{2} is analogous to silica (SiO\textsubscript{2}). The discovery of the rutile type structure from impact craters had led to several experimental investigations on the pressure and temperature stability relationship of these phases (Chao et al 1962; Martini 1978). Thus the
analysis of the SnO$_2$ analogs would make a significantly contribution to the understanding of the transition to the different crystal structures of silica, especially the pyrite-type. The studies of pressure-induced phase transitions had been enabled by remarkable advances in techniques of crystallography that are carried out in situ under high-pressure conditions. Earlier studies showed, that SnO$_2$ undergoes a transition from rutile-type $\rightarrow$ CaCl$_2$-type $\rightarrow$ $\alpha$ PbO$_2$-type phase $\rightarrow$ fluorite-type cubic phase, transformation of cassiterite phase to the $\alpha$-PbO$_2$-type structure and to a cubic structure at higher pressures identified as fluorite-type (Liu 1978; Endo et al 1990). The sequence of pressure driven transition of crystal structures goes like rutile-type $\rightarrow$ CaCl$_2$-type $\rightarrow$ $\alpha$-PbO$_2$-type $\rightarrow$ pyrite-type $\rightarrow$ ZrO$_2$-type orthorhombic phase I $\rightarrow$ fluorite-type $\rightarrow$ cotunnite-type orthorhombic phase II (Gracia et al 2007; Karki et al 1997; Teter et al 1998; Tsuchiya et al 2004; Oganov et al 2005). Crystal structures of the SnO$_2$ polymorphs are shown in Figure 1.3

Figure 1.3 Crystal structures of the SnO$_2$ polymorphs. (a) Rutile (P4$_2$/mnm) and CaCl$_2$ type (Pnnm) (b) $\alpha$-PbO$_2$-type (Pbca) (c) pyrite-type (Pa$\bar{3}$) (d) ZrO$_2$-type (Pbcn) (e) fluorite-type (Fm$\bar{3}$m) and (f) cotunnite-type (Pnam).
Table 1.2 Basic Properties of SnO₂

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>SnO₂</td>
</tr>
<tr>
<td>Molar mass</td>
<td>150.709 g/mol</td>
</tr>
<tr>
<td>Appearance</td>
<td>White powder</td>
</tr>
<tr>
<td>Density</td>
<td>6.95 g/cm³</td>
</tr>
<tr>
<td>Melting point</td>
<td>1630 °C, 1903 K, 2966 F</td>
</tr>
<tr>
<td>Boiling point</td>
<td>1800-1900 °C (sublimes)</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Refractive index (nD)</td>
<td>2.006</td>
</tr>
</tbody>
</table>

The effects on the photovoltaic performance of the incorporation of SnO₂ nanoparticles into the polymer of a solid-state dye-sensitized solar cell (DSC) based on the poly (ethylene oxide)/poly(ethylene glycol) dimethyl ether solid electrolyte are studied in this paper. It has been found that the addition of SnO₂ nanoparticles to the solid electrolyte produces several key changes in the properties of the solid-state DSC that produced a better performance of the device.

Many processes have been developed to the synthesis of SnO₂ nanostructures, e.g., spray pyrolysis, hydrothermal methods, chemical vapour deposition, thermal evaporation of oxide powders and sol-gel method (Raman et al 2010; Zhiwen et al 2003; Bagheri et al 2008; Du et al 2005; Liu et al 2005). Tetragonal phase SnO₂ nanoparticles were synthesized by sol-gel method using SnCl₂·2H₂O and polyethylene glycol (PEG) at different calcination temperatures was reported by (Aziz et al 2013). (Davar et al 2010) reported the synthesis of SnO₂ nanoparticles by thermal decomposition using [bis(2-hydroxyacetophenato)tin(II)], [Sn(HAP)₂], as precursor.

(Gnanam et al 2010) synthesized nanocrystalline tin oxide powders of about 8 to 13 nm in size using different surfactants such as cetyltrimethyl ammonium
bromide, sodium dodecyl sulphate, and polyethylene glycol via hydrothermal reaction at 160°C for 12 hr and studied their structural and photoluminescence properties.

A simple hydrazine-assisted hydrothermal route was employed to synthesize 22.4nm sized nanocrystalline SnO$_2$ powders by (Patil et al 2012). It has high transparency in visible region and high reflectivity in IR region. SnO$_2$ is also having low electrical resistance.

Electrical conduction in transparent solid occurs in just a few systems such as 4d metal oxides SnO$_2$ and In$_2$O$_3$. However, the reason for this coexistence of electrical conductivity with optical transparency is unclear. But it has been postulated that the transparent conductivity is related to the existence of shallow donor levels near the conduction band formed by large concentration of oxygen vacancies (Kilic et al 2002). It has been shown that several dopants (Co, Al, Mg, Cu, Fe) can lead to an increase of surface area of SnO$_2$ powder (Fang et al 2008). These dopants stabilize the surface and promote a reduction in size. Electrical properties such as charge carrier concentration and thus conductivity can further be improved by extrinsic dopants.

Commonly Sb as a cation and F as an anion has been reported to improve the conductivity of SnO$_2$ (Gardan et al 2000). The optical properties of SnO$_2$ nanoparticles have recently been a subject of great interest. Because of its good optical properties (transparent for visible light and reflective for IR) (Chopra et al 1983) allied to good chemical and mechanical stability (Sekizawa et al 2000), it is commonly used in many applications such as oxidation catalysis, gas sensing (Sergent et al 2002; Wang et al 2003; Zhang et al 2004), transparent conducting oxides (Emons et al 2002; Ferrere et al 1997) and optoelectronic devices (Gu et al 2004; Hayakawa et al 2005). The optical properties of SnO$_2$ nanostructures can be enhanced by several ways like impurity doping (Fang et al 2008), coating with surfactants (Wu et al 1997) and annealing (Dieguez et al 1996). One approach to produce strongly luminescent nanoparticles is to introduce small quantities of dopants.
SnO\textsubscript{2} nanoparticles have been successfully doped with transition metal ions (Fe, Co, Mn, Cu) (Gordan et al 2000; Chopra et al 1983) and rare earth ions (Tb\textsuperscript{3+}, Eu\textsuperscript{3+}, Ce\textsuperscript{3+}) (Gu et al 2004; Gu et al 2004; Elhouichet et al 2003). Many results have shown that several dopants (Co, Fe, Cu) can lead to an increase of surface area of SnO\textsubscript{2} by reducing the grain size and crystallinity (Castilo et al 2005; Jin et al 2004; Hays et al 2005; Koroteenkov et al 2004). Thus the final properties of impurity doped SnO\textsubscript{2} nanoparticles are dependent on both the composition and processing method.

(Tan et al 2008) reported the gas sensing properties of nanostructured SnO\textsubscript{2}. (K Jain et al 2006) reported the effect of Ni doping on SnO\textsubscript{2} gas sensors. There are very few number of papers focusing the electrical and optical properties of SnO\textsubscript{2}. (J A Aguiler Martinez et al 2007) reported the microstructure and electrical properties of SnO\textsubscript{2} doped with Co, Sb, and Na. (A V Gaponov et al 2010) have shown the electrical properties of SnO\textsubscript{2} based ceramics with CuO addition. (J Joseph et al 2007) discussed electrical and optical properties of Cu, Fe, Mn doped SnO\textsubscript{2} films.

(Chun-Ming et al 2007) have already reported band gap narrowing effect for doped SnO\textsubscript{2} nanoparticles. However there is no clear understanding of this phenomenon. A direct-indirect transition have been proposed by (Rakhshani et al 1998). In order to explain the band gap narrowing effect, many groups have suggested that alloying effect of parent compound with some impurity phases may be responsible for the band gap narrowing (Park et al 2003).

Cu-doped SnO\textsubscript{2} nanoparticles of size 10.24 nm were synthesized successfully by ultrasonic assisted solvothermal method using ethanol as a solvent. The emissions observed at 405 and 470 nm were due to the formation of doubly ionized oxygen vacancies and the green peak at 520 nm and yellow peak at 557 nm are attributed due to the different luminescent centers such as defect energy levels arising due to tin interstitials or levels formed by copper within the system (Saravanan et al 2014).
Transparent conducting n-type SnO$_2$ semiconductor films were fabricated by employing an inexpensive, simplified spray ultrasonic technique using an ultrasonic generator at different substrate temperatures (300, 350, 400, 450 and 500°C). The structural studies reveal that the SnO$_2$ films are polycrystalline at 350, 400, 450, 500°C with preferential orientation along the (200) and (101) planes, and amorphous at 300°C. The optical transmittance in the visible range and the optical band gap are 80% and 3.9eV respectively. The films thicknesses were varied between 466 and 1840 nm. The resistivity was found between 1.6 and 4 x 10$^{-2}$ Ω cm. This simplified ultrasonic spray technique may be considered as a promising alternative to a conventional spray for the massive production of economic SnO$_2$ films for solar cells, sensors and opto-electronic applications (Bendjedidil et al 2015).

Self-assembled SnO$_2$ nanoparticles embedded in a PVP polymer layer were formed by using spin coating. PL spectra at 300 K for the synthesized SnO$_2$ nanoparticles in the dibutyl ether solution showed the band edge emission (Jin Ku Kwak et al 2010).

Tin sulfide-tin dioxide nanocomposite was synthesized by the pulsed-current electrochemical method on the surface of tin substrate. The synthesized is used as an oxygen gas-sensing agent to construct a new solid-state sensor. This sensor showed high dynamic range, high sensitivity to oxygen gas, fast response time and very low memory effect without any interference of the other gases. (Hassan et al 2013)

Surface modification of nanoporous tin dioxide materials with fluorinated or perylene units is achieved with trialkynyloorganotin compounds. Irreversible chemisorption occurs in solution at room temperature, yielding an organic layer at the oxide surface via the cleavage of the three tin–alkynide bonds of the precursor and the formation of Snbulk–O–Sn–C linkages. The dye-sensitized nanohybrids are suitable for solar-energy conversion devices.(Vilica et al 2006).
1.5.8. Ruthenium (II) Complexes

A large portion of recent interest in these complexes stems from the very interesting photo physical and photochemical properties exhibited by several of its transition-metal complexes, especially those of ruthenium (Ciana et al 1989). In order to improve the efficiency of DSSC devices based on Ruthenium (II) complexes as sensitizers we have to improve its near-IR absorption because of its absorption maxima restricted at around 550 nm and more over the molar absorption coefficient of ruthenium (II) complexes are low causing use of thicker TiO$_2$ layers which further has disadvantage of achieving higher open circuit potential.

The choice of this metal ion was due to the following reasons. First, because of the octahedral complex geometry, specific ligands could be introduced in a controlled manner. Secondly many Ru(II) polypyridyl complexes have been employed to sensitize nanocrystalline titanium oxide semiconductors, since they had broad and intense MLCT bands absorption and appreciable photoluminescence spanning the visible region and a long excited time. These Ru(II) polypyridyl complexes have attracted attention in recent years due to their well-defined spectroscopic, photo physical, photochemical and electrochemical properties (Juris et al 1988). These properties are of particular use in the construction of supramolecular systems (Prasanna de silva et al 2001) and in the development of photo chemically driven molecular devices (Robertson et al 2003).

The ability to tune the excited state properties of these complexes is central to their potential for practical applications. Third, the Ruthenium metal ion possessed stable and accessible oxidation states ranging from I to III (Zakeeruddin et al 1998). The kinetic stability of these oxidation states and the reversible nature of its redox couples had made the Ruthenium metal attractive for use in the DSSC system, where it will be constantly undergoing redox reactions. The metal-to-ligand charge transfer (MLCT) often had intense absorption bands that extend into the visible and infrared region of the spectrum. The position of the MLCT absorption could be modified by altering the substituents on the bipyridine rings and by controlling the d (π) – π* back-
bonding of the nonchromophore ligands (Ardo, S & Meyer, GJ 2009). The molar extinction coefficient of the MLCT absorption was often very intense, regularly around 15,000 M$^{-1}$ cm$^{-1}$, which was necessary to absorb a large portion of light. These complexes also had long lived triplet excited states, often in the microsecond regime. For comparison, electron transfer from the photo excited complexes were often completed in picoseconds and sometimes in femtoseconds (Ardo, S & Meyer, GJ 2009). This ensured that the photoluminescence of the excited complex did not compete with charge injection, ultimately leading to a greater charge transfer efficiency into the metal oxide film. Finally, these complexes were quite robust/photo stable and were generally insensitive to their external environment.

Ruthenium (II) polypyridyl complexes had been widely investigated for improving the solar-to-energy conversion efficiency and long-term stability of dye-sensitized solar cells (DSSCs) based on nanocrystalline TiO$_2$ films. Among the numerous sensitizers, ruthenium(II) polypyridyl complexes had received significant attention owing to their superior performance in DSSCs. [Ru(dcbpy)$_2$(NCS)$_2$] (dcbpy = 4,4'-dicarboxy-2,2'-bipyridine) (N3) (Nazeeruddin et al 1993; Nazeeruddin et al 2005a) and [Ru(tctpy)(NCS)$_3$](-TBA)$_3$ (tctpy = 4,4',4''-tricarboxy-2,2':6',2''-terpyridine and TBA = tetra-n-butylammonium) (N749) (Nazeeruddin et al 2001) were two of the most successful sensitizers and DSSCs sensitized with these complexes had achieved 11% solar-to-energy conversion efficiencies (Chiba et al 2006; Nazeeruddin et al 2005b).

The light-to-electricity conversion efficiencies of the new (Bu$_4$N)$_3$[Ru(dcbpy)$_2$(tmtH)$_2$], (Bu$_4$N)$_4$[-Ru(dcbpy)$_2$(tmtH)] and (Bu$_4$N)$_5$ [Ru(dcbpy)$_2$(tmt)] complexes, where dcbpy = 2,2'-bipyridyl-4,4'-dicarboxylate and tmt = 2,4,6-trimercapto-1,3,5-triazine, were comparable with those obtained with the N719 dye (Guimaraes et al 2013). Carvalho et al (2014) prepared novel cis-[Ru(Me$_2$-phen)(dcbH$_2$)(NCS)$_2$] complex using a one-pot route. The properties of this complex were compared with those on cis-[Ru(R$_2$-phen)(dcbH$_2$)(NCS)$_2$], where R = Ph or H, to establish a relationship between the donor/acceptor character of the R substituent and
the observed behaviour of these compounds. Zalas et al (2014) synthesized a new dinuclear ruthenium (II) polypyridine complex. Its potential application as a sensitizing dye in dye-sensitized solar cells had been checked under AM 1.5 G irradiation conditions (100 mWcm$^{-2}$) and its performance was compared to that of a commercially available mononuclear analogous dye. The overall light-to-electricity conversion efficiency of the photovoltaic device sensitized by the new dinuclear dye had been found to be over 2.5 times lower than that sensitized by the commercial analogue, despite a much higher extinction coefficient of the former dye. Novel ruthenium(II) phenanthroline complex, Ru$^{II}$(4,4',4''-terpyridine)-(4,7-diphenyl-1,10-phenanthroline-disulfonic acid disodium salt) (thiocyanate), [Ru(L1)(L2) (NCS)], [K328] was designed and synthesized as a photosensitizer for the dye sensitized solar cells (DSSCs) using TiO$_2$ and ZnO electrodes. The influence of the semiconductor type on the performance of TiO$_2$ and ZnO based photo voltaics had been tested. The solar cell performance of TiO$_2$ based solar cell showed better efficiencies compared to ZnO based solar cells (Erten-Ela et al 2014).

Two ruthenium complexes with carboxyl and sulfonil groups had been synthesized, [Ru$^{II}$L$_1$(CN)]Cl (where dcpq was 4-26 the observed behaviour of these compounds. Zalas et al (2014) synthesized a new dinuclear ruthenium (II) polypyridine complex. Its potential application as a sensitizing dye in dye-sensitized solar cells had been checked under AM 1.5 G irradiation conditions (100 mWcm$^{-2}$) and its performance was compared to that of a commercially available mononuclear analogous dye. The overall light-to-electricity conversion efficiency of the photovoltaic device sensitized by the new dinuclear dye had been found to be over 2.5 times lower than that sensitized by the commercial analogue, despite a much higher extinction coefficient of the former dye. Novel ruthenium(II) phenanthroline complex, Ru$^{II}$(4,4',4''-terpyridine)-(4,7-diphenyl-1,10-phenanthroline-disulfonic acid disodium salt) (thiocyanate), [Ru(L1)(L2) (NCS)], [K328] was designed and synthesized as a photosensitizer for the dye sensitized solar cells (DSSCs) using TiO$_2$ and ZnO electrodes. The influence of the semiconductor type on the performance of TiO$_2$ and ZnO based photo voltaics had been tested. The solar cell performance of TiO$_2$ based solar cell showed better efficiencies compared to ZnO based solar cells (Erten-Ela et al 2014).

Two ruthenium complexes with carboxyl and sulfonil groups had been synthesized, [Ru$^{II}$L$_1$(CN)]Cl (where dcpq was 4-
carboxy-2-(4′-carboxypyridin-2′-yl)quinoline and CN was a bidentate cyclometalating ligand) FT22 and FT61 had light harvesting property in the near-infrared region and could be used in dye-sensitized solar cells (DSSCs). Modification of the ligand improves photovoltaic performance, and DSSCs sensitized with FT61 showed large photocurrents (N21 mA cm⁻²) as well as a 55% incident photon-to-current conversion efficiency (IPCE) at 800 nm and 25% IPCE at 900 nm. Funaki et al (2014) synthesized FT102, FT90, and FT117 the new class of NCS-free cyclometalated Ruthenium (II) complexes, Ru(tctpy)(O^N^C) (where O^N^C is a tridentate 6-phenylpyridine-2-carboxylate), which could be used as near-infrared (IR) sensitizers in dye-sensitized solar cells (DSSCs). A tridentate donor ligand, 6-phenylpyridine-2-carboxylate was introduced in order to enhance the light harvesting efficiency in the long wavelength region. Modifying the ligand improved the photovoltaic performance and DSSCs sensitized with FT117 exhibited efficient panchromatic sensitization over the entire visible wavelength, extending into the near-IR region. The highest incident photon-to-current conversion efficiency (68%) was found at 600 nm, and the action spectrum onset was near 920 nm.

1.5.9 Objectives

Renewable energy sources have become important approaches for gaining independence from fossil fuels. Utilizing solar energy is certainly one of the most viable ways to solve the world’s energy crisis.

Dye-sensitized solar cells (DSSCs) have emerged as promising candidates for harnessing solar power because of their low cost, flexibility, ease of production, relatively high energy conversion efficiency, and low toxicity to the environment. Several efforts have been made to fabricate highly efficient DSSCs by the introduction of novel components such as electrolytes, dyes, counter electrodes, and semiconductor photo anodes.

Among these DSSC components, the photo anode plays a vital role in determining the DSSC performance. So far, a titanium dioxide (TiO₂) is one of the
most commonly used photo anode materials, and it is promising material for a DSSC because of its low cost, ease of fabrication, relatively high energy conversion efficiency, high specific surface area, and non-toxicity. However, the major limitation associated with using TiO$_2$ as a photo anode is its random electron transport, which will cause the electron-hole recombination process and hence hinder the cell performance$^2,3$. In order to solve this serious issue, designing a photo anode with an efficient charge transport pathway from the photo injected carriers to the current collector seems to be a possible alternative to enhance the performance of DSSCs.

The future directions for the development of DSSC’s include (1) organic dyes that can extend light absorption into the near infrared with good photo and thermal stability (2) synthesis and modification of various type of TiO$_2$, or other semiconductors, nanomaterials and (3) modification of the physical properties of TiO$_2$ nanostructures to extend optical absorption into the visible region.

Lanthanide doped semiconductor has attracted more attention due to the many profitable potential application in photovoltaic devices, and optical communication. This interest is mainly due to their optical properties that affect emission lifetime, structure of emission spectra, luminescence quantum efficiency and concentration quenching. TiO$_2$ is considered as a good host candidate for rare earth doping due to its good properties such as mechanical, thermal, and anticorrosive properties. In this view, an attempt was made in order to find a material with high light harvesting efficiency. Hence the objective of the present work is to synthesize high quality with the lesser crystallite size of pure and ruthenium doped Ti$_{(1-x)}$Sn$_x$O$_2$ ($x$ varies from 0 to 1 in steps of 0.2) alloy for the first time and explore their structural, optical, properties. The work has been targeted at three specific objectives:

i) To carry out a literature survey on semiconductor TiO$_2$, SnO$_2$ nanocrystals and ruthenium complexes and their different characteristics, physical parameters influencing their structural and optical performance and prepare a comprehensive report,
ii) To select suitable cost-effective and reliable synthesis technique and

iii) To study the structural and optical characteristics of the prepared pure and ruthenium doped Ti\(_{(1-x)}\)Sn\(_x\)O\(_2\) (\(x\) varies from 0 to 1 in steps of 0.2) nanocrystals.

1.5.10 Outline of Thesis

The present work has been focused on synthesis and characterization of pure and ruthenium doped Ti\(_{(1-x)}\)Sn\(_x\)O\(_2\) (\(x\) varies from 0 to 1 in steps of 0.2) alloy by using Simple microwave irradiated (SMI) solvothermal technique. The principle goal of this work has been to identify the better photo anode by structural and optical studies for DSSC. The present work is divided into seven chapters which represent the complete picture of the work carried out. First chapter includes the general introduction and a literature survey of the subject. The second chapter covers the materials used for the preparation and characterization techniques employed thereof for pure and ruthenium doped Ti\(_{(1-x)}\)Sn\(_x\)O\(_2\) (\(x\) varies from 0 to 1 in steps of 0.2) nanocrystals. The third chapter deals, with detailed structural analysis of pure and ruthenium doped Ti\(_{(1-x)}\)Sn\(_x\)O\(_2\) (\(x\) varies from 0 to 1 in steps of 0.2) nanocrystals. The fourth chapter deals, with detailed analysis of optical analysis of pure and ruthenium doped Ti\(_{(1-x)}\)Sn\(_x\)O\(_2\) (\(x\) varies from 0 to 1 in steps of 0.2) nanocrystals. The entire research work carried out is concluded with scope for future work in the fifth chapter. The literature cited are listed in the ‘References’ section.