CHAPTER 1

INTRODUCTION

1.1 GENERAL BACKGROUND

Energy is the part and parcel of life. Life is unimaginable without energy. There will be no life after the extinction of energy. It is everywhere in and around us. Energy can be divided into two basic types:

I. Renewable energy

II. Non-renewable energy

The non-renewable forms of energy includes natural gas, oil, radioactive elements, coal, etc. The renewable energy comes from the sun rays, water, wind and many other natural resources. With the alarming rate of depletion of the major energy resources worldwide, it has become an urgent necessity to seek for renewable energy resources that will power the future. In fact, it has been predicted that in the near future the demand for energy will grow at such a rate that it will be completely impossible to find out or meet the demand with the resources that we had been using for so long, such as - oil, gas, coal, etc. This issue throws a positive challenge to the scientific community for the development of new renewable energy resources.

India Energy Storage Alliance, IESA has released the "Energy Storage in India: Market Assessment" report the first of its kind assessment of energy storage market potential in India. The report highlights some of the
potential drivers that could lead to the growth of Integrating Energy Storage System (ESS) in India. India Energy Storage Alliance, IESA estimates the Indian market potential of energy storage to be 15GW by 2020. The anticipated market size (MW) by 2020 for energy storage systems in India is given in Figure 1.1 (http://www.renewindians.com/2013).

![Figure 1.1](http://www.renewindians.com/2013)

**Figure 1.1** The anticipated market size (MW) by 2020 for energy storage systems in India

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

- Wind energy
- Solar thermal energy: using heat from the sun to create electric power.
- Photovoltaic energy: a system that directly converts sunlight into electric power.
• 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.

• Geothermal technology

• Hydroelectric with a capacity of less than 60 megawatts

• Tidal or Wave Action

• 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. Solar energy is the most readily available sources of energy. It does not belong to anybody and is therefore free. It is also the most important of the non-conventional sources of energy because it is non-polluting and therefore, helps in lessening the greenhouse effect. Keeping this in view, scientist concentrates much on the solar energy research.

1.3 SOLAR ENERGY - A RENEWABLE ENERGY RESOURCE

Photovoltaic systems convert the solar energy into electricity. The expected lifetime of such a system is 25-30 years. Majority of the manufacturers offer 25 years standard solar panel warranty, which means that the power output should not be less than 80% of rated power after 25 years. The energy potential of the sun is immense and it is one of the emerging energy sources, which is subsidized in order to secure the distribution of the technology worldwide. The development of solar energy conversion technology is just about the right time to fulfill the green energy demands.
1.4 MATERIALS FOR SOLAR CELL DEVICES

A scientific base for solar PV electric power generation is solid-state physics of semiconductors. Solar cells can be classified into first, second and third generation cells. The first generation cells also called conventional, traditional or wafer-based cells were made of crystalline silicon, the commercially predominant PV technology, that includes materials such as polysilicon and monocrystalline silicon. First generations solar cells with market share more than 80% based on crystalline silicon (Chapin 1954) are not suitable for mass production due to high production cost, which goes to purify and grow crystalline silicon, however the crystalline silicon has high efficiency and reliability.

Second generation cells were thin film solar cells, that include amorphous silicon, CdTe and CIGS cells and are commercially significant in utility-scale photovoltaic power stations, building integrated photovoltaics or in small stand-alone power system. However vacuum technology needed to deposit thin films brings the product cost to high level. The third generation of solar cells includes a number of thin-film technologies often described as emerging photovoltaics - most of them have not yet been commercially applied and are still in the research or development phase. Many use organic materials, often organometallic compounds as well as inorganic substances. Despite the fact that their efficiencies had been low and the stability of the absorber material was often too short for commercial applications, there is a lot of research invested into these technologies as they promise to achieve the goal of producing low-cost, high-efficient solar cells and thus become viable competitors in the PV marketplace. When sunlight strikes a PV cell, the photons of the absorbed sunlight dislodge the electrons from the atoms of the cell. The free electrons then move through the cell, creating and filling in holes in the cell. It is this movement of electrons and
holes that generates electricity. The physical process in which a PV cell converts sunlight into electricity is known as the photovoltaic effect. One single PV cell produces up to 2 watts of power, too small even for powering pocket calculators or wristwatches. To increase power output, many PV cells are connected together to form modules, which are further assembled into larger units called arrays.

Despite the unlimited solar energy, harvesting it is a challenge mainly because of the inefficiency of the panels. Recent works show that different types of methodology have been proposed to improve the efficiency of solar panels (Hua & Shen 1997; Adiyabat & Rokawa 2002; Moghbelli & Vartanina 2006; Olchowik et al 2006).

Various materials display varying efficiencies and have varying costs. Materials for efficient solar cells must have characteristics matched to the spectrum of available light. Some cells are designed to efficiently convert wavelengths of solar light that reach the earth’s surface. However, some solar cells are optimized for light absorption beyond earth's atmosphere as well. Light absorbing materials can often be used in multiple physical configurations to take advantage of different light absorption and charge separation mechanisms. Materials presently used for photovoltaic solar cells include monocrystalline silicon, polycrystalline silicon, amorphous silicon, cadmium Telluride and copper indium selenide/sulfide (Jacobson 2009). Many currently available solar cells are made from bulk materials that are cut into wafers between 180 to 240 micrometers thick that are then processed like other semiconductors. Other materials are made as thin-film layers, organic dyes and organic polymers that are deposited on supporting substrates. Nanopillars are being researched and have shown promising properties in terms of photovoltaic efficiency. A third group is made of nanocrystals and used as quantum dots (electron-confined nanoparticles). Silicon remains the
only material that is well-researched in both bulk and thin-film forms. Most commonly used material for solar cell applications are crystalline and amorphous silicon.

Photovoltaic (PV) or solar cells can be made of many semiconductor materials. Each material has unique strengths and characteristics that influence its suitability for specific applications. For example, PV cell materials may differ based on their crystallinity, bandgap, absorption and manufacturing complexity.

1.5 INORGANIC MATERIALS FOR SOLAR CELLS

The inorganic semiconductor materials used to make photovoltaic cells include crystalline, multicrystalline, amorphous and microcrystalline Si, the III-V compounds and alloys, CdTe, chalcopyrite compound and copper indium gallium di selenide (CIGS). All of these semiconductors have energy bandgaps within the range 1.1 - 1.7 eV that is they are near to the optimum energy bandgap (1.5 eV) for photovoltaic solar energy conversion by a single junction solar cell. Although the use of crystalline Si cells has continued to increase rapidly, the most successful technology at present is that based on the use of multicrystalline Si, which has expanded even faster. The current solar cell industry is dominated by Si with nearly 90% of the market.

1.6 ORGANIC MATERIALS FOR SOLAR CELLS

The idea of organic solar cells began as early as the 1950’s. The inspiration of using organic molecules as light absorbing materials came from the simple observation that photosynthetic systems in plant life on earth use molecular systems to harvest light and convert it into useful chemical energy. The first generation of organic photovoltaic solar cells was based on single organic layers sandwiched between two metal electrodes of different work
functions. (Chamberlain 1983; Wohrle & Meissner 1991) Early experiments, starting in 1958, focused on sandwiching bio-inspired organic dyes such as porphyrins, phthalocyanines, merocyaninines or chlorophylls between metals with large work function offset. These early cells did not exceed efficiencies of < 1%. A significant breakthrough came in 1986, when Tang (1986) published a 2-layer design demonstrating a power conversion efficiency of about 1%. The photovoltaic properties of his device were determined by the interface between two thermally evaporated organic materials, one absorbing light and generating an excited state as electron donor and the other acting as acceptor, pulling away the photo excited electron. This donor-acceptor photo induced charge transfer principle is the fundamental mechanism that all subsequent organic cell design relies on. The rectifying behaviour of single layer devices (Chamberlain 1983; Wohrle & Meissner 1991) was attributed to the asymmetry in the electron and hole injection into the molecular $\pi^*$ and $\pi$-orbitals, respectively (Parker 1994) and to the formation of a Schottky-barrier (Wohrle & Meissner 1991; Gosh et al 1974; Meissner et al 1992; Karg et al 1993) between the p-type (hole conducting) organic layer and the metal with the lower work function. The power conversion efficiencies reported were generally poor (in the range of $10^{-3}$ to $10^{-2}$ %), but reached remarkable 0.7% for merocyanine dyes in the early days (Morel et al 1978; Gosh & Feng 1978).

An important difference to inorganic solid-state semiconductors lies in the generally poor charge-carrier mobility in these materials (Dimitrakopoulos & Mascaro 2001), which has a large effect on the design and efficiency of organic semiconductor devices. However, organic semiconductors had relatively strong absorption coefficients (usually $\sim 10^5$ cm$^{-1}$), which partly balances low mobilities, giving high absorption in even < 100 nm thin devices. Another important difference to crystalline, inorganic semiconductors are the relatively small diffusion length of primary photo
excitations in these rather amorphous and disordered organic materials (Peumans et al 2003; Halls et al 1996; Halls & Friend 1997; Kerp et al 1998; Savanje et al 1998). These excitons are an important intermediate in the solar energy conversion process and usually strong electric fields are required to dissociate them into free charge carriers, which are the desired final products for photovoltaic conversion. This is a consequence of exciton binding energies usually exceeding those of inorganic semiconductors (Sariciftci 1997; Gregg & Hanna 2003). These features of organic semiconductor materials lead generally to devices with very small layer thicknesses of the order ~100 nm. Most of the organic semiconductors are hole conductors and have an optical band gap around 2 eV, which is considerably higher than that of silicon and thus limits the harvesting of the solar spectrum to a great extent. Nevertheless, the chemical flexibility for modifications on organic semiconductors via chemical synthesis methods as well as the perspective of low cost, large scale production drives the research in this field in academia and industry.

Though common materials used for photovoltaics are inorganic, there has been a tremendous effort to develop organic solar cells within the last three decades (Brabec et al 2001; Halls & Friend 2001; Nelson 2002; Nunzi 2002; Brabec et al 2003). The research started by the application of small organic molecules (pigments) and since the development of semiconducting polymers, these materials were incorporated into organic solar cells resulting in remarkable improvements within the past years (Brabec et al 2001; Halls & Friend 2001). The potential of semiconducting organic materials to transport electric current and to absorb light in the ultraviolet-visible (UV-Vis.) part of the solar spectrum is due to the sp\(^2\)-hybridization of carbon atoms. For example, in conducting polymers the electron in the p\(_z\)-orbital of each sp\(^2\)-hybridized carbon atom will form π-bonds with neighboring p\(_z\) electrons in a linear chain of sp\(^2\)-hybridized carbon
atoms, which leads them to dimerization. Due to the isomeric effect, these \( \pi \)-electrons are of a delocalized nature, resulting in high electronic polarizability.

Organic photovoltaic (OPV) represents a potentially cheap and sustainable large scale PV technology. The field has been a very active and continually growing area of research.

Organic solar cells can be broadly classified into 3 types

- Small molecule Solar cell (SM cells)
- Polymer solar cells
- Dye sensitized solar cells

1.6.1 Small Molecule Solar Cell

During the last couple of decades, much effort has been put into the development of solar cells based on small organic molecules (Simon & Andre 1985; Yu et al 1995, Hadziioannou & Hutten 2000; Kaneko 1997). Considerable activity has been spurred by their light weight, potentially low-cost, tuneability of the electronic band gap by chemical synthesis and the simple fabrication of large-area flexible, thin film devices. However, the power conversion efficiency of organic photovoltaic devices is still much lower than that of inorganic photovoltaic devices. This is mainly attributed to lower photogeneration efficiency of charge carriers and high electrical resistivity of organic materials, caused by the low density and mobility of charge carriers. Until recently, the best photovoltaic energy conversion efficiencies for different organic solid state solar cells are typically in the range of 1% (Tang 1986 & Yu et al 1995). The operation processes of an organic small molecule photovoltaic device on the molecular level consist of
three consecutive fundamental steps: (1) absorption of light, (2) creation of separate charges of the donor–acceptor interface and (3) selective transport of the charges through the bulk of the device to the appropriate collecting electrodes. A prerequisite for high efficiency conversion of photons into electrical current is that the holes and electrons should not recombine before being swept out of the device to the external circuit. In order to reduce recombination, the electrons and holes are preferentially transported in different materials or phases. For example, in the case of donor–acceptor devices, an acceptor material with good electron conductivity and a donor material with good hole conductivity is ideal. Therefore, a metastable photo induced charge-separated state and high charge carrier mobilities are important factors.

Recently, organic small molecules competed with the polymeric donor materials in bulk heterojunction solar cells (BHJ) solar cell applications due to their advantages such as facile synthesis, reproducibility of the purity, the number of possibilities for the structural modification of molecules to tune their molecular energy levels for optimizing the photovoltaic device performances (Zhang et al 2011). Presently, the PCE was improved in the range of 4-7% (Fitzner et al 2012; Lee et al 2011; Lin et al 2012) for solution-processed small molecule organic solar cells (SMOSCs) and 10.7% for vacuum-processed tandem SMOSCs. Although small-molecule organic solar cells currently have lower efficiencies than polymer solar cells, they are generally easier to fabricate and their efficiencies are improving.

1.6.2 Polymer Solar Cell

An effort to convert sunlight into electricity, photovoltaic solar cells that use conductive organic polymers for light absorption and conversion
have shown great potential. Organic polymers can be produced in high volumes at low cost, resulting in photovoltaic devices that are cheap, lightweight and flexible. Compared to silicon-based devices, polymer solar cells are lightweight, potentially disposable and inexpensive to fabricate, flexible and customizable on the molecular level and they have lower potential for negative environmental impact. However, it was not until the 1990s that conducting organic polymer solar cells were shown to have an efficiency of 2.9%. In the last few years, much work has been done to improve the efficiency with which these devices convert sunlight into power, including the development of new materials, device structures and processing techniques. The cell efficiency significantly enhanced in polymer solar cells by building a device with a new "tandem" structure that combines multiple cells with different absorption bands. By using cells with different absorption bands, tandem polymer solar cells provide an effective way to harvest a broader spectrum of solar radiation.

1.6.3 Dye Sensitized Solar Cells

A dye-sensitized solar cell (DSSC) is a low-cost solar cell. The DSSC has a number of attractive features; it is simple to make using conventional roll printing techniques, is semi-flexible and semi-transparent, which offers a variety of uses not applicable to glass-based systems and most of the materials used are low-cost. The schematic diagram of the dye-sensitized solar cell (DSSC) is given in Figure 1.2.

Sunlight passes through the transparent electrode into the dye layer where it can excite electrons which then flow into the semiconductor metal oxide. The electrons flow toward the transparent electrode where they are collected for powering a load. After flowing through the external circuit,
are re-introduced into the cell on a metal electrode on the back, flowing into the electrolyte. The electrolyte then transports the electrons back to the dye molecules.

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 the cell. In existing designs, this scaffolding is provided by the semiconductor material, which serves double-duty.

Considering its function in the device, ideally the dye should absorb all the solar energy below a wavelength of about 920 nm and they should inject the photo induced electrons into the semiconductor with a unit quantum yield. This is possible if the LUMO (lowest unoccupied molecular orbital) level of the dyes is well matched to the lower level of the conduction band of the semiconductor and if there is a good electronic coupling between both levels. In order to achieve the electron injection, the dye should be firmly grafted to the semiconductor surface. This is attained through suitable anchoring groups such as: carboxalate, phosphonate or hydroxamate. These groups promote a good overlap between the dye molecule’s excited state orbitals and the empty acceptor levels. In addition, the redox potential of the sensitizer should be high enough to enable the dye regeneration by means of electron donation from the electrolyte. Finally the dye should be stable under solar illumination over the lifetime of 20 years, which implies more than $10^8$ redox turnovers.
A wide range of sensitizers have been developed and tested so far, are classified in chemical terms as Inorganic dyes and organic dyes. Inorganic dyes comprise Polypyridyl metal complexes of ruthenium and osmium, metal porphyrin, phthalocyanine and inorganic quantum dots, while organic dyes include natural and synthetic organic dyes. Up to now polypyridyl - ruthenium complexes have the best photovoltaic performances regarding both conversion and chemical stability. Since the discovery of the ‘ferroin-reaction’ by Blau (1988) more than a century ago, polypyridyl transition metal complexes have been investigated extensively and have found many applications besides analytical and preparative chemistry (Schilt 1969). In the last three decades interest focused on the redox and photophysical properties of such coordination compounds, mainly because of coordinative stability in the oxidation states (Juris et al 1988, Kalyanasundaram 1992; Schneider & Dürr 1991; Willner et al 1998). Especially dye sensitizers of the Ru(II) -polypyridyl type is playing an important role in the study of photo induced electron transfer processes mimicking the processes in the photosynthetic reaction center (Zahavy et al 1995; Magnusson et al 1997;
Dürr et al 1994; Kropf et al 1998; Benniston et al 1998). However, metals such as ruthenium are expensive and are obtained from limited resources.

Recently, many modifications to the Ru-complexes have been proposed for increasing power efficiency. Mainly Ruthenium combined with 2, 2’ bi-pyridine has major properties. The N3 dye, a type of inorganic dye discovered in 1993 by Nazeeruddin and his coworkers had the efficiency of 10%. N3 dye belongs to the promising sensitizers having the general formula ML₂X₂ where L indicates 2,2 bipyridyl-4,4 carboxylic acid , M stands for Ru or Os and X is a halide , cyanide, thiocyanate, acetyl acetonate , thiocarbamate or water substituent. Ruthenium bipydriyl dichloride [Ru(bipy)₃] Cl₂ is one such coordination compound. The Structure of [Ru(bipy)₃]Cl₂ is shown in Figure 1.3.

![Figure 1.3 Structure of [Ru(bipy)₃] Cl₂](image)

Different types Ruthenium complexes prepared by exchanging new ligands instead of 2,2’ bi-pyridine ligand to form [Ru(bipy)₂(L)]²⁺. These type of complexes show different and better properties. The variations in properties are due to MLCT (Metal Ligand Charge transfer). The exchange of a single ligand from [Ru(bipy)₃]²⁺ complexes show a big difference in the photo catalysis, electrical and optical properties etc. The electron transfer
from Ru$^{2+}$ and the substituted ligand is the main reason for the change happened in [Ru(bipy)$_3$]$^{2+}$ complexes. This property of [Ru(bipy)$_3$]$^{2+}$ will depend on the structure and properties of the substituted ligands; some of the examples are given as follows imidazol(in)-2-ylidene ruthenium complexes and [Ru(Cl-phen)$_3$](PF$_6$)$_2$ (where Cl-phen = 5-Chloro -1, 10-phenanthroline) used as catalyst, ruthenium complex of [(5-amino-1,10-phenanthroline)bis(4,4’-dicarboxylic acid-2,2’-bipyridine)] used a photo voltaic cells.

The most important issue of DSSC research is to design effective sensitizing dyes. The main conditions an effective sensitizer should meet are as follows (Nazeeruddin et al 2004)

- Wide range of visible light absorption spectra;
- Strong anchoring on the semiconductor surface;
- Efficient injection of the photoexcited electrons into the semiconductor conduction band;
- The energy of oxidation potential of excited state being higher than that of the conduction band edge of the semiconductor;
- High redox potential of the ground state;
- Long term stability in the solar cell working conditions.

Nazeeruddin et al 1993 & Nazeeruddin et al 1997 have achieved the photon to current conversion efficiencies reached by the devices sensitized with the N3, N719 and black dyes as 10.0%, 11.2% and 10.4% respectively, though these are still not high enough as expected for commercial application in DSSCs. The mainstream research in ruthenium sensitizers is therefore focused on structure modification of the ligands to improve the light harvesting and electron injection efficiency and in consequence, the efficiency of the DSSCs.
DSSC created from nanocrystalline TiO$_2$ films have been intensively investigated over the past decade. The critical component in DSSC is the photoanode, which is typically composed of a porous TiO$_2$ or ZnO nanoparticle film with dye molecules adsorbed onto its surface. To achieve high performance, the photoanode needs to possess a large surface area and good electron transport capability. A TiO$_2$ or ZnO nanoparticle film provides a large enough surface area; however, electron transport is difficult because of the need for electrons to hop across neighboring nanoparticles. Moreover, it is well-known that semiconductor particle surfaces are prone to form defects that can act as electron trapping centers. The presence of these surface traps is detrimental to electron transport because trapping/detrapping events are unavoidable during electron diffusion through the disordered nanoparticle network. By altering the morphology of the photoanode, electron transport pathways may be designed to improve the electron collection (Turner et al 2002; Lagemaat & Frank 2001). Since the sensitizers used in DSSC are critical to the cell's photo-voltaic performance, extensive efforts have been focused on the synthesis of new, highly efficient sensitizers. Among the numerous sensitizers developed for this purpose, Ruthenium(II) polypyridine complexes have received much attention owing to their superior performance in DSSCs. They also have suitable ground- and excited-state energy levels with respect to the nanocrystalline TiO$_2$ conduction-band energy and they match the redox properties of the iodine/triiodide redox couple (Wenger et al 2010; Hara et al 2001; Bouit et al 2009).

From the above discussion, it is clear that, the performance of the DSSC depends on the properties of dye as well as oxide layers. However, more research is being done to improve the power conversion efficiencies in order to turn this technology into a very competitive option in the photovoltaic solar cell market (Yella et al 2011; Burschka et al 2013).
1.7 OBJECTIVES AND METHODOLOGY

1.7.1 Objectives

The objective of the present work is to synthesize high quality with the lesser crystallite size of undoped and doped TiO$_2$, SnO$_2$ nanocrystals and different ligand substituted Ruthenium(II) bipyridine complexes and explore their structural, optical, electrical and photoconducting behavior. The work has been targeted at six specific objectives:

i. To carry out a literature survey on semiconductor TiO$_2$, SnO$_2$ nanocrystals and Ruthenium(II) bipyridine complexes, their different characteristics, physical parameters influencing their electrical and optical performance and prepare a comprehensive report.

ii. To select suitable cost-effective and reliable synthesis technique.

iii. To study the annealing effect by means of phase change and crystallite size of the selected samples.

iv. To study the structural, electrical, optical and photoconducting characteristics of the prepared doped and undoped semiconducting nanocrystals.

v. To study the structural, electrical, optical and photoconducting characteristics of the prepared pure and different ligand substituted Ruthenium(II) complexes.

vi. To study the electrical and photoconducting properties of photosensitizer coated doped semiconductor TiO$_2$, SnO$_2$ nanocrystals.
1.7.2 Methodology

There are many commercially available nanosized TiO$_2$ particles and many methods to synthesize nanosized TiO$_2$ particles. On the other hand, not many commercial TiO$_2$ particles and methods are suitable for highly efficient DSSC. The differences between the particles can be crystal structure, crystallinity, crystal size, surface structure, and the density and distribution of charge traps. These parameters influence electron diffusion coefficient (D), electron life time ($\tau$), and charge injection efficiency (CIE).

In the DSSC system the factors which include the molecular structure of complexes, morphology of semiconductor, electron injection, sensitizer regeneration processes, electrolyte regeneration processes, charge recombination as well as back transfer processes may significantly contribute to lowering the good performance of the DSSC. It is therefore imperative to further examine and understand the chemical properties and synthetic approaches used to obtain materials for the construction of dyes which could enhance the performance of the DSSC in future. It has been reported that the choice of ligand, structure and substituents on nitrogen-based coordinated ligands are paramount in order to influence the photophysical and electro-redox properties of the coordinated Ruthenium complexes thus enhancing the molar absorption coefficient as well as broadening of the metal-to-ligand charge transfer band which may lead to enhanced incident photon to current efficiency (IPCE) in the resulting dye sensitized solar cells.

The most studied complexes are based on [Ru(bpy)$_3$]$^{2+}$ as they have been shown to have long-lived excited states at room temperature that originate from their metal-to-ligand charge-transfer (MLCT) transitions. Hence in the present study an attempt has been made to retard charge recombinations within short time and enhance the absorption and emission of ruthenium bipyridine dye by substituting various ligands such as urea,
thiourea, hydrazine and phenyl hydrazine separately in [Ru(bipy)_3]Cl_2 to form a new dye which have been extensively employed as photosensitizers for the construction of dye sensitized solar cells (DSSCs) in future. Also to improve the properties of semiconductor layers (photo anode), an attempt was made to prepare the pure and divalent metal ion (5.0 mole% of Zn^{2+}, Cd^{2+} and Ni^{2+}) doped (TiO_2 and SnO_2 quantum dots (QDs) by simple microwave irradiated solvothermal method (MIS) and characterized the prepared samples.

1.7.3 Outline of Thesis

The present work has been focused on synthesis and characterization of undoped and doped TiO_2, SnO_2 nanocrystals by using simple microwave irradiated solvothermal (MIS) technique, synthesis of and pure and different ligand substituted Ruthenium(II) bipyridine complexes by chemical refluxing technique. The principle goal of this work has been to identify the better photoanode and photosensitizer materials by the structural, optical, electrical and photoconducting studies.

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 undoped and doped doped TiO_2, SnO_2 nanocrystals as well as pure and different ligand (urea, thiourea, hydrazine and phenylhydrazine) substituted Ruthenium(II) bipyridine dichloride complexes. The third chapter deals, with detailed analysis of pure and divalent metal ion (5.0 mole% of Zn^{2+}, Cd^{2+} and Ni^{2+}) doped TiO_2 nanocrystals. The fourth chapter deals, with detailed analysis of pure and divalent metal ion (5.0 mole% of Zn^{2+}, Cd^{2+} and Ni^{2+}) doped SnO_2 nanocrystals. The fifth chapter deals, with detailed analysis of pure and different ligand (urea, thiourea, hydrazine and phenylhydrazine) substituted Ruthenium(II) bipyridine
complexes. The electrical and optical properties of photosensitizer coated with Cd doped TiO$_2$ and SnO$_2$ nanocrystals are explained in the sixth chapter. The entire research work carried out is concluded with scope for future work in Chapter 7. The literature cited are listed in the ‘References’ section.

1.8 LITERATURE REVIEW

1.8.1 TiO$_2$ Nanoparticles

A significant amount of research on TiO$_2$ had been performed over the last five decades and a number of reviews on various aspects of TiO$_2$ had been published (Carp et al. 2004; Mor et al. 2006; Chen & Mao 2007; Thompson & Yates Jr 2006; Diebold 2003; Linsebigler et al. 1995) to understand and summarize the progress in this field. The Basic properties of TiO$_2$ are presented in Table 1.1.

TiO$_2$ belongs to the family of transition metal oxides. There are four commonly known polymorphs of TiO$_2$ found in nature: anatase (tetragonal), brookite (orthorhombic), rutile (tetragonal) and TiO$_2$ (B) (monoclinic) (Carp et al. 2004). The generation of the phases of TiO$_2$ depends significantly on the synthesis parameters, which in turn affect the product.

1.8.2 Rutile Phase

The vast majority of studies of the bulk and surface properties of TiO$_2$ have been of the rutile phase. The rutile structure, illustrated in Figure 1.4 (a), belongs to the $P42/mnm$ tetragonal space group. The unit cell is defined by the lattice vectors $a$ and $c$ and contains two TiO$_2$ units with Ti ions at $(0,0,0)$ and $(1/2, 1/2, 1/2)$ and O ions at $\pm(u,u,0)$ and $\pm(u+1/2, 1/2-u, 1/2)$ (Muscat et al. 2002). Rutile TiO$_2$ has a tetragonal structure and contains 6 atoms per unit cell (Figure 1.4). The TiO$_6$ octahedron is slightly distorted (Chen & Mao 2007; Thompson & Yates Jr 2006; Diebold 2003). The rutile
phase is stable at most temperatures and pressures up to 60 kbar, where TiO₂ (II) becomes the thermodynamically favorable phase (Norotsky et al 1967); Zhang et al (2000) found that an anatase and brookite structures transformed to the rutile phase after reaching a certain particle size, with the rutile phase becoming more stable than anatase for particle sizes greater than 14 nm. Once the rutile phase formed, it grew much faster than the anatase. The activity of the rutile phase as a photocatalyst is generally very poor. However, Sclafani et al (1990) concluded that the rutile phase can be active or inactive, depending on its preparation conditions.

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### 1.8.3 Anatase Phase

Anatase TiO₂ also has a tetragonal structure with space group \( I4_1/amd \) but the distortion of the TiO₆ octahedron is slightly larger than that of the rutile phase (Mo & Ching 1995; Linsebigler et al 1995), as depicted in Figure 1.4 (b). The unit cell contains two TiO₂ units with Ti ions at (0,0,0) and (0, \( \frac{1}{2}, \frac{1}{4} \)) and O ions at (0,0,u), (0,0,\( \bar{u} \)), (0, \( \frac{1}{2}, \bar{u} + \frac{1}{4} \)) and (0, \( \frac{1}{2}, \frac{1}{2} - u \)). Muscat et al (2002) found that the anatase phase is more stable than the rutile
at 0 K, but the energy difference between these two phases is small (\(\sim 2\) to \(10\) kJ/mol). The anatase structure is preferred over other polymorphs for solar cell applications because of its higher electron mobility, low dielectric constant and lower density (Carp et al 2004). The increased photo-reactivity is because of the slightly higher Fermi level, lower capacity to adsorb oxygen and higher degree of hydroxylation in the anatase phase (Tanaka et al 1991). Selloni (2008) had reported that the reactivity of (0 0 1) facets is greater than that of (1 0 1) facets in an anatase crystal. Yang et al (2008) synthesized uniform anatase crystals containing 47\% (0 0 1) facets using hydrofluoric acid as a morphology controlling agent.

1.8.4 Brookite Phase

Brookite TiO\(_2\) belongs to the orthorhombic crystal system belonging to the space group \(Pnma\). Its unit cell is composed of 8 formula units of TiO\(_2\) and is formed by edge-sharing TiO\(_6\) octahedral. The crystal structure was shown in Figure 1.4 (c). There are four TiO\(_2\) formula units per unit cell with ions at \(\pm (x, \frac{1}{4}, z; x+\frac{1}{2}, \frac{1}{4}, \frac{1}{2}-z)\), where for the Ti ions, \(x=0.264\) and \(z=0.110\); for one O ion, \(x=0.346\) and \(z=0.422\); and for the second O ion, \(x=0.012\) and \(z=0.325\). The Ti ions are nine-fold coordinated to O and the O ions form elongated tricapped trigonal prisms containing the titanium atoms (Muscat et al 2002). It is more complicated that it has a larger cell volume and is also the least dense of the 3 forms and was not often used for experimental investigations (Thompson & Yates, Jr 2006).

Tay et al (2013) had synthesized highly crystalline pure brookite and two-phase anatase/brookite TiO\(_2\) nanostructures via a simple hydrothermal method with titanium sulfide as the precursors in sodium hydroxide solutions. The control of the phase composition had been demonstrated via solution concentration and reaction time, and the phase transformation mechanism had been elucidated. Photocatalytic activities of
the as-synthesized two-phase anatase/brookite TiO$_2$, pure anatase nanoparticles, and pure brookite nanoplates were appraised via photocatalytic hydrogen evolution in aqueous methanol solution.

Besides these polymorphs of TiO$_2$, two additional high-pressure forms had been synthesized from the rutile phase. These were TiO$_2$ (II) (Simons & Dachille 1967) with a PbO$_2$ structure and TiO$_2$ (H) (Cromer & Herrington 1955) with a hollandite structure. All of these crystalline forms of TiO$_2$ occur in nature as mineral, but only rutile and anatase had 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 systems were widely studied on their synthesis, characterizations and photocatalytic properties (Kim et al 1999; Yang et al 2000; Zheng et al 2000). So far anatase phase was known to exhibit higher photocatalytic efficiency compared with rutile phase. Only little efforts had been made in the synthesis, characterization and properties of brookite phase which belonged to the orthorhombic crystal system (Pottier et al 2001; Zheng et al 2000a; Kominami et al 2000). The poor result in brookite phase was due to the difficulty in preparing the pure brookite type TiO$_2$ without mixture of rutile or anatase phase. Recently, the method used to synthesize pure brookite phase TiO$_2$ was reported (Lee & Yang 2005), which means that versatile studies on the brookite phase can be ignited.

1.8.5 **Anatase to Rutile Transition**

The anatase to rutile transformation was not instantaneous; it is time-dependent because it was reconstructive (Jamieson & Olinger 1969; Rao 1961). The kinetics of these processes typically was considered in terms of temperature and time. Consequently, the kinetics of the phase transformation must be interpreted in terms of all of the factors that influence the requisite temperature-time conditions. Pure bulk anatase was considered widely to
begin to transform irreversibly to rutile in air at ~600 °C (Ghosh et al 2003; Hirano et al 2003; Hadjiivanov & Klissurski 1996); however, the reported transition temperatures vary in the range 400-1200 °C (Carp et al 2004; Hirano et al 2003; Kim et al 2001, Shannon & Pask 1965; Zhang & Banfield 2000; Gouma & Mills 2001; Jing et al 2008) owing to the use of different methods of determining the transition temperatures, raw materials, and processing methods. The kinetics of this transition were dependent on variables such as impurities, morphology, sample preparation method, heat flow conditions, etc. In the absence of impurities, dopants, secondary phases, or other types of contamination, rutile forms as fine laths with the product phase’s (1 0 0) planes parallel to the (1 1 2) planes of the parent anatase (Penn & Banfield 1999; Harold 1989; Gouma & Mills 2001). In pure anatase, rutile might nucleate at (1 1 2) twin interfaces in anatase (Gouma & Mills 2001) as these sites were structurally similar to rutile. Both anatase space group \(I4_1/amd\) and rutile space group \(P42/mnm\) are tetragonal in structure. Both crystal structures consist of TiO\(_6\) octahedral, sharing four edges in anatase and two in rutile (Figure 1.4) (Harold 1989; Beltran et al 2006; Muscat et al 2002). The anatase to rutile transformation was reconstructive, which meant that the transformation involves the breaking and reforming of bonds (Batzill et al 2006). The light-induced phase transition of TiO\(_2\) nanoparticles from anatase to rutile structure was reported depending on the surrounding environment, the transition being accomplished under oxygen-poor conditions. The transition mechanism was interpreted in the framework of oxygen adsorption and desorption phenomena with the involvement of surface oxygen vacancies and F centers. It was shown that the observed phase transition was not thermally driven because the local temperature of the nanoparticles during irradiation was about 370 K (Ricci et al 2013).
Won et al (2001) had synthesized TiO$_2$ films with a thickness of 550 nm were deposited on quartz glass at 300 °C by metal organic chemical vapor deposition. The effects of post-annealing between 600 °C and 1000 °C were investigated on the structural and optical properties of the films. They reported that the anatase phase of as-grown TiO$_2$ films began to be transformed into rutile at the annealing temperature of 900 °C. The TiO$_2$ films were entirely changed to the rutile phase at 1000 °C. Wetchakun et al (2012) had synthesized TiO$_2$ nanoparticles with different ratios of anatase to rutile
transformation by the modified sol-gel method. The temperature of anatase to rutile transformation was found between 500 and 600 °C and then completely transformed into rutile phase at 600 °C. Average particle sizes of the nanoparticles were in the range of 10-50 nm at calcination temperature between 400 and 600 °C. The higher temperature clearly favoured the particle growth and agglomerates were corresponded to decrease in the specific surface area.

1.8.6 Synthesis of TiO₂

TiO₂ morphologies had mainly included nanostructures such as nanotubes (Varghese et al 2003), nanowires (Wen et al 2005), nanorods (Wu & Qi 2007) and mesoporous structures (Yi et al 2001). In recent years, a variety of synthesis methods such as hydrothermal method (Andersson et al 2002), solvothermal method (Wahi et al 2006), sol-gel method (Bazargan et al 2012), direct oxidation method (Ryu et al 2008), chemical vapour deposition (CVD) (Shinde et al 2008), electrodeposition (Tan et al 2009), sonochemical method (Arami et al 2007), and microwave method (Corradi et al 2005) had been used for the preparation of TiO₂ nanocrystals. Recently, TiO₂ had been prepared in the form of powders, crystals, thin films, nanotubes and nano rods.

Dawson et al (2010) subjected mixed phase TiO₂ powders with different compositions and particle sizes to hydrothermal reaction with NaOH. The anatase phase component of the starting material was easily converted to trititanate nanotubes at 140 °C. At 170 °C, the rutile phase reacted to form trititanate plates and belts. TiO₂ nanoparticles can be obtained by hydrothermal treatment of peptized precipitates of a titanium precursor with water (Luo et al 2013). The precipitates were prepared by adding a 0.5 M isopropanol solution of titanium butoxide in deionized water ([H₂O] / [Ti]) =150), and then they were peptized at 70 °C for 1 hr in the presence of tetraalkylammonium hydroxides.
Besides TiO$_2$ nanoparticles, TiO$_2$ nanorods have also been synthesized by the hydrothermal method. Zhang et al (2000) obtained TiO$_2$ nanorods by treating a dilute TiCl$_4$ solution at 333-423 K for 12hr in the presence of acid or inorganic salts (Zhang & Gao 2003; Tang et al 2013). Yana et al (2010) synthesized pure rutile nanotubes by a hydrothermal process in NaOH water-ethanol solution starting from rutile-anatase TiO$_2$ particles. The nanotubes were up to several micrometers in length and had diameters of less than 20 nm. The type of alcohol and the ratio of alcohol to water had a great impact on the morphology and structure of the final products. The rutile nanotubes exhibited different optoelectronic properties to those of the raw TiO$_2$. Mozia et al (2010) prepared modified titanate nanotubes (TNTs) via a hydrothermal method and focused on their application for the decomposition of Acid Red 18 (AR18) in water.

Pradhan et al (2003) grew TiO$_2$ nanorods on a Tungsten carbide-Cobalt (WC-Co) substrate by metal-organic chemical vapour deposition (CVD). The diameter and length of the nanorods were about 50-100 nm and 0.5-2 mm, respectively. Nanorod growth was observed at 500 °C, while most particles were deposited at 600 °C and a thin coating was formed at 400 °C. Limmer et al (2004) used sol electrophoretic deposition for template-based growth of TiO$_2$ nanorods. Uniform nanorods of approximately 45-200 nm in diameter and 10-60 μm in length were grown over large areas with almost unidirectional alignment. Attar et al (2008) fabricated aligned anatase and rutile TiO$_2$ nanorods and nanotubes with diameters of about 80-130 nm. Byun et al (2000) prepared TiO$_2$ thin films at 287-362 °C using titanium(IV) tetraisopropoxide (TTIP) precursor and O$_2$ gas. Djerdja et al (2005) reported nanocrystalline TiO$_2$ films by CVD on different substrates at relatively low temperature of 320 °C using TiCl$_4$ as a precursor and found that the nature of substrates influence the size and distribution of nanograins in the films.
Liu et al (2013) had prepared TiO$_2$ nanowires by electrodeposition process. The electrodeposition was carried out in 0.2M TiCl$_3$ solution with pH= 2 with a pulsed electrodeposition approach, and titanium and/or its compound were deposited into the pores of the anodic alumina membrane (AAM). By heating the above deposited template at 500 ºC for 4 hr and removing the template, pure anatase TiO$_2$ nanowires can be obtained. The enhancement of characteristics (sensitivity, selectivity, response time, etc.) of metal oxide gas sensors was possible by addition of other metals as dopants or mixtures (Edelmam et al 2000; Scotter et al 2005). One further application of TiO$_2$ nanotubes was in photo anodes for excitonic solar cells, where the straight tubular structure acts as transparent electron conductor and at the same time, hosts dye molecules were responsible for light absorption (Galstyana et al 2012). Xiao et al (2008) have prepared the bioactive Titania (Titanium dioxide, also known as titanium(IV) oxide or titania, is the naturally occurring oxide of titanium, chemical formula TiO$_2$) nanotube arrays by anodic oxidation in hydrofluoric (HF) electrolyte with the addition of 5-10 g/L Na$_2$HPO$_4$. They showed that the HF concentration and anodic voltage had the important effect on the appearance and sizes of Titania nanotube arrays. The formation of Titania nanotube arrays were the results of the combined action of the anodization and chemical dissolution. Nam et al (2010) had prepared metallic-nanoparticle-embedded one-dimensional titanium dioxide (1D-TiO$_2$) via a one-step electrospinning process.

Microwave radiation was applied to prepare various phases of TiO$_2$ nanostructured particles (Russo et al 2013; Kruth et al 2013). Komarneni et al (1999) had synthesized TiO$_2$ nanoparticles by forcing hydrolysis in hydrothermal condition starting from a 0.5 M solution of TiOCl$_2$ with the employment of both a conventional and a microwave thermal treatment. Wu et al (2005) synthesized TiO$_2$ nanotubes by microwave radiation via the reaction of TiO$_2$ crystals of anatase, rutile, or mixed phase and NaOH aqueous.
solution under a certain microwave power. Recently Dar et al (2014) had synthesized ~7 nm and ~100-400 nm of anatase Titania by exploiting the chemical nature of solvents through a microwave based approach.

1.8.7 Doped TiO$_2$ Semiconductor

In literature, N-doped TiO$_2$ nanoparticles had been prepared by various methods such as ion implantation, sputtering, sol-gel (hydrothermal growth, microwave, etc.), chemical vapor deposition, decomposition of N-containing metal organic precursors and oxidation of TiN (Diwald et al 2004; Ghicov et al 2006; Ryu et al 2007; Sun et al 2008; Peng et al 2008a; Liu et al 2008). Hydrothermal growth and microwave methods were comparatively used for synthesis of nanomaterials and they were less expensive. Although literature contains many valuable studies on preparation and applications of N-doped TiO$_2$, a systematic comparison of the influence of structural differences in amine sources was presented in none of them. However, the basic strength, and consequently the tendency to react with titanium precursors and/or TiO$_2$ surface of an amine change depended mainly on its structure (Ananpattarachai et al 2009).

Doping TiO$_2$ with anionic species had received more attention due to some drawbacks of metal doped TiO$_2$ nano powders (Choi et al 1994; Qiu et al 2007; Liu et al 2008). The visible light response of anion-doped TiO$_2$ was discovered by Sato (1986) and became more of an issue in conjunction with the studies of Asahi et al (2001). Among anionic dopants, nitrogen was one of the most effective ones for photocatalytic applications (Qiu et al 2007; Diker et al 2011). The improvement observed in photocatalytic activity had been described by either mixing of nitrogen 2p states with oxygen 2p states on the top of the valence band or a creation of N-induced mid-gap level (Sato
Asahi et al 2001; Diwald et al 2004; Sathish et al 2005). However the Ultraviolet radiation occupies approximately 5-6 % in day light source, which limits the applicability of TiO₂ as a photocatalyst. Doping was one of the techniques to overcome such limitation (Narayan et al 2011). Doping TiO₂ with metal ions like Fe, Sb, Co, etc., could extend the absorption spectrum to infrared radiation i.e., in the visible light spectrum (400 nm -800 nm), where the daylight source could be utilized effectively (Myung et al 2007). Sikong et al (2010) had prepared a Fe doped TiO₂/ SnO₂ by sol-gel method and tested for photo activity with E.Coli killing. The Fe doping exhibited the highest photocatalytic activity and E. coli inactivation efficiency. The E. coli was completely killed within 90 min under UV irradiation or 99.7% inactivated under visible light exposure. Chen et al (2008) had studied the doping behaviours of eight transition metal ion dopants on the crystal phase, particle sizes, XRD patterns, absorption spectra, anatase fraction and photoreactivity of TiO₂ nanoparticles. The pristine and ion-doped TiO₂ nanoparticles of 15.91-25.47 nm were prepared using the sol-gel method. Among the ions investigated, Ni-doped TiO₂ nanoparticles had shown the highest photoreactivity at the concentration of 0.002% at about 1.9 times that of the pristine TiO₂. Xiao-qing et al (2004) had synthesized nanocrystalline Fe-doped TiO₂ with a size of 60 - 70 nm by a sol-gel technique, followed by freeze-drying treatment for 2 hr. The Fe doping increased the UV and visible light activity for calcined catalyst, one such observation was reported by Nahar et al (2007), where they prepared Fe doped TiO₂ by impregnation and calcination method using TiO₂ particle and Ti element, respectively. Similarly Cobalt (Co) also seemed to improve photo degradation slightly or selectively for some organic compounds as found by Paola et al (2002). Amadelli et al (2008) also studied the photo degradation of 4-chlorophenol and Bisphenol A to assess the photocatalytic activity of the Co-TiO₂ and TiO₂ and showed that
the activity of the former was higher, both under UV and visible light irradiation, depending on the degree of doping.

TiO$_2$ based photocatalysts doped with 10 wt% Nd$^{3+}$ or 1.8 wt% nitrogen was synthesized by a sol-gel method using Ti-butoxide and Nd(NO$_3$)$_3$ or aqueous ammonia as starting materials. The doping with 10% Nd affected the activity of the catalysts negatively (Kralchevska et al 2012). However, Huang et al (2006) studied the doping of TiO$_2$ with different concentration of Nd$^{3+}$ can inhibit the photocatalytic activity. The optimum amount of Nd$^{3+}$ doping was 0.1%, at which the photocatalytic activity of Nd$^{3+}$/TiO$_2$ was 3.5 times higher than that of undoped TiO$_2$ (Huang et al 2006). Doping with nitrogen had insignificant influence on the catalyst activity when ultra-pure water was used to dissolve the pollutant. However, the N-doped catalyst was much more effective when tap water was used (Kralchevska et al 2012). Recently, doping TiO$_2$ with lanthanides (Ln) attracted much attention (Han et al 2009; Dimitrov et al 2011). Neodymium was found to be one of the most promising choices among the lanthanides. In some papers it is shown that the Nd$^{3+}$ doped material had a higher activity than pure TiO$_2$ and Degussa P25 commercial product (Xie et al 2005) and was recommended (Xu et al 2002) as the second most efficient after Gd$^{3+}$ because of an increase in the interfacial electron transfer rate. The promotion action of lanthanides and activity differences between different Ln$^{3+}$ were ascribed to changes in the amount of surface hydroxyl groups resulting from the interaction between the rare earth oxides and titanium (Xu et al 2002), differences in the standard redox potentials of Ln$^{n+}$/Ln$^{(n-1)+}$ ion pairs (Xie et al 2005), reduction of the band-gap energy because of the defect energy level induced by the 4f-atomic orbitals (Zhao et al 2006), differences in oxygen affinity of the dopant ions, production of a localized charge perturbation when dopant with larger ionic
radius (like Nd$^{3+}$) presents substitutionally in TiO$_2$ (Rengaraj et al 2007), efficient separation of the charge carriers, higher adsorption and 4f electron transition of heavily rare earths doped samples (Stengl et al 2009). Quan et al (2009) had reported in Lanthanide-doped TiO$_2$ photocatalysts by coprecipitation and sol-gel methods and Rhodamine B were used to evaluate their photocatalytic activity. Aqueous ammonia solution was commonly used as a nitrogen source. Wang et al (2007a) had synthesized nitrogen-doped titanium dioxide powders by wet method, that was, the hydrolysis of acidic tetra-butyl titanate using aqueous ammonia solution, followed by calcination at temperatures about 350 °C.

1.8.8 Application of TiO$_2$ Nanoparticles

Titanium dioxide (TiO$_2$) is considered very close to an ideal semiconductor for photocatalysis because of its high stability, low cost and safety toward both humans and the environment. Various investigations had established that TiO$_2$ was much more effective as a photocatalyst in the form of nanoparticles than in bulk powder (Han & Ba 2009). When the diameter of the crystallites of a semiconductor particle falls below a critical radius of about 10 nm, each charge carrier appears to behave quantum mechanically as a simple particle in a box as showed in Figure 1.5 (O'Regan & Grätzel 1991). As a result of this confinement, the band gap increased and the band edges shifted to yield larger redox potentials (Hoffmann et al 1995). However, the solvent reorganization free energy for charge transfer to a substrate remain unchanged. Because of the increased driving force and the unchanged solvent reorganization free energy, the rate constant of charge transfer in the normal Marcus region increased (Marcus 1990). Size-quantized semiconductor particles increased the photo efficiency of systems in which the rate-limiting step was charge transfer. Mill & Hunte (1997) reported that because the
absorption edge blue shifts with decreasing particle size, the redox potentials of the photo generated electrons and holes in quantized semiconductor particles increased. In other words, quantized particles show higher photo activity than macro crystalline semiconductor particles.

![Molecular orbital model](image)

Figure 1.5 Molecular orbital model for particle growth of N monomeric units. The spacing of the energy levels (i.e. Density of states) varies among systems (Regan & Grätzel 1991).

The semiconductor band must allow the radiation of the visible part of the solar spectrum which could be employed in photo electrochemical devices (Bak et al 2002). TiO₂ was a rather stable material and its band gap or even doped TiO₂ make it as one of the most promising material in the photochemical generation of hydrogen from water in the presence of the solar light (Nowotny et al 2007). The photo electrochemical response was strongly dependent on the methods of synthesis and the materials employed in the
preparation of the photo electrodes. Even though TiO$_2$ was widely investigated for its general properties, one of the disadvantages of TiO$_2$ was associated to the band gap (3 eV for rutile phase, 3.2 eV for anatase phase) and a higher resistance to the charge transfer (Bak et al 2002; Nowotny et al 2007).

The degradation of an azo dye Orange G (OG) on nitrogen-doped TiO$_2$ photocatalysts had been investigated under visible light and sunlight irradiation by Sun et al (2008). Liu et al (2005a) had examined the photocatalytic degradation of three azo dyes, Acid Orange 7 (AO7), Procion red MX-5B (MX-5B) and Reactive Black 5 (RB5) using a new type of nitrogen-doped TiO$_2$ nanocrystals. The nitrogen-doped TiO$_2$ polycrystalline powders were synthesized by calcination of the hydrolysis product of tetra-butyl titanate with ammonia by Wang et al (2005a). They considered that nitrogen atoms in doped TiO$_2$ polycrystalline powder were responsible for the significant enhancement in the doped TiO$_2$ photoactivity under visible light irradiation. The review (Qiu & Burda 2007) was focused on the synthesis, physical properties, as well as applications of nitrogen-doped metal oxide nanoparticles, with a special emphasis on Titania-based nanomaterials. The enhanced photocatalytic activity in nitrogen doped mesoporous TiO$_2$ was attributed to the generated abundant surface states (Liu et al 2009). It was believed that mixing of 2p states of N (substituting oxygen in the TiO$_2$ lattice) with 2p states of O was responsible for the reduction of the band gap of Titania (Kosowska et al 2005).

Paulose et al (2006a) had fabricated the nanotube arrays using anodic oxidation of titanium foil in a pH 4.0 electrolyte containing potassium fluoride, sodium hydrogen sulfate monohydrate and sodium citrate tribasic dihydrate. A highly ordered array of micron-length undoped Titania nanotubes exhibited an unprecedented variation in electrical resistance of about 8.7 orders of magnitude (50 000 000 000%), at room temperature, when
exposed to alternating atmospheres of nitrogen containing 1000 ppm hydrogen and air. Xiao et al (2008) had prepared the bioactive Titania nanotube arrays to form dye-sensitized solar cells. The random network of Titania nanoparticles served both as a high-surface-area support for dye molecules and as an electron-transporting medium. Electron diffusion lengths could be increased by transporting charge through highly ordered nanostructures such as Titania nanotube arrays. Varghese et al (2009) had reported that the fabrication of transparent Titania nanotube array films on transparent conducting oxide glass with lengths between 0.3 and 33.0 µm using a novel electrochemistry approach. Dye-sensitized solar cells containing these arrays yielded a power conversion efficiency of 6.9%. The incident photon-to-current conversion efficiency ranged from 70 to 80% for wavelengths between 450 and 650 nm.

Optimized coating of an MgO layer of TiO₂ nanoparticles enhanced the energy conversion efficiency as much as 45% compared to that of the uncoated TiO₂ electrode. This indicated that controlling the extrinsic parameters such as the specific surface area was very important to improve the energy conversion efficiency of TiO₂-based solar cells (Jung et al 2005). Mor et al (2006) had described the use of highly ordered transparent TiO₂ nanotube arrays in dye-sensitized solar cells (DSCs). Highly ordered nanotube arrays of 46-nm pore diameter, 17-nm wall thickness, and 360-nm length were grown perpendicular to a fluorine-doped tin oxide-coated glass substrate by anodic oxidation of a titanium thin film.

In a dye sensitized solar cell, N719 dye, using TiO₂ nanowire arrays 2-3 µm long achieved an AM 1.5 photoconversion efficiency of 5.02% (Feng et al 2008). Chang et al (2010) had synthesized TiO₂ nanoparticle by sol-gel method and further applied TiO₂ nanoparticle coating on the surface of the multi-wall carbon nanotube (MWCNT). As a result, TiO₂-CNT composite
nanoparticles were prepared to serve as photoelectrode material in dye-sensitized solar cell (DSSC). Experimental results showed that the photoelectric conversion efficiency of DSSC using CNT/TiO$_2$ photoelectrode and N719 dye was increased by 41% from the original 3.45% to 4.87%.

Angelis et al (2007) had performed fully first principles quantum mechanical calculations of the ground and excited-state properties of the [cis-(NCS)$_2$ - Ru(II) -bis(2,2'-bipyridine-4,4'-dicarboxylate)] dye, N719, adsorbed onto a model TiO$_2$ nanoparticle. A flexible DSC using TiO$_2$ nanotube arrays on a Ti foil as a working electrode and polyethylene naphthalate (ITO/PEN) as counter electrode in combination with solvent-free ionic liquid electrolyte achieved 3.6% photovoltaic conversion efficiency under simulated AM 1.5 sunlight (Kuang et al 2008).

The photocatalytic activity of samples was tested for degradation of methyl orange (MO) solutions. Although the photocatalytic activity of undoped TiO$_2$ was found to be higher than that of Co/TiO$_2$ under UV irradiation, the presence of 0.5% Co dopant in TiO$_2$ resulted in a catalyst with the highest activity under visible irradiation (Hamadanian et al 2010). A novel photoelectrochemical biosensing platform for the detection of biomolecules at relatively low applied potentials was constructed using porphyrin-functionalized TiO$_2$ nanoparticles. The functional TiO$_2$ nanoparticles were prepared by dentate binding of TiO$_2$ with sulfonic groups of water-soluble [meso-tetrakis (4-sulfonatophenyl) porphyrin] iron (III) monochloride (FeTPPS). The functional nanoparticles showed good dispersion in water and on indium tin oxide (ITO) surface. The resulting FeTPPS-TiO$_2$-modified ITO electrode showed a photocurrent response at +0.2 V to a light excitation at 380 nm, which could be further sensitized through an oxidation process of biomolecules by the hole-injected FeTPPS. Using glutathione as a model, a methodology for sensitive photoelectrochemical biosensing at low potential was thus developed. Under optimal conditions, the proposed
photoelectrochemical method could detect glutathione ranging from 0.05 to 2.4 mmol L\(^{-1}\) with a detection limit of 0.03 mmol L\(^{-1}\) at a signal-to-noise ratio of 3. The photoelectrochemical biosensor had an excellent specificity against anticancer drugs and could be successfully applied to the detection of reduced glutathione in glutathion injection, showing a promising application in photoelectrochemical biosensing (Tu et al 2010). Nam et al (2010) had prepared metal-nanoparticle-embedded 1D-nanostructures of TiO\(_2\) via electrospinning might be useful as electrodes in lithium-ion batteries.

1.8.9 \textbf{SnO}_2 \textit{Nanoparticles}

SnO\(_2\) is an n type semiconductor crystal with direct band gap (3.7 eV at 300 K) having high excitonic binding energy (130 eV) (Kucheyev et al 2005; Suda et al 2003). SnO\(_2\) possesses several polymorphs such as the rutile-type (P4\(_2\)/mmn), CaCl\(_2\)-type (Pnmn), \(\alpha\)-PbO\(_2\)-type (Pbnm), pyrite-type (Pa\(\bar{3}\)), ZrO\(_2\)-type orthorhombic phase I (Pbcn), fluorite-type (Fm\(\bar{3}\)m), cotunnite-type orthorhombic phase II (Pnam) with ninefold coordination (Gracia et al 2007; Karki et al 1997; Teter et al 1998; Tsuchiya et al 2004; Oganov et al 2005). All these structures were sequentially obtained when the most commonly available and stable rutile phase was subjected to high mechanical pressure. Thus, the most important form of naturally occurring SnO\(_2\) is cassiterite, a phase of SnO\(_2\) with the tetragonal rutile structure. Rutile has tetragonal D\(_{4h}^{14}\) symmetry. The structure of the conventional rutile unit cell of SnO\(_2\) is characterized by two lattice parameters, \(a (=b)\) and \(c\), and an internal parameter \(u\) associated with the O atomic position. Atomic positions are determined by the c/a ratio and the internal parameters \(u\) (Wyckoff 1963). The cations are at (000) and \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) and are surrounded by a distorted octahedron of anions at \(\pm (u, u, 0)\) and \(\pm (\frac{1}{2}+u, \frac{1}{2}-u, \frac{1}{2})\). Each cation has a distorted octahedron of anions at \(d_1 = \sqrt{2} ua\) and four at \(d_2 = \sqrt{2}(\frac{1}{2}-u)^2 + (\frac{1}{2}a)^2 a\). The experimental values of the lattice constant are: \(a = 4.737\ \text{Å}, c = 3.186\ \text{Å}\), and \(u = 0.306\) (Munnix & Schmeits 1983).
1.8.10 Phase Transition of SnO$_2$

The phase transitions in SnO$_2$ attract special attention because SnO$_2$ is analogous to silica (SiO$_2$). 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 significant 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 1.6.

During room-temperature compression of SnO$_2$ to 49 GPa, Haines & Leger (1997) first observed the rutile to CaCl$_2$-type transformation near 12 GPa. The authors also found out that the cubic phase was actually a modified-fluorite or pyrite-type structure of SnO$_2$ and appeared above 21 GPa at ambient temperature. It was also found that CaCl$_2$ $\rightarrow$ cubic transition was very slow at room temperature and in order to obtain maximum conversion, the sample was needed to heat for several hours at different pressures between
24 and 48 GPa (Shieh et al. 2006). SnO$_2$ in the rutile-type (P4$_2$/mnm) structure transforms to orthorhombic CaCl$_2$-type structure (Pnnm) at 13.6 GPa under hydrostatic conditions and persist up to 50 GPa during room-temperature compression. Suito et al. (1975) reported the high-pressure orthorhombic phase of SnO$_2$ in a dense form at 15.8 GPa and temperature of 1073 K. The orthorhombic structure was also found in diamond-anvil SnO$_2$ experiments by Liu et al. (1978), who found that it was formed from a higher-pressure fluorite-type phase upon release of pressure. Liu et al. (1997) reported that intense irradiation of cassiterite particles by an electron beam can also produce orthorhombic phase. The interesting part of the study was that, half of the material showed orthorhombic phase at the beginning of 12.6 GPa during compression, but the other half of this material showed orthorhombic phase on decompression (Haines & Leger 1997). Chen et al. (2006) reported the formation of a pure orthorhombic thin films by pulsed-laser deposition (PLD) from rutile-type SnO$_2$ target at an oxygen partial pressure of 3x10$^{-2}$ Pa and substrate temperature of 320 ºC. The cotunnite-type phase was stable upon compression to 117 GPa and 2400 K (Haines & Leger 1997).

Jiang et al. (2001) reported that rutile-to-pyrite type transformation was sluggish with an onset transition-pressure ($P_{BT}$) about 18 GPa during the room-temperature (300 K) compression. Ono et al. (2005) contradicted this finding as rutile to pyrite type transformation did not occur at 300 K. The discrepancies were mainly attributed to the kinetic effect during phase transition at room temperature. The transition to $\alpha$-PbO$_2$ type SnO$_2$ was observed at 800 K. When the temperature was increased to 1100 K, the intensity of the XRD peaks due to the $\alpha$-PbO$_2$ type structure started to decrease and the peaks due to the pyrite type structure appeared. The XRD peaks due to the $\alpha$-PbO$_2$ type structure eventually disappeared at 1300 K. A
report showed that the transition boundary was represented by the linear equation,\[ P \text{ (GPa)} = 16.7 \pm 0.5 - 0.0021 \pm 0.0015 [T \text{ (K)} - 1000]. \] If \( \text{SnO}_2 \) was not heated sufficiently within the pressure range of stability of the \( \alpha \)-\( \text{PbO}_2 \) type phase, complete transformation would not occur.

1.8.11 Synthesis of \( \text{SnO}_2 \) Nanoparticles

It is well known that the particle size and morphology of materials have a great influence on their properties. Therefore, the synthesis of nanomaterials with well-controlled size and morphology may open up new opportunities for exploring a material’s chemical and physical properties. \( \text{SnO}_2 \) nanostructure can be fabricated using different methods such as: ion sputtering (Ruske et al 1999), sol-gel (Ning et al 2008), reverse cell (Ahmed et al 2008), thermal evaporation (Luo et al 2005) and surfactants mediate (Pal & Chauhan 2009; Liang et al 2003). As early as in 1984, Nagano et al (1984) reported the growth of \( \text{SnO}_2 \) whiskers with ‘globule’ at the tip. It was suggested that Sn was the principal constituent of the globule, which was essential for the growth by the VLS mechanism and considered to be melted during the growth process. The oxide assisted growth technique had been utilized in producing \( \text{SnO}_2 \) nanostructures. In this method, catalyst was not needed for the growth of one-dimensional nanostructures. In this mechanism, the vapour phase of metal oxide was generated by thermal evaporation, which was the key component. It was found that precipitation, nucleation and growth of nanostructures always occurred in the area near the colder regions of the furnace. Oxide assisted growth for the \( \text{SnO}_2 \) nanoribbon and belt via large scale rapid oxidation of elemental Sn and Fe \((\text{NO}_3)_3\) powders at 1080 °C were reported by Hu et al (2002). Iwanaga et al (1987) reported growth of straight and bent \( \text{SnO}_2 \) whiskers by oxidizing Sn. Straight whiskers showed
preferential growth along [0 1 1], [1 0 0], and [1 1 1] directions. Bent whiskers were composed of two coherent elements.

Figure 1.6 Crystal structures of the SnO$_2$ polymorphs. (a) Rutile (P4$_2$/mm) and CaCl$_2$ type (Pnmm), (b) α-PbO$_2$-type (Pbcn), (c) pyrite-type (Pa$_3$), (d) ZrO$_2$-type (Pbca), (e) fluorite-type (Fm$\overline{3}$m), and (f) cotunnite-type (Pnam).

Table 1.2 Basic Properties of SnO$_2$

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>SnO$_2$</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/cm$^3$</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>
Leite et al (2002), Berengue et al (2009) & Wang et al (2005b) described the growth of SnO$_2$ nanoribbons by a controlled carbothermal reduction process. The nanoribbons have a well-defined shape, with a typical width in the range of 70-300 nm. The growth of nanoribbon-like structures was ascribed to the VS process. Very recently, Wang et al (2013) obtained plate like shape and chrysanthemum shape SnO$_2$ nanostructures grown on single silicon substrates by Au-Ag alloying catalyst assisted carbothermal evaporation of SnO$_2$ and active carbon powders. SnO$_2$ nanograsses had been synthesized by metallic catalyst-assisted thermal evaporation of graphite and SnO$_2$ powder (Wang et al 2005c). Preparation of square shaped oriented SnO$_2$ arrays were reported by Liu et al (2004) and Liu & Liu (2005). The precursor solution was prepared by dissolving Sn (II) -2-ethylhexanoate in absolute ethanol. The resulting solution was then pumped into a specially designed nanomizer, where the precursor solution was mixed with high purity oxygen, producing a microscale mist in a flame. The process, which was a combustion CVD technique, was utilized at 950 ºC and 1150 ºC for 30 min and 60 min. The four peripheral surfaces were determined to be 11 0 planes and the tubular crystals grew along the [0 0 1] direction.

Qin et al (2008) demonstrated catalyst free growth of cube like SnO$_2$ structures by CVD technique. The spontaneous self-organization of adjacent rods into cubes was aided by oriented attachment through coalescence along common crystallographic faces. The side surfaces of nanocubes were (1 1 0) planes, while their cube axes were [0 0 1] direction. Dai et al (2001) discussed the vapor transport synthesis at elevated temperatures of around 1050-1150 ºC, in concert with the control of entrainment flow rates and reactant mixtures. Calestani et al (2005) grew SnO$_2$ nanowires and nanobelts successfully by low cost CVD method directly on large area (100 mm$^2$) Al$_2$O$_3$, SiO$_2$ and Si substrates. The nanocrystals were distributed in a very uniform entanglement in the growth plane over a
deposited thickness of about 0.3 mm. The lateral size ranged from 50 to 700 nm and the length achieved was several hundreds of micrometers.

The preparation of SnO$_2$ thin films had been intended by many different procedures, either by using wet routes (Yoon & Nam 1995), chemical vapor deposition procedures (Liu et al 1995) or other methods working under vacuum sputtering conditions (Meng et al 1994). A general problem with many of these procedures was the formation of Sn$^{2+}$ or even SnO species that, if not well controlled, may led to undesired microstructural properties of thin films. SnO$_2$ films close to stoichiometric condition had low free carrier concentration and high resistivity, but non-stoichiometric SnO$_2$ films had high carrier concentration, conductivity and transparency. This came about from an oxygen vacancy in the structure so that the formula for the thin film material was SnO$_{2-x}$, where x is the deviation from stoichiometry (Coutts et al 2000). Lilach et al (2005) showed that it was possible to precisely control the overall structure of SnO$_2$ nanowires by pulse modulating the flow rate of the carrier gas in which oxygen (one of the reactants) was entrained. Diskette like product could be obtained using either SnO or SnO$_2$ powders under a higher pressure (500-600 Torr) compared to ~3x10$^4$ Pa used for the nanobelt system (Dai et al 2003; Wang 2003). The typical diameter of the diskettes was 8-10 μm. It was found that the substrate temperature has significant influence of the morphology and phase structure of oxide nanostructures. Huang et al (2005) reported the use of plasma to modify the microstructure of the SnO$_2$ thin films deposited by plasma enhanced CVD (PECVD). After plasma treatment, uniform one dimensional SnO$_2$ nanorods were grown from the two-dimensional films. Liu et al (2005b) reported a highly porous and nanostructured SnO$_2$ thin-film gas sensors with Pt interdigitated electrodes fabricated via a combustion chemical vapour deposition process.
Leonardy et al (2009) described the synthesis method to thermally deposit tilted nanowire on the Au/sapphire (SA) (1 0 0) and Au/sapphire (SA) (1 1 0) substrates. The alignment of the nanowire was ascribed to the epitaxy of the substrates. Ma et al (2008) obtained cone shaped SnO₂ nanorod arrays by conventional thermal approach evaporation approach on a common stainless steel mesh without any catalyst. Chen et al (2004) worked on three-dimensional SnO₂ nanoflowers which were formed on a titanium substrate by thermal-pyrolysis of a Sn organometallic precursor dibutyltin dilaurate. Vertically aligned SnO₂ nanorod had been grown on gold (Au) coated Si substrates by high frequency inductive heating in the presence of graphite powder by Li et al (2009) and in the presence of zinc chloride (ZnCl₂) powder on Si substrates by Wang et al (2011). Microwave plasma enhanced CVD was employed to obtain nanopin like morphology on an Au coated Si substrate (Wang et al 2007c).

Porous rutile SnO₂ fibers were prepared by synthesized from a precursor solution of poly (ethylene oxide) (PEO), chloroform (CHCl₃) and dimethylinedeodecanoate Sn (C₂₂H₄₄O₄Sn) (Wang et al 2007b). Krishamoorthy et al (2012) demonstrated a large-scale production of aligned SnO₂ nanofibers with a multi-nozzle electrospinning method combined with an air-shield enclosed rotating drum collector. The production rate by this multi-nozzle approach was several times higher than that of the single-nozzle electrospinning. Wang et al (2013a) recently reported SnO₂ hollow Microtubes for efficient photocatalytic characteristics, with ultra-fast degradation and stable repeatability. A novel hydrogen peroxide based on Ag/SnO₂ composite nano-tubes were obtained by direct sintering of the electrospun poly (vinylpyrrolidone)/SnCl₂ precursor composite fibers (Miao et al 2013).
Periathai et al (2013) showed that the size of SnO$_2$ nanoparticles was influenced by the pH of the solution. SnO$_2$ nanoparticles with tetragonal rutile structure were almost regularly synthesized by soft chemical synthesis route (pH ~8) (Ghan et al 2002). Wang et al (2013b) showed by molecular dynamics simulation that the minimum concentration required to prevent rapid thermal growth of nanoparticles corresponds to ~0.7 monolayer coverage. It was concluded that surface hydration layers not only stabilize SnO$_2$ nanoparticles, but also induce size-dependent structural modifications. Yang et al (2004) prepared bipyramidal octahedron shaped SnO$_2$ nanocrystals by one pot solution routes without using templates by stabilizing certain crystallographic planes while the zero dimensional nanocrystallites form and undergo two dimensional self-aggregation. Rizzato et al (2001) and Broussous et al (2002) studied the effect of acetylacetone (acac) complexing ligand on the formation and growth of SnO$_2$-based nanoparticles during thermohydrolysis at 70 ºC of a Sn precursor SnCl$_{4-n}$ (acac)$_n$ (0 ≤ n ≤ 2) solution. Das et al (2011a, 2011b) carried out low temperature synthesis at ambient pressure in order to obtain pyramidal shaped nanostructures. SnO$_2$ nanorods were synthesized through an aqueous hexamethylenetetramine (HMTA) assisted route. Lupan et al (2008) synthesized single-crystalline SnO$_2$ microcubes in catalyst free hydrothermal method where the dimensions vary as a function of concentration and synthesis temperatures.

structure, a multishell structure, and a multichamber structure (Lou et al 2007). Carbon microsphere was dispersed in organic solvent and layer-by-layer growth of SnO₂ precursor on it resulted in hollow spheres (Sun et al 2006b). Lee et al (2009) prepared SnO₂ hollow spheres by encapsulating the Sn-precursor on Ni spheres and then removing the metal templates by dilute acid.

Meng et al (2011) obtained highly structured-tunable SnO₂ nanotube arrays of high aspect ratio, which features atomic layer deposition of SnO₂ on AAO templates using SnCl₄ and H₂O as precursors. A low temperature synthesis of highly crystalline nanorod was reported by Zhang et al (2003a). Square-shaped single-crystalline SnO₂ nanowires and its sphere-like hierarchical structures were synthesized with a template-free hydrothermal approach (Xi & Ye 2010). Vayssieres & Graetzel (2004) reported one step aqueous growth for aligned SnO₂ nanorods on a transparent conducting glass substrate. Wang et al (2010) reported nanorod with square-shaped cross section on Ti-substrate. Liu et al (2009) obtained highly aligned SnO₂ nanorod on large-area flexible metallic FeCoNi alloy and Ni foil substrates via a hydrothermal process.

1.8.12 Doped SnO₂ Semiconductor

SnO₂ is a n-type semiconductor widely used for technical applications and can be considered as a good model to study the effect of surface excess on nanoparticles stability due to its high stability (rutile phase) up to 1300 ºC (Bueno et al 2008), even when highly doped and synthesis easiness. Studies concerning SnO₂ based nanoparticles obtained by chemical route and doped with a vast variety of ions (Szendrő et al 2001; Dobler et al 2003; Castro et al 2005) had shown that surface excess was a constant in this material and some surface related properties, such as specific surface area, sintering and physical-chemical properties like isoelectric point and electronic
properties were dramatically changed as a consequence of the segregation of dopants on the surface. The quantification of the amount of dopant segregated on the surface was of prime importance in understanding the role of the surface energetics in the nanostructure evolution. Most of the reliable quantitative studies concerning segregation were based on X-ray photoelectron spectroscopy (XPS) or Auger electron spectroscopy (AES) (Gulino et al 1995; Nowotny 1989; Szczuko et al 2001).

These data allowed the calculation of the free energy of segregation, which can be used to predict the driving force for segregation and indirectly the total energy contribution to the stability of the system. In this work the chemical procedure was used to wash off the ions from the surface to quantify to surface segregated amount and isolate the surface excess effect on the nanoparticle stability. Mg had been reported to change the surface properties of SnO₂ even at very low concentrations (0.5%) due to surface segregation and promoted the stability of high surface areas (Seneviratna et al 2007). Since MgO was soluble at pH lower than 7 (Segall et al 1978) and SnO₂ showed very low solubility in acid or basic condition (Dadze et al 1981), this system (SnO₂,MgO) was particularly interesting since it offered the possibility of washing off Mg ions from the surface of SnO₂ by using a chemical route, allowing quantitative analysis of surface excess. The surface excess quantification was then correlated with nanoparticles stability by confronting data with microstructure analysis, such as specific surface area, crystallite size, lattice strain, and TEM.

Lu et al (2011) noticed that for Mn-doped SnO₂, the larger the Mn substitution, the greater the enhancement of interaction between Mn 3d states and the Sn 5p, or O 2p states. With the increase of doping, the conduction band gradually moves to the valence band. Zhang et al (2013) mentioned that Sn vacancies too were easily formed at the nearest distance from the doped
Zn atom. However, the influence of the positions on the formation energy of Sn vacancy was weak compared to that of an oxygen vacancies. For F doped SnO$_2$, the increase in the concentration of F doping increased the density of the electronic states at the Fermi level. Various dopants like Al, In, Cu, etc. had been used to improve sensitivity and selectivity performance of the gas sensors based on the SnO$_2$ nanoparticles (Zhang et al 2009; Menini et al 2004; Thomas et al 2008). Menini et al (2004) had investigated the CO response of a nanostructured SnO$_2$ gas sensor doped with palladium and platinum. Microstructure In/Pd-doped SnO$_2$ sensor for low level CO detection had been studied by Zhang et al (2009). Thomas et al (2008) had examined the influence of Cs doping in spray deposited SnO$_2$ thin films for LPG sensors. Though a large number of studies on the gas sensors based on SnO$_2$ nanoparticles (in various forms) had been carried out, a very little attention had been paid to the investigation of the Zn-doped SnO$_2$ nanoparticles for gas sensing applications (Ding et al 2010).

1.8.13 Application of SnO$_2$ Nanoparticles

SnO$_2$ has been applied in many applications such as transparent conducting coating of glass, gas sensors, solar cell and heat mirror (Diéguez et al 1996; Kudo et al 2007; Choudhury & Sehgal 1989). Owing to its low resistivity and high transmittance, SnO$_2$ transparent conducting oxide thin films were used as window layers and heat reflectors in solar cells (Frank et al 1983; Colen 1981). Sensor technology has gained popularity as the need for physical, chemical and biological recognition systems. Gas sensors are used to detect gas, to discriminate odour, or generally to monitor changes in the ambient gas atmosphere. The basic detection principle of this sensor is the change of the resistance (or conductance) of the sensing layer with gas adsorption. The observed variations of the resistance were due to the chemical catalytic reactions that occur at the surface, resulting in the modulation of
conduction barriers between the oxide grains (Ducéré et al 2011). \(\text{SnO}_2\) nanostructures, such as nanorod, nanowire, nanobelt, nanotubes, hollow sphere have been used effectively to act as room temperature sensors for NO\(_x\), CO, O\(_2\), H\(_2\) and ethanol. Moreover, sensor arrays of SnO\(_2\) can be patterned and miniaturized with good mechanical strength. Owing to its direct band gap, transitions are faster, which couple with high mobility of electrons results in fast response to small concentration of gas. The sensitivity and selectivity of the sensors could be varied by changing the dimensions of these nanostructures. It is known that a specific surface area sharply increases with the decrease of grain size. A high specific surface area and comparison of grain size (D) with thickness of the surface space charge layer (L\(_s\)) offers advantages for developing highly sensitive gas sensors. It was shown that the sensing behavior of SnO\(_2\) greatly increased if the grain size was smaller than 6-10 nm (Xu et al 1991; Yamazoe 1991; Bârsan 1994; Korotcenkov 2007).

Very recently, Kida et al (2013) studied gas sensor responses to H\(_2\), CO and H\(_2\)S as a function of operating temperature for films with different particle sizes. Results revealed that the diffusion of CO and H\(_2\)S was limited by small pores because of their lower diffusion rates compared with that of H\(_2\.\) It was revealed that additives and dopants had several effects on the gas sensing applications, including inhibiting SnO\(_2\) grain growth, modifying the electron Debye length and modifying the interaction between the gas and the surface of the sensing materials. Important features of doped SnO\(_2\) as gas sensors were provided in a review article by Miller et al (2006). Thus the introduction of dopants into the SnO\(_2\) sensing materials can improve sensor performance. Noble metal catalysts Pt, Pd, Ag, Rh, Au and Ir were often used as additives in SnO\(_2\) sensors (Khakani et al 2001; Park & Akbar 2003; Korotcenkov et al 2003; Kumar et al 2009; Korotcenkov et al 2011; Korotcenkov et al 2013 ). Influence of copper (Cu) on the sensor properties of SnO\(_2\) thin film was also reported (Rumyantseva et al 1996). Sysoev et al
(2009) showed that sensors consisting of percolating nanowires show superior long time stability over the thin layer of pristine SnO$_2$ nanoparticles. The advantages could be attributed to the absence of nooks and necks which facilitates direct adsorption and desorption of gas molecules, improving the dynamic behavior of the sensors (Ramírez et al 2009).

Cox et al (1982) pointed out that the energy of the surface states was strongly influenced by the high polarizability of the Sn$^{2+}$ ion. When the adsorption involves the oxygen sites through an acid-base mechanism, weak differences were expected for the reducible oxides. The conductivity of oxide films were related to the oxygen vacancies generated during oxide growth. SnO$_2$ exhibits considerably selective sensitivities to detect CO, CO$_2$, NO$_x$ gases and water vapour. The characteristic response of the gas sensor was attributable to the evolution of the concentration of various species present on the surface and the corresponding charge transfers including conductivity variations (Ducéré et al 2011).

Kolmakov et al (2005) showed enhanced gas sensing of single SnO$_2$ nanowires configured as resistive elements by surface decoration with Pd nanoparticles. A massive improvement in sensitivity to oxygen and hydrogen was attributed to the enhanced catalytic dissociation of the molecular adsorbate on the Pd nanoparticle surfaces (Choi & Jang 2010; Wang et al 2011). This process greatly increased both the quantity of oxygen that can repopulate vacancies on the SnO$_2$ surface and the rate at which this repopulation occurs, resulted in a greater (and faster) degree of electron withdrawal from the SnO$_2$ (and at a lower temperature) than for the pristine metal oxide nanowire. Liu et al (2005b) reported nanostructured SnO$_2$ thin-film gas sensors had a sensitivity of 1075 to 500 ppm ethanol vapour, and the corresponding response time and recovery time were 31 and 8 sec, respectively. Similar results were recently obtained by Jang et al (2013) with
Pt catalyst for hydrogen sensing and Jin et al (2012) with an Au catalyst for ethanol sensing. Both the response and recovery times of the SnO$_2$ nanobelts were decreased by Au-functionalization regardless of the ethanol concentration. The functionalized nanobelt sensor was superior to the bare SnO$_2$ nanobelt sensor in terms of both response and rate of sensing. Zhan et al (2013) reported SnO$_2$ nanopowder doped poly-diallyldimethylammonium chloride (PDDAC) deposited on Polyimide (PI) substrate based sensor. PDDAC acted both as the binder promoting the adhesion between SnO$_2$ and the flexible P substrate. The obtained sensor had a detection limit of 10 ppm at room temperature and showed good selectivity to ethanol.

One of the important factors affecting the sensing properties of semiconductor gas sensors was the microstructure of the polycrystalline thin film. In general, the crystallite of semiconductor oxide had an electron-depleted surface layer (space-charge layer) to a depth of Debye length (L). If the diameter (D) of the crystallite decreased to about 2 L, the whole crystallite was depleted of electrons; as a result, the sensitivity of the element to a reducing gas would change with D. In the case of SnO$_2$, L for a thin sputtered film had been reported to be as short as 3 nm. Thus, the critical crystallite size of SnO$_2$ was expected to be about 6 nm. Such small crystallites of pure SnO$_2$ were only stable at temperatures below 400 °C (Serrini et al 1997) and could not be maintained during the processes of sensor fabrication, which include high-temperature thermal treatment to stabilize the physical properties of the sensitive layers. The addition of foreign elements, however, had proven to be an effective way to control D to such small sizes, even after treatment at 700 °C (Xu et al 1989). SnO$_2$ sensors evoke particular interest in detecting inflammable gases and organic compounds, such as methanol (CH$_3$OH) (Oyabu 1982; Amamoto et al 1990). The use of ethylene (C$_2$H$_4$), on the other hand, offered problem because of its strong double bonds and hence, there were difficulties in dissociating it at modest temperatures.
The analysis of the experimental data on the gas sensing properties of SnO$_2$ was based on the following factors: (1) morphology and structure, (2) bulk electrophysical properties of SnO$_2$ through the change of the point defects concentration, (3) the change of the height of intergrain potential barrier through the influence on the surface stoichiometry (4) surface reactivity change and (5) the change of the phase content in gas sensing matrix (Pan et al 2010; Korotcenkov et al 2013).

The crystallinity and morphology of SnO$_2$ nanoparticles were of functional importance in determining electro physical properties and gas sensitivity of the final product (Tjong 2004). The adsorption/desorption processes had activation energies and the atomic level of chemical bonding had a great crystalline structure and surface morphology dependence (Xi et al 2008, Kalinina et al 2003). In detail, the particle crystallinity and morphology had great influences on crystallographic planes, surface state density, energetic position of levels, adsorption/desorption energies of interacted gas molecules, concentration of adsorption surface states, which could influence the gas sensitivity of the product significantly (Kalinina et al 2003). In addition, the size decrease of SnO$_2$ nanoparticles changed the particle crystallinity and morphology, which could in turn lead to a variety of sensing responses of final gas sensors.

SnO$_2$ semiconductor nanoparticles could be widely used in many fields such as catalytic materials, transparent conducting electrodes and especially semiconductor gas sensors for its low operating temperature (Willett et al 1998; Manifacier et al 1977; Zhang & Gao 2004; Lou et al 2009). The working principle of SnO$_2$ gas sensor was related to the change of electrical conductivity of SnO$_2$ grains, which results from the reaction between oxygen and reducing gases (Korotcenkov et al 2008). Generally, SnO$_2$ nanoparticles with high surface area were in favour of improving the
gas sensitivity of sensors, which could be achieved by decreasing the particle size (Davis et al 1998). Many literatures could be found on optimization of the particle size and gas sensitivity of SnO$_2$ sensors (Sequinel et al 2009; Xi et al 2008). Zhang et al (2004) and Neri et al (2008) had addressed that SnO$_2$ nanoparticles with a particle size of less than 6 nm display fully depleted electrons and could result in higher gas sensitivity. Leite et al (2000) described a novel method in obtaining SnO$_2$ nanoparticles with decreased particle size below 6 nm by adding Nb$_2$O$_5$ in SnO$_2$ precursor to suppress particle growth of SnO$_2$ nanoparticles in order to enhance the gas sensitivity of SnO$_2$ sensors.

1.8.14 Ruthenium(II) Bipyridine Complexes

The research efforts in the field of bipyridine containing ligands and their metal complexes have strongly increased within the last few years. In particular, the central focus had shifted from analytical purposes (complexation of metal ions) to the creation of new materials and polymers (Schubert & Eschbaumer 2002; Schubert & Eschbaumer 2002a). A large portion of recent interest in this ligand stems from the very interesting photophysical 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. Hence, research to find optimum ruthenium-based sensitizers have been focused primarily on enhancing the molar absorption coefficient as well as broadening of the metal-to-ligand charge transfer band. For this reason, Gratzel and coworkers had increased the molar extension coefficient
of Ruthenium(II) complexes by introducing extended $\pi$-conjugation concept in the molecular structure (Wang et al 2005; Wang et al 2004).

In the present study the same concept was adopted for increasing the molar extinction coefficient and reported a few Ruthenium(II) polypyridyl complexes. 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, photophysical, 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 photochemically 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 $d(\pi) - \pi^*$ 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 photoexcited 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/photostable 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(R₂-phen)(dcbH₂)(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''-tri-tert-butyl-2,2':6',2''-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 TiO₂ and ZnO electrodes. The influence of the semiconductor type on the performance of TiO₂ and ZnO based photovoltaics had been tested. The solar cell performance of TiO₂ based solar cell showed better efficiencies compared to ZnO based solar cells (Erten-Ela et al 2014).

Two ruthenium complexes with carboxyl and sulfonyl groups had been synthesized, [Ru^{II}(L1)₂(NCS)₂] Ru^{II}bis(4,7-diphenyl-1,10-phenanthroline-disulfonic acid disodium salt)-di(thiocyanate) [K313],[Ru^{II}(L1)₂(dcbpy)] Ru^{II}bis(4,7-diphenyl-1,10-phenanthroline-disulfonic acid disodium salt)(4,4'-dicarboxy-2,2'-bipyridyl) [K314] as photosensitizers. Photovoltaic properties of dye sensitized nanocrystalline semiconductor, solar cells based on Ruthenium complexes which bear carboxyl and sulfonyl groups had been tested under standard AM 1.5 sunlight. Under the standard global AM 1.5 solar conditions, K314 and K313-sensitized solar cells demonstrated short circuit photocurrent densities of 14.92 mA/cm² and 11.23 mA/cm² and overall
conversion efficiencies of 5.09 % and 4.02 %, respectively (Erten-Ela & Ocakoglu 2014).

Funaki et al (2013) synthesized a new class of thiocyanate-free cyclometalated Ruthenium(II) complexes [Ru(dcpq)$_2$(C$^\text{N}$)]Cl (where dcpq was 4-carboxy-2-(4′-carboxypyridin-2′-yl)quinoline and C$^\text{N}$ 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$^\text{N}_2$C) (where O$^\text{N}_2$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.