SUPPRESSION OF RECOMBINATION
CHANNELS OF DYE–SENSITIZED
SOLAR CELLS BY INCORPORATING
NANO-PARTICLES OF METALS AND
INSULATORS TO THE
SEMICONDUCTOR FILM

By

GONIYA MALIMAGE LASANTHA PRIYANITH
APONSU

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Thesis submitted to the University of Sri Jayewardenepura for the award of the Degree of Doctor of Philosophy in chemistry on 2009.
DECLARATION

“The work described in this thesis was carried out by me under the supervision of Prof. K. Tennakone, Director (former), Institute of Fundamental Studies, Hanthana Road, Kandy and Prof. Pradeep Jayaweera, Professor in Chemistry, Department of Chemistry, University of Sri Jayewardenepura, Nugegoda and a report on this has not been submitted in whole or in part to any university or any other institute for another Degree/Diploma”.

Signature of the candidate
"We certify that the above statement made by the candidate is true and that thesis is suitable for submission to the University for the purpose of evaluation".

Prof. K. Tennakone,
Director (former),
Institute of Fundamental Studies,
Hanthana Road,
Kandy.

Prof. Pradeep Jayaweera
Senior Lecturer
Department of Chemistry,
University of Sri Jayawardanapura
Nugegoda.
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ABSTRACT

In the conversion of solar energy into electricity, devices made of high band gap semiconductor materials are more stable comparable to those made of low band gap semiconductor materials. However, under these circumstances, an efficient absorber material is very essential. In this work, particular dye (Indoline) as a sensitizer and high band gap semiconductors such as TiO₂ and SnO₂ were utilized in the construction of dye-sensitized solar cells.

The performance of dye-sensitized solar cells based on SnO₂ film is inferior due to existing of shallow trap levels belong to it. On the other hand, the existing of these defects on TiO₂ film is minimum and hence, improvement of cell performance based on composite systems becomes marginal for TiO₂ semiconductor. However, the efficiency of indoline-149 sensitized photoelectrochemical solar cells increases significantly when the nanocrystalline TiO₂ is doped with Cu to a concentration similar to the dye concentration. Indoline-149 possesses sulfur in rhodanine rings in addition to carboxylate ligand. Therefore, sulfur in rhodanine rings of indoline-149 too could coordinate with copper in TiO₂ in addition to the anchoring of this dye to TiO₂ surface via the carboxylate ligand. And hence it suppresses the aggregation of the dye molecules. The firm bonding of the indoline-149 molecule to the TiO₂ surface at two points
covers TiO$_2$ surface without leaving any voids. Therefore, suppression of recombination through these voids may increase both photovoltage as well as photocurrent.

Depositing nano–particles of gold on SnO$_2$ particles showed enhancement of both photovoltage as well as photocurrent. As many articles in literature claims, the surface plasmon resonance of the gold nano–particles deposited on semiconductors enhances the performance of the dye–sensitized solar cells accompanied by an increment of photocurrent. Since the above device improves photovoltage as well, it is realized that in addition to the surface plasmon resonance effect, there may be several factors which dominates the mechanism of this device. The Fermi level of SnO$_2$ particles rises when it is in contact with a metal having lower work function. Since the particles are in nano–range, to achieve the equalization of Fermi levels of gold and SnO$_2$ particles, the potential of the conduction band edge of SnO$_2$ rises up together with the shallow traps. This will result to suppress the recombination of germinated electrons with acceptors in electrolyte which increases the photocurrent. The shift of the conduction band edge to a higher level attributes to higher photovoltage as well.

ZrO$_2$ is an insulating material with its energy gap in between 5–7 eV. Suppression of recombination processes through the incorporation of the insulating material, ZrO$_2$ improved cell performance significantly. Many articles in literature revealed that the enhancement of the photocurrent is impossible in coupled type heterostructures formed between insulator and semiconductor. And therefore, the formation of ZrO$_2$ shell around the SnO$_2$ crystallites in the [SnO$_2$] ZrO$_2$ (capped type heterostructures) can not be ruled out in this regard. This ZrO$_2$ shell around SnO$_2$ prevents the recombination of germinated electrons with acceptors in electrolyte. And accumulation of these electrons in SnO$_2$ particles rises up quasi–Fermi level (QFL) of the [SnO$_2$] ZrO$_2$ composite. This will attributes to higher photovoltage and photocurrent of the cell.
CHAPTER 1

SOLAR CELLS

1.1 Introduction

Civilization in the twentieth century was mainly based on large scale consumption of valuable and irreplaceable reserve of fossil fuel that has formed over millions of years from the remains of animals or plants. Large scale consumption of fossil fuel such as petroleum has lead to rapid corruption of the global environment. And also, experts predicted that these fossil fuel reserves would last further for several years. Therefore, scientific community all over the world realized the necessity of finding out a new clean sustainable source of energy. The invention of photovoltaic solar cell which converts solar energy into electricity is one of the solutions in this regard.

In many countries, solar photovoltaic field has attained a priority area of research, thereby gaining considerable interest and funding. This worldwide interest in the field of photovoltaic solar cell can be attributed to a variety of factors such as: search for new energy sources due to heavy pressure on conventional fuels; the simplicity, cleanliness, and direct conversion of solar energy in to electricity by solar cells; and a rapid growth of technical material. Photovoltaic cells or the so called solar cells generate an electromotive force (photovoltage) as a result of the absorption of light. There are many advantages of the utilization of solar cells over conventional methods of power generation, some of which are:
i) The ability of solar cells to directly convert the solar radiation into electricity using the photovoltaic effect without going through a thermal process.

ii) The reliability, durability, and the ease of maintenance of solar cells.

iii) The ease with which, solar cells can be located at the place of use and hence canceling the requirement of a distribution network.

Solar cells had been the standard source of power for space vehicles and satellites during the past 45 years and are still one of its most important applications. This would also remain so for supplying electricity for terrestrial applications, if the problem of economics required for making available solar cells for such usage can be solved. The challenges of producing reliable and competitive solar electrical power for terrestrial applications have led to intensive research activities in almost all advanced countries during the past three and half decades and are expected to being continued to fulfill the goal. There are several semiconductor materials used to construct solar cells. Among these materials silicon (Si) and gallium arsenide (GaAs) have given encouraging results. The single crystal stable Si solar cell under terrestrial sunlight has given an efficiency of 14%, but still due to its high cost, it is not used widely for terrestrial applications. On the other hand, thin film cells such as: GaAs is less costly compared to Si solar cells, but these cells are less stable and therefore lead to limitations in their applications. Therefore, attempts are made to reduce the cost of the Si solar cells and also examine some other combinations of new materials to construct stable, highly efficient, low cost solar cells. The invention of the polycrystalline Si thin film solar cells as well as amorphous Si thin film solar cells are some of the achievements made as a result of these efforts.
In thin film technology, reduction of cost is achieved by using small amounts of material and inexpensive processing techniques. However, semiconductor thin film could be low purity which leads to decrease in efficiency of solar cell through high recombination process of photo-generated electron-hole pairs, because mobile charge carriers are produced in the same material. In this regard, the invention of the dye-sensitized solar cell is a great achievement to the recombination problem arises in thin film solar cells. Injection of carriers (electrons or holes) into a semiconductor band (conduction or valence) by a dye molecule attached to its surface upon irradiation occurs in these devices.

During the past few decades, a great deal of work has been done to make dye-sensitized solar cell practically usable device. Its short lifetime and low conversion efficiency are the major drawbacks of this cell to give a commercial value. To increase the life time of the cell, developments have been done on many aspects such as improving the dye as well as the electrolyte to resist photo degradation. To improve the cell efficiency, the major task is to avoid recombination of the generated charges. One of the possibilities is to use composite semiconductor material thin film as the photo electrode facilitating rapid separation of the generated charges. Therefore in this work we have investigated ways to overcome the recombination in dye-sensitized solar cells by utilizing composite semiconductor materials.
1.2 History

The photovoltaic technology remained the province of research scientists only until the advent of the space program. Although the basic material selenium [1] was discovered in 1817 by Berzelius, an understanding of the operation of the solar cells took nearly 100 years. The photovoltaic effect was first observed in electrolytic cells by a French scientist called Bacquerel in 1839. He also discovered that the current generated by absorption of light (photocurrent) depend on several parameters such as: intensity and the wavelength of light and so on. The photoconductivity in selenium was discovered by Willoughby in 1873. In 1876, Adams and Day observed the photovoltaic effect in solid-state selenium structures and also the spectral sensitivity of the selenium photoconductors. The first selenium photovoltaic cell was described by Fritts in 1883. In 1904, the photosensitivity of the combined copper-cuprous oxide structure was observed by Hallwacks. By 1905, it was well known that the number of electrons emitted from an element depends on the intensity of light at a given wavelength.

Later Einstein published his famous paper in which he explained the mechanism photoelectric effect or effectively the behavior of these emitted electrons and precisely formulated the maximum kinetic energy of these electrons as a function of the wavelength of light which was later proved experimentally by Millikan in 1916. The existence of a barrier layer in photovoltaic effect was first established in 1914. A new interest emerged with the development of copper/copper-oxide rectifier and the interest initially based on selenium devices was rapidly transferred to the copper/copper-oxide photovoltaic devices. In 1941, a single-crystal silicon photovoltaic device was prepared using a technique called 'grown p-n junction' at Bell Telephone Laboratory. A team of scientists comprising
Chapin, Fuller, Pearson and Prince at Bell Telephone Laboratory and Rappaport, Loferski, and Jenny at the RCA further developed this device using impurity diffusion method in the formation of a p-n junction and acquired efficiency up to 6% in 1950. With the improved design technique and fabrication process, the device in producing a 14% efficiency. By this time, many big electronic companies such as: RCA, Texas Instruments and International Rectifier had entered the solar photovoltaic field and had started the production of solar cells for terrestrial applications. However, the relatively high cost of these devices coupled with the poor demand drive of these companies leads to a reduction in their production.

The first major application of solar cells in the space programme appeared in 1958 when U.S.A. launched its first space craft ‘Vanguard I’ powered by solar cells containing 6 small arrays of 108 Si chips providing power to 5 mW radio transmitter. Presently, all satellites are powered by photovoltaic systems.

In October 1973, the National Science Foundation [2] organized a workshop to achieve the reduction in cost of photovoltaic systems for terrestrial applications through inexpensive processing techniques. Therefore, scientists all over the world made great attempts to reduce the cost of the Si based solar cells. The invention of the polycrystalline Si thin film solar cells as well as amorphous Si thin film solar cells are some of the fulfillments achieved as a result of this great effort. They also tested for some other combination of new materials. Various cell structures such as: p-n junctions, heterojunctions, schottky barriers, metal insulator semiconductors (MIS), semiconductor insulator semiconductor (SIS), etc. were invented as results of these studies.
1.3 Thin Film Solar Cell Technology

It appears that thin-film technology is essential for the development of terrestrial solar cells. In the thin-film approach, reduction of cost is achieved by using small amounts of material and inexpensive processing techniques. Thin films are necessary not only for producing photo electrically active layers but also to be used as good electrical contacts, window materials, antireflection coatings, transparent conducting coatings, and passivating layers. Film deposition techniques, therefore, play an important role in the field of thin film solar cells. In addition to standard methods such as physical vapour deposition (PVD), sputtering, molecular beam epitaxy (MBE), chemical vapour deposition (CVD), and chemical deposition, other recently developed methods like spray pyrolysis deposition (SPD), sole-gel processing and electrochemical deposition need to be considered.

1.4 Synthesis and Preparation of Semiconductor Films

Synthesis and preparation techniques strongly affect the physical and chemical properties of thin films of semiconductor material. Researchers working on this area have already presented many preparation techniques of semiconductor films consisting of particles in the nano–meter range. To achieve the reduction in cost of photovoltaic systems, adoption of inexpensive processing techniques is very important as well as the utilization of low cost materials. However, for the completeness of the literature, highly sophisticated and expensive methods in addition to inexpensive techniques have also been discussed here.
1.4.1 Gas Phase Synthesis of Semiconductor Films

Nano-structured films of semiconductors can be fabricated by condensation of gas phase compounds on a suitable substrate. Physical vapour deposition (PVD), Chemical vapour deposition (CVD), Molecular beam epitaxy (MBE) and Sputtering are some techniques adopted here. A general discussion on each method is given below.

1.4.1.1 Physical Vapour Deposition (PVD)

In this technique, material in one solid phase is transferred via a vapour-phase stage, into another physical phase without changing its chemical composition. However, when the starting material has a complex chemical composition, the amorphous growth of semiconductor film without known chemical composition can not be avoided. This technique is commonly utilized to prepare amorphous thin films of materials such as CuInS₂, CuInSe₂ [3–4].

1.4.1.2 Chemical Vapour Deposition (CVD)

Chemical vapour deposition (CVD) is widely used to fabricate large area thin films of hydrogenated amorphous silicon (a-Si:H) and its derivatives such as a-SiN:H, a-SiC, etc. by thermal decomposition of inorganic gaseous precursors.

\[
\text{SiH}_4(\text{g}) \xrightarrow{\text{heat}} \text{a-Si:H} (\text{s}) + \text{H}_2(\text{g})
\]

\[
\text{SiH}_4(\text{g}) + \text{NH}_3(\text{g}) \xrightarrow{\text{heat}} \text{a-SiN:H} (\text{s}) + \text{H}_2(\text{g})
\]

This thermal CVD technique is widely used to produce high-purity thin films of semiconductor materials.
1.4.1.3 Molecular Beam Epitaxy (MBE)

Molecular Beam Epitaxy (MBE) is a high technology development of the physical vapour deposition (PVD) technique. It allows fabricating compositionally controlled epitaxial layers of complex chemical materials. A schematic of the MBE system is shown in Figure 1.1.

![Figure 1.1 Schematic diagram of MBE system](image)

An ultra high vacuum (UHV) chamber is outfitted with a number of evaporation cells, each controlled by a separate shutter, which supplies fluxes of molecular beams of the desired atomic species. The beam can be turned on and off within 0.1 seconds. Growth rates are typically 5 Å/sec. An ion beam sputtering gun is used to ion etch the surfaces, to remove
impurities and imperfections. The substrate is maintained at about 500–700 °C during growth. Various spectroscopic capabilities, such as mass spectrometry, Auger spectrometry, and refraction high-energy electron diffraction (RHEED), are included in the chamber to control the process and provide analytical data on the quality of the films. The atomic species that can be produced by MBE include Ga, Al, In, As, Sb, Sn, Be, Ge, Se, Te, Cd, Hg, Zn, Mn, Pb and Si.

1.4.1.4 Sputtering

Sputtering is one of the most commonly used methods for depositing semiconductor films. This involves ejection of material from the surface of a solid through collision of energetic particles such as ions, neutrons, electrons or photons to the substrate. Generally argon atmosphere is used in most sputtering techniques where Ar produces the ion beam to sputter. Metal thin films (for example, Au, Ag, Pt) as well as polycrystalline films (for example titanium oxide) have been prepared using sputtering [5]. This method is a high cost technique compared to other methods.

1.4.2 Liquid Phase Synthesis of Semiconductor Films

Liquid phase synthesis of semiconductor films requires relatively simple equipment for deposition and also can be fabricated on a large scale even on irregular surfaces. Therefore, these types of techniques are less expensive and economical. Further, since liquid phase synthesis of semiconductor films involve only one phase transition; i.e., transition from liquid to solid phase, where in gas phase synthesis two transition states are involved, these
techniques can be recommended to produce better films if all other deposition conditions are correctly chosen.

1.4.2.1 Chemical Deposition
Chemical deposition is another method widely utilized to deposit thin semiconductor film on the substrate. In this technique, a solution-phase reaction occurs producing an insoluble, often a crystalline precipitate.

1.4.2.2 Electrochemical Deposition
Several attractive, useful, and advantageous features occurs in electrochemical deposition of semiconductor films are: (a) It involves relatively simple and inexpensive equipment; (b) Films can be fabricated on large and irregular surfaces; (c) The deposition occurs closer to equilibrium than in many high temperature methods and inter-element diffusion is not a problem; (d) The process can be rather precisely controlled because of its electrical nature. This method can be readily used to deposit thin films of low band gap semiconductors such as n-CdS, p-CdTe, p-ZnSe [6] and high band gap semiconductors such as n-ZnO, p-CuI, p-CuCNS etc. [7-8].

1.4.2.3 Spray Pyrolysis Deposition (SPD)
In spray pyrolysis deposition technique, spray gun is place above the glass substrate and the solution is sprayed onto the heated substrate using compressed air as a carrier gas. This is a promising method since the technique is quite simple, economical, and applicable to
produce thin films on a large scale. Synthesizing of semiconductor thin films such as SnO$_2$ [9] and Cu$_2$O are most prominent to form by utilizing this technique.

1.4.2.4 Sol–gel Method

An important technique that can be used to synthesize many materials and prepare them in a variety of sample shapes and forms is sol–gel process. The starting point of this method is a sol which is a colloidal dispersion of small particles suspended in a liquid. The sol can be stabilized by peptization, i.e., the addition of peptizing agents (e.g., HNO$_3$ to TiO$_2$), which form an electrically charge layer around each particle and this electrostatic repulsion then prevents particles being aggregation together.

![Diagram of gel formation and precipitation from a sol.](image)
Under suitable chemical and thermal conditions, particles in some soles can be made to react or interact electrostatically so that they form a continuous, three-dimensional net work of connected particles known as a gel, instead of aggregate to form larger, but discrete, particles as happens in precipitation. Sol–gel method is a convenient method to produce high band gap semiconductors such as ZnO, TiO₂, and SnO₂.

1.5  Fundamentals of Photovoltaic Conversion

1.5.1  Semiconductor Materials

Depending on the ability of the material to carry electrical current, materials are grouped into three categories: conductors, insulators, and semiconductors. In a conductor, electrons in the conduction band are free to move and they are not bound to any specific site in the material. Therefore, they readily conduct electricity. On the other hand, in an insulator, the outer shell of the atom contains six or seven electrons and therefore such electrons are tightly bound and they are unable to carry electric current. In a semiconductor which lies between these two extremes, atoms may have three, four, or five electrons in the outer shell, and these electrons can be freed only if some additional energy is supplied. Under the required circumstances, these semiconductors conduct current slightly. The conductivity of a semiconductor can be changed by introducing new foreign elements called dopants.

Semiconductors as other materials can exist in three forms named: crystalline, polycrystalline or amorphous. In the crystalline form, atoms or molecules are arranged in a ordered array and the array is periodic throughout the bulk of the sample. In a polycrystalline sample, atoms within the subsection (crystallite) are symmetrically arranged similar as in
crystalline form while subsections are totally irregular and jumbled. In an amorphous form of a material, atoms are not arranged in an orderly pattern on any macroscopic scale.

So far single crystal silicon solar cells are widely studied and used all over the world. And therefore, this particular solar cell is discussed here to provide a clear understanding of the fundamentals of solar cells. The silicon p-n junction crystalline solar cell also works the same way as other solar cells and therefore, this can be considered as an illustrative model to understand the behavior of solar cells.

1.5.2 Electron–hole Concentration and Fermi level

In a equilibrium state of a crystal, electrons constantly seek and occupy lower energy levels. But they get being excited to higher states due to interactions with photons and also phonons. The Pauli Exclusion Principle limits the number of electrons that can exist in any allowed energy level. The highest occupied state of electrons under this condition is called the Fermi level, and its energy, denoted by $E_F$, is called the Fermi energy. The distribution of electrons in a solid obeys the (quantum) Fermi–Dirac statistics. According to the above statistics, Fermi-Dirac probability function, which is denoted by $p(E)$, is given by

$$p(E) = \frac{1}{e^{\frac{E-E_F}{kT}} + 1} \quad (1.2)$$

In which $E$, $E_F$, $k$, and $T$ are the energy of an allowed state, the Fermi energy, the Boltzmann's constant, and the absolute temperature, respectively. At absolute zero, $p(E)$ is equal to unity up to an energy equal to $E_F$ and then it becomes zero above this energy $E_F$. By definition, the Fermi energy, $E_F$ is the energy at which the probability of a state being filled by an electron is exactly one-half.
If we consider a particular isolated atom, the filling of energy levels by electrons obeys Pauli Exclusion Principle. Now let us bring two atoms closer together so that the outer electrons in either atom can be influenced, through slightly, by forces exerted on it by the other atoms. Under these circumstances, their wave functions overlap with each other and each energy level splits into two (Figure 1.3). By extension, if we bring N atoms together to form a lattice, each level of the isolated atom become N levels of solid. Therefore, as atoms are brought together to form a lattice, the levels of the isolated atoms split, eventually forming bands of closely lying levels in between which there are forbidden gaps.

Figure 1.3  Size quantization effect. Discrete molecular electronic levels gradually convert into energy bands with increasing particle size.
A semiconductor is a material in which the allowed energy bands of the highest energy for electrons (the valence band) is almost totally occupied. An intrinsic semiconductor is one in which the free electrons in the conduction band and the free holes in the valence band arise solely due to thermal excitation across the band (Figure 1.4a). In an intrinsic semiconductor, the Fermi level is exactly at the middle of the energy gap and also the number of electrons in the conduction band is equal to the holes in the valence band. An extrinsic semiconductor is one in which additional electrons are present in the conduction band because of ionized donor imperfections (Figure 1.4b), or one in which additional holes are present in the valence band because of ionized acceptor imperfections (Figure 1.4c). The Fermi level in an extrinsic semiconductor gets shifted towards the donor level $E_D$ or towards the acceptor level $E_A$.

A degenerate semiconductor is one in which so many donor (acceptor) imperfections are present that the states at the bottom of the conduction band are almost totally occupied by electrons (states at the top of the valence band are almost totally occupied by holes) and the Fermi level lies within the conduction (valence) band.

The electrical conductivity of a semiconductor can be controlled by the incorporation of suitable donor or acceptor imperfections. Such imperfections can be achieved by having a desired impurity added in the preparation of the material or by introducing the impurity at a later time by diffusion, ion implantation, or by some other suitable method.
Figure 1.4  Energy level diagrams for semiconductors

(a) An intrinsic semiconductor,

(b) Extrinsic n-type with electron donor imperfection level $E_D$, and

(c) Extrinsic p-type with electron acceptor imperfection level $E_A$.

In a non-degenerate semiconductor, the Fermi level lies within the band gap of the material as shown in Figure 1.4 a. For the conduction of thermal equilibrium between the conduction and valence bands, the total density of free electrons, $n_e$ in an n-type material can be written as;
\[ n_0 = N_C e^{-\left(\frac{E_E - E_F}{kT}\right)} \]  

(1.3)

where \( k \) and \( T \) are the Boltzmann's constant and the absolute temperature, respectively. The term \( N_C \) is called the effective density of states in the conduction band and is given by

\[ N_C = \frac{1}{\Pi^2} \sqrt{\frac{\Pi}{2}} \left( \frac{m_e^* k T}{\hbar^2} \right)^{3/2} \]  

(1.4)

where \( m_e^* \) is the effective mass of the electrons in the conduction band and \( \hbar \) is the Planck's constant.

Similarly, the total density of free holes, \( p_0 \), in a p-type material is given by

\[ p_0 = N_V e^{-\left(\frac{E_F - E_V}{kT}\right)} \]  

(1.5)

where \( N_V \) is called the effective density of states in the valence band and is given by

\[ N_V = \frac{1}{\Pi^2} \sqrt{\frac{\Pi}{2}} \left( \frac{m_{vh}^* k T}{\hbar^2} \right)^{3/2} \]  

(1.6)

where \( m_{vh}^* \) is the effective mass of the holes in the valance band.

The product of equation [1.3] and [1.5] gives

\[ n_0 p_0 = N_C N_V e^{-\left(\frac{E_E - E_V}{kT}\right)} \]  

(1.7)

\[ = N_C N_V e^{-\frac{E_E}{kT}} \]
It shows that $n_0 p_0$ is a constant for a particular temperature depending on the band gap $E_g = E_C - E_V$ of the material. Equation (1.7) is an expression illustrating the law of mass action, and it is always true at thermal equilibrium. In an intrinsic semiconductor, $n_0 = p_0$, and an intrinsic density $n_i$ can be defined such that

$$n_i^2 = n_0 p_0$$

(1.8)

Since this is a restatement of Eq. (1.7), Eq. (1.8) remains true for extrinsic semiconductors, where $n_0 \neq p_0$. It is sometimes convenient to regard the position of the Fermi level in an intrinsic semiconductor as a reference level $E_i$. Then from (1.3) and (1.5)

$$E_i = E_{F,\text{intrinsic}} = \left( \frac{E_C + E_V}{2} \right) + \frac{kT}{2} \ln \frac{N_V}{N_C}$$

(1.9)

The intrinsic level $E_i$ usually lies quite close to the center of the band gap and is a weak function of temperature. The Fermi level in extrinsic semiconductors can then be described in terms of $E_i$

$$E_F = E_i + \frac{kT}{2} \ln \frac{n_0}{p_0}$$

(1.10)

where $n_0 \neq p_0$. 
1.5.3 p–n Junction

If a semiconductor is doped with a donor impurity increasing the number of electrons in the conduction band, then it is known as a n–type semiconductor material. If a semiconductor is doped with an acceptor impurity leaving excess holes in the valance band, then it is known as a p–type semiconductor material. If these n–type and p–type crystals are joined together, a charge dipole is created in the vicinity of the junction and hence, a strong electric field develops in the junction. Then, according to the definition of Fermi level, Fermi levels in the two regions should be at the same energy which leads to an energy displacement configuration as illustrated in Figure 1.5a. The built in electric field over the p–n junction balances the strong tendency of large diffusion currents from p-region to n-region and hence, reaches an equilibrium point.

Suppose that a voltage is applied across this p–n junction in the mode as shown in Figure 1.5b known as ‘reverse biased condition’. Under this condition, majority carriers (electrons in the n–region and holes in the p–region) are drawn away from the junction and will make the inherent electric field even stronger resulting in no flow of current. Due to the high potential barrier accompanied by the strong electric field, majority carriers are not permitted to diffuse, but it helps the minority carriers (electrons in p–region and holes in n–region) to drift across the p–n junction. This results in a negligible current due to minority carriers from the n-type material to the p–type material called saturation current (leakage current), which is denoted by I_s.
If the voltage is applied in the opposite direction as shown in Figure 1.5c called as 'forward bias condition', an applied electric field is established opposite to the existing field across the p-n junction such that the resulting electric field across the p-n junction reduces. This leads to a decrease in potential barrier for the diffusion of majority carriers. Therefore, it increases the diffusion current and these majority carriers recombine at this junction. For each recombination of a free electron and a hole, an electron from the negative terminal of the battery enters the n-type material, whereas a hole from positive terminal of the battery enters the p-type material and they drift towards the p-n junction.
Therefore, a considerable current in the external circuit from the p to n direction can be observed. In the absence of light, the current through the p–n junction with the applied voltage is given by:

\[ I_j = I_s \left( \frac{qV}{e^{kT} - 1} \right) \]  \hfill (1.11)

where \( q \) is the electronic charge and \( I_s \) is the saturation current. The saturation current is dominated by the diffusion of minority carriers and is given by:

\[ I_s = \frac{qD_p n_{p0}}{L_p} + \frac{qD_e n_{p0}}{L_e} \]  \hfill (1.12)

where \( n_{p0} \) and \( p_{n0} \) are the thermal equilibrium densities of electrons on the p–side and holes on the n-side of the junction respectively; \( L_e \) and \( L_h \) are the electron diffusion length on the p-side and hole diffusion length on the n-side respectively; and \( D_e \) and \( D_h \) are the electron and hole diffusion coefficients respectively. These diffusion coefficients are given by:

\[ D_e = \frac{kT}{q} \mu_e \]  \hfill (1.13)

and

\[ D_h = \frac{kT}{q} \mu_h \]  \hfill (1.14)

where \( \mu_e \) and \( \mu_h \) are electron and hole mobility, respectively.
The electron and hole diffusion lengths are given by:

\[ L_e = \sqrt{D_e \tau_e} \]  
\[ L_h = \sqrt{D_h \tau_h} \]

where \( \tau_e \) and \( \tau_h \) are the electron and hole life times of minority carriers.

When light (phonon) is incident on the junction, electron-hole pairs are generated and the electric current will be the difference between the normal current \( I_j \) (dark) and the light generated current \( I_L \) (illuminated) i.e.

\[ I = I_L - I_j = I_L - I_s \left( \frac{qV}{e^{kT}} - 1 \right) \]

Figure 1.6 Typical current–voltage characteristic of a solar cell under (a) dark, and (b) illuminated conditions.
The curves (a) and (b) in Figure 1.6 respectively show the voltage–current characteristics when the p–n junction is not illuminated and when it is illuminated. From the photovoltaic energy conversion point of view, the power quadrant illustrated in Figure 1.6 is very important as it gives the ideal current voltage output of the solar cell.

The behaviour of a solar cell can be characterized using three parameters, namely, the open circuit voltage ($V_{OC}$), the short circuit current ($I_{SC}$), and the fill factor (FF) as shown in Figure 1.6. $V_{OC}$ is defined as the voltage output of the photovoltaic solar cell when the load impedance is much larger than the device impedance resulting in no current in the circuit. And this is the maximum possible voltage which can possibly be acquired by the cell. On the other hand, $I_{SC}$ is the current output when the load impedance is much smaller than the device impedance i.e. the maximum possible current. FF is the ratio of the maximum possible power ($V_m I_m$) to the theoretical limit ($V_{OC} I_{SC}$) if both voltage and current were simultaneously at their maximum.

The open circuit photovoltage ($V_{OC}$) is obtained by substituting $I = 0$ into Eq. (1.17)

$$V_{OC} = \frac{kT}{q} \ln \left( \frac{I_L}{I_s} + 1 \right)$$

(1.18)

The short–circuit photo-current ($I_{SC}$) is obtained by substituting $V = 0$ in Eq. (1.17), leading to

$$I_{SC} = I_L$$

(1.19)

The fill factor (FF) as defined is given by

$$FF = \frac{V_m I_m}{V_{OC} I_{SC}}$$

(1.20)
The energy conversion efficiency ($\eta$) of a solar cell at maximum power point is expressed by:

$$\eta = \frac{W_e}{W_s} = \left( \frac{I_{SC} V_{OC} FF}{W_s} \right) \times 100 \quad (1.21)$$

where $W_s$ and $W_e$ are the incident solar energy and the electric energy converted by the cell, respectively.

Incident photon to current conversion efficiency (IPCE) of a cell represents the ratio of the current of photo-generated electrons to the photon flux incident on the system for a particular wavelength $\lambda$, i.e.

$$\text{IPCE} = \frac{I_{ph}}{\Gamma(\lambda)} \quad (1.22)$$

Where $I_{ph}$ is the photocurrent density for a given wavelength, $\Gamma(\lambda)$ is the photon flux and $q$ is the elementary charge. $\Gamma(\lambda)$ can be expressed in term of the optical power $P$ given by

$$\Gamma(\lambda) = \frac{P \lambda}{hc} \quad (1.23)$$

Therefore,

$$\text{IPCE} = \frac{I_{ph}}{q} \left( \frac{P \lambda}{hc} \right) \quad \Rightarrow \quad \text{IPCE} = \frac{1240 I_{ph}}{P \lambda} \quad (1.24)$$

In practice IPCE is calculated by the final formula. Here the units of $I_{ph}$, $P$, $\lambda$, and the product $hc$ are respectively in $\mu A/cm^2$, $\mu W/cm^2$, nm and in $eVnm$. 
A simplified steady state equivalent circuit of a solar cell is shown in Figure 1.7 in which $R_L$, $R_s$, and $R_{sh}$ are the load resistance, series resistance, and shunt resistance, respectively.

![Equivalent circuit of a solar cell.](image)

Figure 1.7  Equivalent circuit of a solar cell.

The effect of series resistance ($R_s$) and shunt resistance ($R_{sh}$) on the current voltage curve for solar cells is illustrated in Figure 1.8 and 1.9, respectively.

![Current I vs Voltage V with different resistances](image)

Figure 1.8  The effect of series resistance ($R_s$) on the current voltage curve for solar cells

Where $R_1 > R_2 > R_3 > R_4$ and $R_{sh}$ is considerably high.
Where $R_d > R_3 > R_2 > R_1$ and $R_s$ is considerably low.

Figure 1.9 The effect of shunt resistance ($R_{sh}$) on the current voltage curve for solar cells

1.5.4. Interfaces

In the earlier sections, we have seen that photons entering a semiconductor colloid with valance band electrons and, if of sufficient energy, produce hole–electron pairs in the semiconductor. These hole-electron pairs will, if undisturbed, recombine in a time dictated by the bulk life time and surface recombination velocity of the semiconductor. Under these conditions, the energy represented by the absorbed photons is converted into heat within the semiconductor. However, if a local electric field is present within the semiconductor, it can be used to separate the constituent parts (holes and electrons) of the hole-electron pairs. Once separated, the collected charge carriers (holes and electrons) produce a space charge that result in a voltage across the semiconductor. This voltage is known as the photovoltage. If the separated charge carriers are allowed to flow through an external load before eventually
recombining, they constitute a photocurrent. The product of the photovoltage and the photocurrent represents a net flow of energy from the solar cell to the external load. This energy originated in the sun and was converted from photon-energy to electrical energy when the photos were absorbed within the solar cell and the resultant hole-electrons pairs were separated by the internal electric field. Therefore, the existence of an internal electric field within the semiconductor is most important for the separation of photo-generated holes and electrons. This can be achieved by using different semiconductor interfaces in the construction of solar cells. The three type semiconductor interfaces to be examined are given below. They are

(a) semiconductor-semiconductor homo-junction,
(b) semiconductor-metal schottky-junction, and
(c) semiconductor-semiconductor hetero-junction.

1.5.4.1. Homo—junction

The junction between n and p—type portions of the same material is the simplest to treat theoretically, and the theory of such a homo junction is well established. Such junctions are usually formed by the diffusion of free charge carriers into the opposite direction. When two layers of semiconductor material of opposite carrier types are intimately joined, an exchange of charge takes place so that the Fermi level becomes same in both layers. Electrons from the n—type material adjacent to the junction flow into the p—type material and holes flow from the p—type section to the n—type side. This leaves uncompensated donors and acceptors on either side of the junction as indicated in Figure 1.1Ob. Therefore, free carriers are depleted in the region near the boundary, and the presence of the net positive charges of donors in the n—type semiconductor and the net negative charges of acceptors in the p—type semiconductor cause
band bending. The magnitude of the band bending is equal to the difference in the Fermi energies of n and p type semiconductors.

Figure 1.10 Formation of a homo-junction.

1.5.4.2 Schottky–junction

When two materials having different work functions are in contact, free carriers in the material with a lower work function material transfer to the high work function material, and consequently an electrical double layer is formed at the interface. Because of this double layer, the potential in the higher work function material becomes lower than that in the other material, and the Fermi levels of both materials coincide. When an n-type semiconductor is in contact with a higher work function metal, electrons in the conduction band of the semiconductor are transferred to the metal. The density of free carriers in the semiconductors are usually low, and hence, free carriers lying in the semiconductor from the surface to the
deep bulk must be transferred to the metal in order to line up the Fermi level (Figure 1.11a). The vacant layer produced is called a depletion layer. In this layer, net positive charges (or negative charges) are present from ionized donors (or acceptors), and therefore it is also called a space charge layer. A parabolic potential gradient arises in the depletion layer which causes bending of the bands of the semiconductor and an energy barrier, termed the Schottky barrier, is formed. If we assume that surface states or defect states are not present in the semiconductor (this assumption is not valid for covalent semiconductors such as silicon), the magnitude of the band bending at equilibrium (eV_b) is equal to the difference of the work function of the metal (\( \Phi_m \)) and that of the semiconductor (\( \Phi_s \)).

\[ eV_b = \Phi_m - \Phi_s \]  

(1.25)

\( V_b \) is often called the built-in potential. The energy barrier for the flow of the electrons from the semiconductor conduction band to the metal is \( \Phi_m - \Phi_s \), while the movement of the electrons in the metal to the semiconductor is \( \Phi_m - X_s \) (\( X_s \) is the electron affinity of the semiconductor). When a negative voltage is applied to the semiconductor, the band bending is reduced by the magnitude \( eV \), and the barrier for the electron flow from the metal is unchanged by applied voltage (either forward or reverse). This value is called the barrier height (\( \Phi \)) of the Schottky barrier.

\[ \Phi = \Phi_m - X_s \]  

(1.26)

As shown in Figure 1.11a, a Schottky barrier is formed in the case of \( \Phi_m > \Phi_s \) (or \( \Phi_m < \Phi_s \)) for n-type (p-type) semiconductors. In the opposite case of a semiconductor-metal junction (Figure 1.11b), electrons in the metal transfer to the n-type semiconductor. If a high density of electrons is accumulated in the semiconductor conduction band, a very thin negatively charged
layer is formed at the semiconductor surface. Here the double layer at the metal-semiconductor interface becomes very thin. As charge carriers can easily tunnel through this thin layer, a current flows freely between the semiconductor and the metal in both directions. Such contact is called an Ohmic Contact.

![Figure 1.11 Metal semiconductor interfaces](image)

(a) for metal/semiconductor contact when $\Phi_m > \Phi_s$ (schottky–junction), and

(b) for the metal/semiconductor contact when $\Phi_m < \Phi_s$ (ohmic–contact).
1.5.4.3 Hetero—junction
This type of junction is formed between two different semiconductor materials (Figure 1.12). The use of a hetero-junction with a large band gap window material and a small band gap absorber material is a means to minimize the surface recombination loss that might otherwise dominate in direct band gap materials. The use of hetero—junctions extends the type of semiconductor material that can be used for solar photovoltaics enormously.

![Diagram of hetero-junction](image)

Before contact  After contact

Figure 1.12  Formation of a hetero-junction.

1.5.5. Composite Semiconductor Nano—cluster and Quantum well
Composite semiconductor nano—clusters can be classified into two categories. They are;

(a) capped type hetero structures, and

(b) coupled type hetero structures.
In capped type nano-cluster, one semiconductor (core material) is surrounded by thin outer shell of second semiconductor (shell material) where as in the couple system two semiconductor nano-clusters are in contact with each other.

A single quantum well is possible to be formed when one semiconductor is sandwiched between two layers of second material, which could be a semiconductor having a larger band gap or an insulating material. They create the potential barriers on either sides of the small band gap semiconductor, forming finite or infinite quantum wells. In this configuration, the difference between the conduction band edges of the two materials forms a potential well for electrons, while the well depth for holes is the corresponding valence band offset (Figure 1.13).

![Quantum well diagram](image_url)

**Figure 1.13** Quantum well formed by sandwiching a thin layer of low band gap semiconductor between two layers of high band gap semiconductors.
Multiple quantum well structures consist of a series of quantum wells (i.e., a series of alternating layers of wells and barriers). If the barrier width is narrow, photo-excited high energetic electrons and holes respectively, have sufficient energy to penetrate through the narrow barrier and transport towards the back contacts (Figure 1.14).

Figure 1.14  Transportation of high energetic electrons and holes penetrating through the narrow barrier.

On the other hand, the thicker barrier width prevents further penetration of photo-excited electrons through it. Broad barrier width confines these electrons to the potential well. In this case, the suggestion is that the trap-mediated transportation of charge carries is feasible as discussed later.
According to the classification of composite semiconductors, capped type and coupled type composite semiconductors could be utilized to build quantum wells as depicted in Figure 1.15. In the capped type composite semiconductor the second material could be either a high band gap semiconductor or an insulator, as the capping thickness could be finely controlled. Depending on the nature of the second material, the structure could be a finite or infinite potential well. But for couple type composite semiconductors, high band gap semiconductors could only be utilized for favorable conductivity.

![Figure 1.15](image)

Figure 1.15  Nano–cluster composite structures with (a) capped semiconductors (b) coupled semiconductors.
CHAPTER 2

DYE–SENSITIZATION

2.1 Introduction

Conventional solar cell can be fabricated by interfacing window material with an absorber material. Generally, the band gaps of two materials are selected such that they both cover the total visible spectrum of solar radiation. In that sense, utilization of high band gap materials for solar cell fabrication seems as useless. But these high band gap materials are found to be photo–stable even in electrolytic media of photo-electrochemical solar cells (PECSCs) [10–11]. Therefore, utilization of high band gap materials is a solution for the photo corrosion of semiconductor electrodes of PECSCs. But an efficient absorber material is essential when wide band gap semiconductors are utilized for solar cell construction.

Carrier injection of optically excited dye molecules into the band of wide band gap semiconductor material provides a solution to the absence of absorber material, which is an interesting application of the concept called dye–sensitization that had first observed more than a century ago. Injection of carriers (electrons or holes) into a semiconductor band (conduction or valence) by a dye molecule attached to its surface upon irradiation is referred to as dye–sensitization.
2.2 History

The phenomenon of dye-sensitization of the semiconductor surface was first observed more than a century ago and still continues to arouse the interest of both physicists and chemists. This effect was first discovered by Vogel [12] in 1873, that dye coated silver halide on a photographic plate sensitized absorption spectrum of the dye. Later his invention paved the way for development of colour photography and xerography, but until 1970, it was not realized that dye-sensitization could be utilized for conversion of solar energy into electricity at higher efficiencies. Earlier, dye-sensitized photo-electrochemical solar cells had minute photocurrents and efficiencies, so that it was limited only for academic curiosity. Work of Tsubomura et.al. [13] revealed that possibility exists for devising high efficient (~1-2%) PECSCs using porous ZnO electrodes sensitized with Rose Bengal dye. Porous electrodes increased the light absorption cross-section by increasing the surface concentration of the dye at monolayer level. But in planer electrodes, thicker dye layers electrically insulated the semiconductor and also caused concentration quenching i.e., release of energy as heat by excited dye molecules due to their mutual interaction. A major invention of dye-sensitized PECSCs was reported around the 1990s by M. Gratzel and collaborators [14]. They have used nano-porous film of TiO$_2$ of high surface roughness, i.e., ~800-1200 times the geometrical area of the surface of the film and specially synthesized dye (ruthenium bipyridyl dye) to achieve efficiency exceeding 10%. Dye-sensitized PECSCs of this category are currently being considered as possible cheap alternative to silicon solar cells.
2.3 Theoretical Aspect of Dye-sensitization

In large organic dye molecules, there are often energy levels of excited state and ground state which do not change when electrons are added or removed from the molecules. These dye molecules have two features that make them useful for study.

(i) They absorb the visible light, so light of right wavelength can be passed through a wide band gap semiconductor electrode with no minority carrier generation, and

(ii) They have high extinction coefficient so the light is absorbed by the dye very near the semiconductor surface so that monolayer of dye is sufficient to absorb the light energy.

Basically two types of sensitization processes have been identified. Namely they are; (a) anodic sensitization and (b) cathodic sensitization. In anodic sensitization, the photo excited dye molecule on the surface of the semiconductor injects an electron into the conduction band (Figure 2.1.a), i.e.,

\[ D + h\nu \rightarrow D^* \]
\[ D^* \rightarrow D^- + e^- \quad (CB) \quad \text{(Electron goes to the conduction band.)} \]

Where as in cathodic sensitization, the excited dye molecule injects a hole to the valence band of the semiconductor (Figure 2.1.b), i.e.,

\[ D + h\nu \rightarrow D^* \]
\[ D^* \rightarrow D^- + h^+ \quad (VB) \quad \text{(Hole goes to the valance band.)} \]
Figure 2.1 Mechanism of dye-sensitization (a) Anodic sensitization, and (b) Cathodic sensitization.
Anodic sensitization is favourable if the excited state $D^*$ of the dye molecule is located above the bottom of the conduction band of the semiconductor whereas cathodic sensitization occurs if the ground state $D$ of the dye is situated below the valence band. From this point of view, it is revealed that n-type semiconductor shows anodic sensitization and p-type semiconductor shows cathodic sensitization.

The process involved in dye-sensitization is seemed to be very basic as far as its definition is concerned. However, this process is rather complicated and still; it is not fully understood quantitatively. The injection of a carrier could occur through a singlet or a triplet state of the dye. And also, charge injection from dye molecule to semiconductor is an ultra-fast process and details of which are little understood. But the preliminary process is that the transfer of charge carriers from excited states of dye molecules to continuous spectrum of semiconductor band. The Fermi Golden Rule of perturbation theory explains this type of transitions using quantum mechanics. The formula governing the process is given by the matrix element,

$$ R_{ds} = \frac{2\pi}{\hbar} \left| \langle \Phi_s | H | \Phi_d \rangle \right|^2 \rho_s $$

Where, $R_{ds}$ is the transition rate; $\Phi_s$ and $\Phi_d$ are electronic states in semiconductor and dye respectively; $\rho_s$ is the density of final states of the semiconductor. The Hamiltonian theory ($H$) of the process is complicated and depends on the details of the problem that remains unelucidated. Dye-sensitized carrier injection is an ultra-fast process because the density of final states of the semiconductor is a continuum. The fastness of electron injection has been demonstrated by time resolved measurements [15–16]. And also, the height of the
excited level of the dye (above the bottom of the conduction band) is an important parameter that determines the rate of charge injection. In dye-sensitization, electrons could also be injected to trap states of n-type semiconductor material [17]. Location of excited level of the dye below the conduction band motivates the transformation of carriers to trap levels either in bulk or at the surface. Here again, the Fermi Golden Rule gives at least qualitative explanation. When the density of trap levels become high, the electron transformation process to these states become significant and shallow traps and surface states play an important role in dye-sensitization.

An advantageous property of dye-sensitization process is that the semiconductor material could be a low purity polycrystalline material. The reason for this is that dye-sensitization involves only one band (the conduction band in an anodically sensitized process and the valance band in a cathodically sensitized process) and electrons and holes are both not produced in the same material. Consequently, recombination arising from impurity and defects are nonexistent.

2.4 Dye-sensitized Photovoltaic Solar Cells

Dye-sensitization has several favourable attributes that are important for photovoltaics.

i) The ability to use high band gap semiconductors that are photo stable even at electrolytic media and they avoid photo corrosion.

ii) Since the dye-sensitization is being a single band (conduction or valence band) process, semiconductor could be a low purity nano–porous material and hence, the porosity of the semiconductor material increases the light harvesting efficiency.
iii) The electrons or holes produced by the dye are not in the same material, so that recombination losses arising from impurities and defects are elucidated.

Dye-sensitized photovoltaic solar cells can be classified into two categories. They are:

(i) Dye-sensitized solid-state photovoltaic solar cells, and

(ii) Dye-sensitized photo-electrochemical solar cells.

2.4.1 Dye-sensitized Solid-state Photovoltaic Solar Cells

In dye-sensitized solid-state photovoltaic solar cell, dye mono-layer is sandwiched in between n-type and p-type semiconductor material, respectively. No electrolytic media is present in this cell and hence, generally it is called “dry cell”. The mechanism of photocurrent generation of this cell is fairly well understood (Figure 2.2).

On the illumination of the dyed electrode, electrons injected to the conduction band of n-type semiconductor, reached back-contact and they are driven to the counter electrode via the external circuit while holes injected to the valance band of p-type semiconductor are carried to the counter electrode.
Figure 2.2  Mechanism of photocurrent generation in dye-sensitized solid-state photovoltaic solar cell.

The process is summarized in the following equations.

\[ D + h\nu \rightarrow D^* \]

\[ D^* \rightarrow D^+ + e^- \quad (\text{CB}) \quad \text{(Electron goes to the conduction band.)} \]

\[ D^+ \rightarrow D + h^+ \quad (\text{VB}) \quad \text{(Hole goes to the valance band.)} \]

The alternative process;

\[ D + h\nu \rightarrow D^* \]

\[ D^* \rightarrow D^- + h^+ \quad (\text{VB}) \]

\[ D^- \rightarrow D + e^- \quad (\text{CB}) \]

is also possible.
The most important thing to note in this cell is the restriction of electrons and holes into two different materials separated by an insulating dye layer. Thus the problem of bulk recombination does not arise. The availability of continuum states in conduction band of n-type material and valence band of p-type material facilitates the injection of electrons and holes into two different materials, which is a kinetically feasible ultra-fast process. This type of dye-sensitized solid-state solar cell was first devised by Tennakone and co-workers in 1988 using plane electrodes and late in 1995 with a nano-porous electrodes [18-19]. The selection of p-type material is restricted and hence the construction of dye-sensitized solid-state cell is even more challenging than electrochemical cell.

2.4.2 Dye-sensitized Photo-electrochemical Solar Cells

In the dye-sensitized photo-electrochemical solar cell, liquid electrolyte is utilized as hole-collector instead of p-type semiconductor in dye-sensitized solid-state solar cell. Therefore, generally it is called "wet cell". Figure 2.3 illustrates the mechanism of photocurrent generation in dye-sensitized photo-electrochemical solar cell.

On illumination of the dyed electrode, electrons are injected to the bulk semiconductor and they are carried to the counter electrode via the external circuit. The positive charge on the dye cation, in the photo electrode is scavenged by the oxidizing specie X in the electrolyte to form $X^+$, which diffuses to the counter electrode and transfers the positive charge while reducing to its original state X.
Figure 2.3  Mechanism of photocurrent generation in dye-sensitized photoelectrochemical solar cell.

The process is summarized in the following equations.

\[ D + h\nu \rightarrow D^+ + e^- \quad \text{(Electron goes to the conduction band)} \]

\[ D^+ + X \rightarrow X^+ + D \quad \text{(at the dye coated electrode and the electrolyte interface)} \]

\[ X^+ + e^- \rightarrow X \quad \text{(at the counter electrode)} \]

If the number of electrons produced by the dye is equal to the number of species X oxidized in electrolyte, it will be a regenerative cell. If not, chemical reactions take place involving X and D or other species in the electrolyte and electrode itself, resulting free energy storage
or dissipation. It is impossible to think of existence of perfectly regenerative systems, but the life time of such devices turn out to be sufficient for practical applications.

2.5 Hot Carrier Generation in Dye—sensitized Process

Hot carrier generation is referred as the excitation of an electron to a higher energy than the band gap energy of a semiconductor by absorption of a photon. (Figure 2.4.a). Generally, the excess free energy of hot electrons is given out as thermal radiation or transferred to kinetic energy of the electron before they relax to the conduction band. If it is possible to avoid this radiation loss, a significant increase in the efficiency of solar energy conversion can be attained because of the additional free energy content of the non-thermal electrons. In dye—sensitization process, electron injected to the conduction band of the semiconductor is most likely to be a hot carrier, as excited state of the dye molecule always locates above the conduction band edge (Figure 2.4.b).
Figure 2.4. Generation of hot electrons (a) by photo excitation of semiconductor
(b) by photo excitation of dye molecules attached to the semiconductor.
CHAPTER 3

EXPERIMENTAL TECHNIQUES

The experimental techniques that have been used to fabricate and characterize the composite semiconductor films and dye-sensitized solar cells made from these films are described in this chapter.

3.1 Film Deposition Methods

The Spray Coating method was utilized to prepare composite films of SnO$_2$ while Doctor Blade method was used to prepare composite films of TiO$_2$ in different composite semiconductor systems. Film deposition methods are discussed in detail under relevant chapters.

3.2 Film Thickness

The measurement of the thickness of the deposited film is an important parameter because many properties of thin films are thickness dependant. The applicable methods to measure the thickness of a thin film are listed below.

<table>
<thead>
<tr>
<th>Method</th>
<th>Device</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical methods</td>
<td>Interferometry, absorption and emission spectroscopy, ellipsometry.</td>
</tr>
<tr>
<td>Mechanical Methods</td>
<td>Crystal oscillators and gravimetric methods, stylus-method profilometry.</td>
</tr>
<tr>
<td>Electrical Methods</td>
<td>Measurement of resistivity, capacitance, q-factor change and ionization.</td>
</tr>
<tr>
<td>Nuclear Methods</td>
<td>Rutherford backscattering spectrometry and nuclear reaction analysis.</td>
</tr>
<tr>
<td>Electron microscopy</td>
<td>Scanning electron microscopy (SEM) and transmission electron microscopy (TEM).</td>
</tr>
</tbody>
</table>

In this work, thicknesses of the films were determined using SEM images.
3.3 Determination of Crystalline Structure and Crystalline Size

X-ray diffraction is a powerful tool to analyze the crystallinity of a material and crystalline size. A beam of X-rays exposed to crystal lattice interferes constructively according to the path difference, \(2d\sin\theta\), between the two rays, which leads to Bragg equation,

\[
2d \sin \theta = n \lambda
\]  

(3.1)

Where \(\lambda\) is the wavelength of the X-rays and \(n\) is the order of the reflection, it was found that very small crystals causes broadening of the diffracted beam, which leads to formulation of Scherrer's equation,

\[
B_{\text{sher}} = \frac{0.9 \lambda}{B \cos \theta}
\]  

(3.2)

This was used to estimate the particle size of a small crystal \(B_{\text{sher}}\), by measuring the broadening of the diffraction line \(B\), at half its maximum intensity in radians. In this work Shimadzu XD-D1 model X-ray diffractometer with Cu-\(k_\alpha\) radiation (1.54Å) was used to identify diffraction peaks and Scherrer's formula was used to calculate the mean grain size. The calculated values are compared with the sizes of the particles observed from SEM images.

3.4 Calculation of the Particle Size of Powders

The particle size distribution of the powder samples were determined by gradient centrifuging using a Horiba (CAPA 700) particle size analyzer. For this purpose 15 mg of the oxide was dispersed in a 0.01 M solution of sodium hexametaphosphate by ultrasonic agitation. The sodium hexametaphosphate was used to disperse the clusters of oxide particles [20].
3.5 Calculation of Roughness Factor and Porosity

3.5.1 Roughness Factor

Generally the morphological and roughness data of films are obtained from atomic forced microscopy (AFM). But SEM images also give more or less information on the morphology of the film. The strategy we used to calculate the roughness factor was quite simple. The dye incorporated into a film was desorbed into 1 mM solution of KOH and concentration was determined spectrometrically with the help of pre-drawn calibration curve (Figure 3.1). When the number of dye molecules absorbed on the surface of the film and the surface area covered by each dye molecule (~100 Å² for indoline) is known, electrochemically active area (effective surface area) can be calculated assuming monolayer of dye is absorbed on the film. The roughness factor is defined as the ratio between the effective area and geometrical area, so that the roughness factor can be estimated very easily.
3.5.2 Porosity

The ratio between the volume of the pores and film volume is defined as the porosity of a film. Most of the times it is expressed as a percentage. The volume of the film can be simply obtained by multiplying surface area and thickness. As we know the effective surface area $A$, the pore volume, $V$ can be estimated if average pore diameter $D$ is known. i.e.,

$$ V = \frac{DA}{4} \quad (3.3) $$

An average value for pore diameter can be derived from Washburg equation, which is true for capillary flow in a single cylindrical tube as well as for more complex materials.
It reads as:

\[ L^2 = \frac{\gamma D t}{4 \eta} \]  

(3.4)

Where,

- \( L \) - Length,
- \( \eta \) - Viscosity of liquid,
- \( D \) - Average pore diameter,
- \( \gamma \) - Surface tension, and
- \( t \) - Time.

Therefore expression for the pore volume is,

\[ V = \frac{L^2 \eta A}{\gamma t} \]  

(3.5)

3.6 Finding the Band Gap and Band Edge Position

3.6.1 Band Gap

Semiconductors absorb light below a threshold wavelength \( \lambda_g \), the fundamental absorption edge, which is related to the band gap energy via

\[ \lambda_g \text{ (nm)} = \frac{1240}{E_g \text{ (eV)}} \]  

(3.6)

3.6.2 Band Edge

Conduction band edge of n-type semiconductor material and valence band edge of p-type semiconductor material can be determined from Mott-Schottky plot with reference to some
known electrode potential such as normal hydrogen (NHE) or standard calomel electrode (SCE). Mott-Schottky relation read as,

\[ \frac{1}{C^2} = \frac{2}{q N_{SC} \kappa \varepsilon_0 A^2} \left( V - V_{fb} - \frac{\kappa T}{q} \right) \]  \hspace{1cm} (3.7)

Where \( C \) - capacitance, \( \kappa \) - relative permittivity, \( \varepsilon_0 \) - permittivity of free space, \( q \) - electric charge, \( N_{SC} \) - doping density, \( V \) applied voltage and \( V_{fb} \) flat band potential. Therefore the plot of \( 1/C^2 \) vs. \( V \) is a straight line where intersection of \( V \) axis gives the flat band potential \( V_{fb} \), neglecting the \( \kappa T/q \) factor, which is very small (0.0257) at room temperature. The experimental set-up consists of three-electrode system (Figure 3.2). The electrolyte was 0.5M Na₂SO₄ at pH 7. The capacitance and voltage measurements were taken using Hewlett-Packard LCZ Meter 4191 and Keithly digital multimeter.

Figure 3.2  Experimental set up for band edge measurement
3.7 Transient Photocurrent

A digital oscilloscope (Hewlett-Packard) coupled to a computer was used to measure the current transients. Chopped white light or monochromatic light from a filament lamp is used as the light source. A schematic representation of the experimental set-up is illustrated in Figure 3.3.

![Schematic representation of time resolved photocurrent measurement system.](image)

3.8 Fluorescence Spectrum

Fluorescence is the stimulation and emission of radiation from a subject by the impact of higher energy radiation upon it. Fluorescence, unlike phosphorescence, ceases almost immediately when excitation is removed. Luminescence is a general term for the emission of radiation that incorporates fluorescence and phosphorescence, as well as other electrochemical phenomena like bioluminescence. Fluorescence is the result of a three-
stage process that occurs in certain substances called fluorescent dyes. The entire fluorescence process is cyclical.

The fluorescence spectrums were taken using the Shimadzu RF-5000 spectrofluorophotometer in the experiments.

3.9 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR is most useful for identifying chemicals structures of organic or inorganic materials. It can be utilized to quantitate amount of some compound in unknown mixture. The analyzing of solids, liquids, and gases is possible with the FTIR spectroscopy. The term Fourier Transform Infrared Spectroscopy (FTIR) refers to the fairly recent development technique in which the data are collected and converted from an interference pattern to a spectrum. Today's FTIR instruments are computerized which makes them faster and more sensitive than the older dispersive instruments. FTIR is perhaps the most powerful tool for identifying functional groups of chemicals. The wavelength of light absorbed is the characteristic of the chemical bond of the compound. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. For any given bond, there are several specific frequencies at which it can vibrate. According to quantum mechanics, these frequencies correspond to the ground state (lowest frequency) and several excited states (higher frequencies). One way to cause the frequency of a molecular vibration to increase is the excitation of the bond by the absorption of light energy. For any given transition between two states, the light energy (determined by the wavelength) must exactly equal the difference in the energy between the two states (usually
ground state and the first excited state). The energy corresponding to these transitions between molecular vibrational states is generally 1 to 10 kilocalories/mole which corresponds to the infrared region of the electromagnetic spectrum.

Samples for FTIR can be prepared in number of ways depending on its nature; solids, liquid and gases. For solid samples, it can be milled with potassium bromide (KBr) to form a very fine powder. This powder is then compressed into a thin pellet which can be analyzed for particular requirement. KBr is transparent in the IR region. Alternatively, solid samples can be dissolved in a solvent such as methylene chloride, and the solution is placed onto a single sodium chloride (salt) plate. Salt is also transparent to infrared light. The solvent is then evaporated off, leaving a thin film of the original material on the plate. This is called a cast film, and is frequently used for polymer identification. For liquid samples, the easiest method is to place one drop of sample between two plates of salt. The drop forms a thin film between the plates. Solutions can also be analyzed in a liquid cell. This is a small container made of NaCl (or other IR-transparent material) which can be filled with liquid.

3.10 Dark I–V Measurements
Since solar cells convert light energy into electricity it might seem odd to measure the photovoltaic properties of the cell in the dark. However, dark IV measurements are valuable in examining the diode properties. Dark IV measurements use the injection of carriers by the applied electric potential rather than the injection of light generated carriers into the circuit. In most cases, the dark IV measurements give extra information about the
cell for diagnostic purposes. Dark IV measurement produces usually the exponential curve so characteristic of the diode.
CHAPTER 4

ENHANCEMENT OF PHOTOVOLTAIC EFFECTS OF INDOLINE—SENSITIZED
SOLAR CELL OF NANO—CRYSTALLINE TiO₂ SURFACE DOPED WITH
COPPER

4.1 Introduction

The discovery of the concept of dye-sensitized photo—electrochemical solar cell based on
nano—crystalline oxide semiconductors more than two decades ago, continues to receive
wide attention as a cheaper alternative to the conventional photovoltaics [21–22]. Basically,
the mechanism of operation of these devices depends on absorption of light by a pigment
anchored to a nano—crystalline high band—gap n—type oxide semiconductor, following
injection of electrons to the semiconductor by the excited dye molecules. The positive
charge on the dye cation scavenged by a donor species in the electrolyte is diffusively
transported to a counter—electrode. The energy conversion efficiency achievable depends on
many factors; (1) the bulk properties of the semiconductor (i.e., band—gap ,band—positions,
conduction band density of states) and the structure of the film (i.e., crystallite size,
porosity, roughness factor), (2) Photophysical properties of the dye (i.e., LUMO and
HOMO positions, extinction coefficient) and the mode of anchoring of the dye molecules to
the semiconductor surface, (3) nature of the redox electrolyte and electrocatalytic properties
of the counterelectrode. Significant improvements have been made in structuring the
nano—crystalline films, synthesis of superior sensitizers and redox electrolytes and
fabrication techniques [23]. An important recent development is the identification of metal
free organic dyes capable of delivering energy conversion efficiencies approaching that of the best Ru-bipyridyl dyes [24–29]. In this context high extinction coefficient indoline D–149 dyes are quite promising because of the good stability [24–25], low cost and ease of synthetic procedures. We have found that the efficiencies of dye–sensitized solar cells based on indoline D–149 can be further enhanced by surface doping of TiO₂ with copper. Evidence presented show that copper doping increases the open–circuit voltage and suppresses recombination of the injected electron with acceptors in the electrolyte.

4.2 Experimental Details

In order to obtain reproducible results and easy comparison a simple procedure was used to prepare TiO₂ films. A mixture of TiO₂ powder (Degussa P25, 200 mg, median particle size 30 nm), 95% ethanol (2 ml), glacial acetic acid (10 drops) and Triton X–100 (one drop) was ground to form a thick paste. The paste was doctor bladed onto fluorine doped conducting tin oxide (FTO) glass plates (sheet resistance 15 ohm/sq, 0.5x1.5 cm², active area 0.25 cm²) and heated in air at 550°C for 30 min. Copper doped TiO₂ films were prepared by the same method after incorporating a measured volume of 0.025 M CuCl₂ in ethanol to the mixture used for preparation of the paste. Both types of films used for fabricating cells had a thickness of ~ 10 μm. The surface concentration of Cu atoms in the films was calculated from the knowledge of Cu incorporated into a known weight of TiO₂. After sintering, plates were washed with water to remove any un–reacted CuCl₂ and again sintered at 550°C for 5 min. The specific surface area of the sample films were estimated by determining the amount of the N3 dye adsorbed after depletion of the dye into alcoholic alkaline solution and spectroscopic estimation. To determine the exact amount of copper in
the film, the water used for rinsing the plates was tested for copper by atomic absorption spectroscopy. Indoline D-149 was coated on TiO₂ surface by soaking the plates in the dye solution (1.5x10⁻⁴ M in t-butyl alcohol + acetonitrile, 1:1 by volume) for 2 hrs. The amount of dye adsorbed was estimated by measuring the depletion of the dye in the coating solution spectrophotometrically. Photoelectrochemical cells were fabricated by clamping a platinum sputtered FTO glass plate onto the dyed surface and filling the capillary space with the electrolyte (0.5 M tetrapropyl ammonium iodide + 0.05 M iodine in 1:4 by volume mixture of acetonitrile + ethylene carbonate). I–V characteristics of the cells at 1000 Wm⁻² 1.5 AM simulated sunlight were recorded using a Keithly source meter. The simulator lamp was calibrated using a silicon diode to set the light intensity at 1000 Wm⁻². The Mott–Schottky plots of TiO₂ and copper doped TiO₂ films in 0.1 M Na₂SO₄ were recorded using a Hewlett Packard 4276A LCZ meter and a HJ Instruments potentiostat recorded the dark I–V curves. A He–Ne laser and mechanical shutter were used to record photovoltage transients using an oscilloscope.

4.3 Results and Discussion

During the sintering process, copper gets deposited on the TiO₂ surface via the reaction

\[ 2x\text{CuCl}_2 + O_2 \rightarrow 2\text{Cu}_x\text{O} + 2x\text{Cl}_2 \]  \hspace{1cm} (5.1)

As sintering is at a relatively low temperature for a short duration, Cu dopes on the TiO₂ crystallite surface. Nevertheless, Cu remains firmly bonded to TiO₂ surface and its removal requires prolonged warming with strong HNO₃. On increasing the sintering temperature or prolonging sintering at 550⁰C, the efficiency falls below that the cells made from bare TiO₂ films subjected to similar variations. This suggests that the diffusion of the dopant into the
bulk of the crystallites is detrimental. At the level doping used in the experiments, the U.V–visible diffuse reflectance spectra did not indicate any features significantly different from the undoped films, indicating that the doping has no major effect on the band–gap. When indoline D–149 is used as the sensitizer, the efficiency of the cell gradually increases above that of bare TiO$_2$ as the surface concentration of Cu ($S_{Cu}$) is increased, reaching an optimum when $S_{Cu} = 1.67 \times 10^{14}$ cm$^{-2}$ (Figure 4.1). At much higher values of $S_{Cu}$, the efficiency goes well below that of the cells made of bare TiO$_2$. IV characteristics of indoline sensitized cells with Cu doped and undoped TiO$_2$ films shown in Figure 4.2. Table 4.1 gives the I–V parameters ($I_{sc}$ = short–circuit photocurrent, $V_{oc}$ = open–circuit voltage, $\eta$ = efficiency, $FF$ = fill factor) of the cells. At the optimum $S_{Cu}$ the efficiency of the doped cell reaches 8.1% compared to 5.8% for an equivalent cell with an undoped TiO$_2$ film. It is seen that Cu doping enhances other I–V parameters as well (Table 4.1). The photocurrent action spectrum of the Cu doped cell presented in Figure 4.3 corresponds to a peak (581 nm) incident photon to photocurrent conversion efficiency (IPCE) of 82%. In the undoped system, the peak point in photocurrent action spectrum is red–shifted by $\sim$ 68 nm with an IPCE of 78%. It is interesting to note that the effect of Cu doping disappears on incorporation of 4–tert- butylpyridine to the electrolyte, in complete contrast to the behavior of cells made of undoped TiO$_2$ (Table 4.1). A comparison of dark I–V characteristics (Figure 4.4) of the indoline sensitized cells based on Cu doped (at optimum $S_{Cu}$) and bare TiO$_2$ films shows that current onset under reversed bias occurs at $\sim$ 0.60 and 0.10 V in the two systems. On incorporating 4–tert butylpyridine into the electrolyte, the opposite behavior was observed; here the onset under reversed bias occurred at a higher
voltage in the cells with undoped TiO$_2$ films. The above difference in dark I–V characteristics of the doped and undoped cells is a clear indication that the recombination is better suppressed in the former cell. The photovoltage transients of the two cells shown in Figure 4.5 confirm the same. Exceedingly fast decay of the photovoltage of the doped cell compared to the undoped one implies that doping effectively suppresses the recombination loss. The fast decay indicates a decrease in the carrier trapping rate, one of the main causes of recombination.

Figure 4.1. Variation of the efficiency of the cell (1000 W m$^{-2}$, 1.5 AM illumination) with the surface concentration of copper atoms on the TiO$_2$ surface.
Figure 4.2. I–V characteristics of indoline D–149 sensitized cells constituted of (a) un–doped TiO₂ in the electrolyte without 4–tert butylpyridine (b) TiO₂ optimally doped with Cu in the electrolyte without 4–tert butylpyridine (c) undoped TiO₂ in the electrolyte with 4–tert butylpyridine (d) TiO₂ optimally doped with Cu in the electrolyte with 4–tert butylpyridine (e) TiO₂ sensitized with indoline D–149 complexed with Cu²⁺ in the electrolyte without 4–tert butylpyridine (f) TiO₂ sensitized with indoline D–149 complexed with Cu²⁺ in the electrolyte with 4–tert butylpyridine.
Table 4.1 I–V parameters (Isc= short–circuit photocurrent, Voc = open–circuit voltage, η = efficiency, FF = fill-factor) of different systems sensitized with indoline D–149. (a) undoped TiO₂ in the electrolyte without 4–tert butylpyridine (b) TiO₂ optimally doped with Cu in the electrolyte without 4–tert butylpyridine (c) un-doped TiO₂ in the electrolyte with 4–tert butylpyridine (d) TiO₂ optimally doped with Cu in the electrolyte with 4–tert butylpyridine (e) TiO₂ sensitized with indoline D–149 complexed with Cu²⁺ in the electrolyte without 4–tert butylpyridine (f) TiO₂ sensitized with indoline D–149 complexed with Cu²⁺ in the electrolyte with 4–tert butylpyridine.
Figure 4.3. Photocurrent action spectrum of the indoline D-149 sensitized cell with (a) Cu doped TiO$_2$ (b) undoped TiO$_2$

Figure 4.4. Dark I–V characteristics (a) Cu doped cell (b) undoped cell in an electrolyte without 4-tert butylpyridine
Figure 4.5. Photovoltage transients of the cells with TiO$_2$ films (a) doped with Cu (b) undoped.

The Mott–Schottky plots for TiO$_2$ and Cu doped TiO$_2$ (doping level = $S_{Cu}$) shown in Figure 4.6 indicates that the doping shifts the flat-band potential (FB) of the latter film in the negative direction by 0.17 V. When the doping concentration is increased beyond $S_{Cu}$ corresponding to optimum performance, FB becomes more negative.
Figure 4.6. Mott–Schottky plots for (a) Cu doped TiO$_2$ and (b) TiO$_2$ (supporting electrolyte 0.1M Na$_2$SO$_4$).

The above observations can be understood on basis of the following hypothesis. If an even distribution of Cu atoms on the TiO$_2$ surface is assumed, the average distance between the Cu atoms ($\sim [S_{Cu}]^{1/2}$) is $\sim 0.8$ nm, a distance, of the same order of magnitude as the linear dimension of the indoline D–149 dye molecule. Alternatively, the dye surface concentration ($S_{dye}$) is same order of magnitude as $S_{Cu}$ (The measured value of dye on the film is $9.3 \times 10^{16}$ molecules cm$^{-2}$, a roughness factor of $\sim 840$ yields $S_{dye} = 1 \times 10^{14}$ cm$^{-2}$). Thus at the optimum, each dye molecule is associated with one copper atom indicating an interaction between copper and the dye. Indoline D–149 anchors to TiO$_2$ surface via the
carboxylate moiety. FTIR signals originating from carboxylate ligand in indoline coated TiO₂ and copper doped TiO₂ are identical, suggesting that in both cases, the carboxylate binds to TiO₂. Sulfur in rhodanine rings of indoline D-149 could coordinate with copper and a schematic diagram indicating a possible mode of bonding of indoline D-149 to Cu atoms on the surface of TiO₂ is shown in Figure 4.7. The distinctive differences in the photocurrent action spectrum of the doped cell compared to the undoped one (Figure 4.3) is a clear indication of an interaction of indoline with copper atoms on the TiO₂ surface. In addition to the blue-shift of the peak position in the doped cell, there are other distinct differences in the two spectra. The sharp peak at 510 nm in the undoped cell is smoothed out in the doped cell and its profile is narrower. The distinction of two spectra also supports the assumption that copper atoms reside on the TiO₂ surface, permitting interaction with the dye. When Cu²⁺ ions are introduced to an indoline D-149 solution, Cu complexes with dye accompanied by a colour change. In the absorption spectra of alcoholic solutions of indoline D-149 and the same complexed with copper, the absorption peaks are located at 515, 521 nm respectively (Figure 4.8). The complexed dye adsorbs well onto TiO₂, but the efficiency is drastically reduced (Table 4.1). Obviously, the complexed dye would not coordinate with Cu on the TiO₂ surface. Possibly, photo-induced electron delocalization pattern in the dye molecule also undergoes a change on coordination of rhodanine rings with Cu. Interaction of the dye with Cu could also suppress aggregation of the dye molecules as suggested by blue-shift of the absorption peak of the doped cell. If the electron is driven towards the metal (Cu), the injection rate to TiO₂ via the carboxylate linkage will be reduced. A natural question that arises is about the, most probable point of injection of the electron to TiO₂ (i.e., carboxylate ligand attached to TiO₂ or coordination of
a rhodanine ring moiety to a Cu atom. Although there is no experimental evidence, an involvement of the coordination of rhodanine to Cu atoms (attached to TiO₂) may have important implications on electron injection and geminate recombination kinetics. Indoline D–149 forms non-quenching J-aggregates on the TiO₂ surface [25].

![Chemical structure of indoline D-149](image)

Figure 4.7. Schematic diagram suggesting the mode of interaction of indoline D–149 with the TiO₂ surface.

The broadening of the action spectrum indoline D–149 sensitized cells and extension of the responsivity towards the red region results from this effect. It is natural to expect that when this dye is bonded to both Cu atoms and TiO₂ (Figure 4.7), the aggregation is circumvented. The narrower profile of the action spectrum of the doped cell compared to the undoped, seems to originate from prevention of aggregation in the former system.
Many factors seem to be responsible for the dramatic improvement of efficiency of the cell on Cu doping of TiO$_2$. The shift of the flat–band potential of copper doped TiO$_2$ in the negative direction increase the open–circuit voltage as observed. The higher dark current onset potential of Cu doped cell compared to the undoped one indicates that the recombination probability of the injected electron with acceptors in the electrolyte is lesser in the former system. Figure 4.9 (i) and (ii) shows the variation of the energy conversion efficiency and the open–circuit voltage of the two cells with the intensity of illumination. In the un–doped cell, the efficiency decreases faster with the increase of the light intensity compared to the doped cell. In the doped cell, the open–circuit voltage remain nearly
constant at higher intensities (i.e., > 900 Wm\(^{-2}\)), whereas in the undoped cell a saturation voltage is not approached even at very high intensities. The pumping of electrons into TiO\(_2\) via sensitized injection raises the quasi–Fermi level (QFL), the height of which determines the open–circuit voltage. Recombinations limit the build–up of the QFL. Results further confirm that copper doping suppress recombination, enabling upward lift of the QFL even at lower light intensities when the electron pumping rate is slow. Despite the significantly higher efficiency of the doped cell compared to the undoped one, the peak IPCEs of the two cells are of the same order of magnitude. IPCEs are measured at very low intensities (~ 50 \(\mu\)W cm\(^{-2}\)) where the recombination losses are less pronounced. Copper doping of TiO\(_2\) resembles the effect of 4–\(\text{tert}\) butylpyridine, the adsorption which shifts the flat–band potential in the negative direction and suppresses recombination increasing the open–circuit voltage. 4–\(\text{tert}\) butylpyridine \([30–32]\) is believed to passivate intra–band gap defects in TiO\(_2\) which act as recombination centers \([33]\). Presumably, the copper atoms are also attached to defect sites on TiO\(_2\).
Figure 4.9. Variation of (i) efficiency (ii) open-circuit voltage of (a) Cu doped and (b) un-doped cells with the light intensity.

When Cu doped and undoped films are sensitized with the N3 dye, the efficiency and other IV parameters of the doped cell decreases in complete contrast to the behavior of indoline
D-149. Clearly, the interaction of indoline and Cu also plays a crucial role in enhancing the efficiency. Mechanism involved is not fully understood. Perhaps, the firm bonding of the indoline D-149 molecule to the TiO₂ surface at two points (i.e., carboxylate link to TiO₂ and coordination of sulfur in the rhodanine rings to Cu atoms as in Figure 4.7) covers TiO₂ surface without leaving any voids. Recombinations occur at the voids where the electrolyte is in direct contact with the TiO₂ surface. The observation that 4-tert butylpyridine in the electrolyte interferes with the beneficial effect of Cu doping can be understood. The stronger bonding of 4-tert butylpyridine to Cu could yield the link of indoline D-149 molecules to Cu. This happens if Cu atoms are located on the TiO₂ surface.

4.4 Conclusion

The efficiency of indoline D-149 sensitized photoelectrochemical solar cells increases significantly when the nanocrystalline TiO₂ is surface doped with Cu to a concentration similar to the dye concentration. The prescription adopted to prepare TiO₂ films in this investigation is not optimized standard procedure. However, the efficiency increased from 5.8 to 8.1% on doping the TiO₂ film with Cu. We believe that the efficiency can be further improved by optimization of the TiO₂ film casting procedure. Preliminary experiments indicate that copper doped cell is stable as the undoped cell. There is no evidence that Cu leaches into the electrolyte. Possibly, the coordination of the dye to the copper, adds to the chemical stability copper bonded to the TiO₂ surface and also suppress the aggregation of the dye molecules. The exact mode of coordination of the dye to copper sites in the TiO₂ surface is not clear. As the surface concentration of Cu on TiO₂ is very low, the resolution of the FTIR measurements is not sufficient to obtain any clues as to the mode coordination
of indoline D–149 dye to the copper doped TiO₂ surface. The involvement of both sulfur and nitrogen in the rhodaine rings is not ruled out. The present investigation suggests that surface modification of TiO₂ and incorporation of suitable accessory ligands to dye molecule are promising strategies to enhance the efficiencies of dye-sensitized solar cells. Although conclusive evidence is not available to single out one mechanism, increase in efficiency and the behavior of photocurrent transients suggests that Cu doping suppresses recombination.
5.1 Introduction

Dye-sensitized solar cells (DSSCs) based on nanoporous films of metal oxides have gained much attention as alternative approach to the silicon solar cells because of their prospect for the low cost photovoltaic energy conversion. In this contest, the promising solar energy into electrical energy conversion efficiencies of more than 10% have been achieved for DSSCs based on TiO$_2$ [34]. However the efficiency of DSSCs constructed with other candidates of metal oxides such as ZnO, Nb$_2$O$_5$, SnO$_2$ etc., lies much more behind [35]. Even though, an impressive enhancement of the efficiencies comparable to TiO$_2$ have been noted in cells made from composite films of ZnO / SnO$_2$ and SnO$_2$ films coated with an ultra thin layers of MgO and other insulating oxides [35–36]. The mechanisms involved here are not fully understood.

SnO$_2$ is an attractive semiconductor material for DSSCs as well as for other optoelectronic devices because of its high photo–stability and good carrier mobility. SnO$_2$ is a high band gap semiconductor utilized as that of TiO$_2$ and ZnO. But the conduction band edge of SnO$_2$ locates at a lower level in the energy scale [37]. Due to this reason, one would expect a low value of the open–circuit photovoltage for DSSCs constructed with SnO$_2$. 
There are many articles in literature reporting observations of photo responses in visible region by deposition of nano-particles of gold or silver on to TiO$_2$ [38-40]. The optical absorption in visible region of the above mentioned metals embedded to TiO$_2$ films is ascribed to the surface plasmon resonance of the metal particles [38]. In some of the reports TiO$_2$ films deposited with these metals have been used to construct DSSCs. Enhancement in photocurrent of DSSCs constructed with metal/TiO$_2$ electrodes can be explained based on different mechanism. Few of them are, the band edge fluctuations induced by the surface metal particles, formation of the schottky barrier at the TiO$_2$/metal interface and the plasmon resonance effect induced by optical absorption of nano-particles of metals [39-40]. Some investigators have observed higher efficiencies in DSSCs by depositing gold nano-particles on the surface of TiO$_2$ films prior to the deposition of the dye. The enhancement of efficiencies of these cells can be explained as given below. The ability of gold nano-particles to act as an electric relay that accept electrons and quickly shuttle upon, raise the Fermi level, conduction band and shallow traps of the semiconductor [41].

In this article we have reported our experimental results of construction of DSSCs with composite film made by embedding gold nano-particles in SnO$_2$. Here the efficiency of the solar cell is enhanced by increment of both the photocurrent and the photovoltage. Our experimental results clearly indicate that the conduction band edge of SnO$_2$ shift up in the energy scale when gold nano-particles are incorporated, which increases the photovoltage of DSSC. Simultaneously, the shallow traps and the Fermi level of the SnO$_2$ are shift up together with the conduction band edge. The existence of these shallow traps of SnO$_2$ far away from the redox level of the electrolyte suppresses recombination via trap
states, so that photocurrent of the cell increases. Surface plasmon resonance of metal particles supports the injection of electrons to the semiconductor and transportation of electrons in the film. This phenomenon will only enhance the photocurrent of the cell. However, there is no any mean to increase the photovoltage of a cell significantly by the above stated plasmon resonance effect. According to our experimental observations, shift in the energy of the conduction band (CB) of SnO₂ is more dominant for the enhancement of the efficiency of a DSSC than the plasmon resonance effect when gold nano-particles are embedded in SnO₂ films.

5.2 Experimental Details

We have prepared gold embedded SnO₂ films which we refer as Au/SnO₂ to fabricate films of DSSCs. The performance of the DSSCs constructed with above films was compared with bare SnO₂ films in this study. In the preparation of the Au/SnO₂ films; 1 ml of SnO₂ colloidal solution (Alfa chemicals, 15 % SnO₂ colloidal in H₂O), few drops of glacial acetic acid and sufficient amount of ethanol were added together in to an agate mortar and mixed well. Known volume of gold chloride hydrate (AuCl₄H) from 3x10⁻⁵ M solution was added to the above mixture. The mixture was dispersed in 30 ml of ethanol and ultrasonically agitated for several minutes. The solution was sprayed onto 0.5x 1.0 cm² conducting fluorine doped tin oxide (FTO) glass plates (sheet resistance 13 Ω/sq) heated to 150 °C and then sintered at 550 °C in a furnace for 30 min. The size of SnO₂ particles in the film was around 100 nm and the thickness was maintained at ~ 10μm. Bare SnO₂ films were prepared by the same method adopted above without the incorporation of AuCl₄H solution. Indoline D-149 dye was coated on surface of the electrode by soaking plates in the dye-
solution (1.5x $10^{-4}$ M in $t$-butyl alcohol + acetonitrile, 1:1 by volume) for 1.5 hrs. Photoelectrochemical cells (PECs) were fabricated by clamping a Pt sputtered FTO glass plate onto the dyed surface and filling the capillary space with the electrolyte (0.5 M tetrapropyl ammonium iodide + 0.05 M iodine in 1:4 by volume mixture of acetonitrile + ethylene carbonate). I-V characteristics of the cells were recorded using a Keithley 2420-3A source meter and a 1.5 AM, 1000 Wm$^{-2}$ solar simulator lamp. Photocurrent action spectra were recorded with a monochromator (Nikon Monochromator Autoscan). An Eko pyranometer (MS 80) measured the light intensities. Absorption spectra of the dye solution were recorded with a Shimadzu UV-1600 Spectrophotometer. The flat band potential of SnO$_2$ and Au/SnO$_2$ electrodes were measured by Mott-Schottky measurements. 0.5 M Na$_2$SO$_4$ solution was used as the electrolyte and voltage is measured with respect to a standard calomel electrode (SCE).
5.3 Results and Discussion

Figure 5.1 shows the absorption spectra of (a) Indoline D-149 dye, and (b) the Au/SnO$_2$ composite film. The surface plasma resonance of gold nano-particles due to optical absorption occurs at around 540 nm in visible region. Since the optical absorption of Indoline D-149 dye also peaked at around 530 nm, the light absorbed by the dye partially masks the surface plasma resonance of gold particles on SnO$_2$.

![Absorption spectra of (a) Indoline D-149 dye and (b) Au/SnO$_2$ film.](image)

Significant difference could not be observed in the action spectra of dye coated bare SnO$_2$ electrode and the gold embedded SnO$_2$ electrode, other than the higher photocurrent of the Au/SnO$_2$ electrode (Figure 5.2). Chelations of indoline D-149 dye on the surface of
SnO₂ red shift the action spectra of the cell to 600 nm. Since the action spectrum of Au/SnO₂ composite film also red shift by the same amount to 600 nm, the dye is most probably adsorb on the surface of SnO₂ rather than on Au particles of the Au/SnO₂ composite film. SEM pictures were unable to sight these gold nano-particles embedded in SnO₂ film because of their very low concentration as well as small in size (few nanometers). The average particle size of SnO₂ is around 100 nm and gold particles are around 10 nm. The photo excitation of the dye as well as the plasmon resonance effect of gold nano-particles could contribute to the photocurrent of the cell at different extents, which is difficult to quantify with the action spectrum.

Figure 5.2 Action spectra of dye-sensitized electrochemical solar cells made of (a) SnO₂ and (b) Au/SnO₂ composite films.
IV characteristics of indoline D-149 dye sensitized cells with Au doped and undoped SnO$_2$ are shown in Figure 5.3 and Table 5.1 which gives I–V parameters ($I_{sc}$ = short–circuit photocurrent, $V_{oc}$ = open–circuit voltage, $\eta$ = efficiency, FF = fill factor) of the cells. Introduction of gold to the composite film gradually increases both the photocurrent and the photovoltage of the cell and reaches their maximum when the gold content of the Au/SnO$_2$ film is 1.4x10$^{-3}$ % by weight. At that optimum point, the efficiency of the Au doped cell reaches 3.9 % compared to 2.4 % for an equivalent cell of an undoped SnO$_2$ film. And also the doping has enhanced other I–V parameters as well (Table 5.1). Further increment of gold in the composite film decreases the photocurrent of the cells.

![Figure 5.3](image_url)

**Figure 5.3** I–V characteristic curves of dye-sensitized electrochemical solar cells made of Au/SnO$_2$ composite films of (a) 0 % (b) 0.9x10$^{-3}$ (c) 1.4x10$^{-3}$ (d) 1.9x10$^{-3}$ (e) 2.4x10$^{-3}$ of gold by weight, respectively.
keeping the photovoltage at the maximum voltage around 600 mV. Increment of the photovoltage due to incorporation of Au to TiO$_2$ is marginal because of TiO$_2$ alone produces a higher photovoltage with indoline D–149 dye. However, the photocurrent of TiO$_2$ cells increases considerably with the incorporation of Au nano–particles. This is one of the reasons for selecting SnO$_2$ as the semiconductor material of our study to fabricate the Au/SnO$_2$ composite films. The experimental results reveal that the incorporation of Au particles to SnO$_2$ increases both the photovoltage and the photocurrent. The significant improvement of the photovoltage of a cell merely by surface plasma resonance of gold particle is difficult to elucidate. This can only be described by the rise of the conduction band edge during the formation of schottky barrier at the metal semiconductor interface.

<table>
<thead>
<tr>
<th>Cell configuration</th>
<th>Au by weight (% x 10$^{-3}$)</th>
<th>$I_{sc}$(mA/cm$^2$)</th>
<th>$V_{oc}$(mV)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.0</td>
<td>9.2</td>
<td>524.4</td>
<td>48.6</td>
<td>2.4</td>
</tr>
<tr>
<td>b</td>
<td>0.9</td>
<td>9.7</td>
<td>598.0</td>
<td>57.9</td>
<td>3.4</td>
</tr>
<tr>
<td>c</td>
<td>1.4</td>
<td>10.1</td>
<td>604.7</td>
<td>63.0</td>
<td>3.9</td>
</tr>
<tr>
<td>d</td>
<td>1.9</td>
<td>6.3</td>
<td>600.9</td>
<td>66.4</td>
<td>2.5</td>
</tr>
<tr>
<td>e</td>
<td>2.4</td>
<td>2.9</td>
<td>594.9</td>
<td>70.4</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table 5.1  I–V parameters ( $I_{sc}$= short–circuit photocurrent, $V_{oc}$ = open-circuit voltage , $\eta$ = efficiency , FF = fill-factor ) of different systems sensitized with indoline D–149. (a) un–doped SnO$_2$ and doped SnO$_2$ of (b) 0.9x10$^{-3}$ (c) 1.4x10$^{-3}$ (d) 1.9x10$^{-3}$ (e) 2.4x10$^{-3}$ of gold by weight, respectively.
When two materials having different work functions are in contact, free carriers in the material with a lower work function material transfer to the high work function material, and consequently Fermi levels of both materials coincide. When an n-type semiconductor is in contact with a higher work function metal, electrons in the CB of the semiconductor are transferred to the metal. The density of free carriers in the semiconductors are usually low, and hence, free carriers lying in the semiconductor from the surface to the deep bulk must be transferred to the metal in order to line up the Fermi level [42]. As a consequence, bands of semiconductor bend at the interface forming a depletion layer, which could extend even to a maximum depth of one micrometer (Figure 5.4b). But the situation is rather different at a metal semiconductor interface when the particles are in nano-range. Build up of a depletion layer in the interface is questionable because of the small size of the semiconductor and the metal particles [43]. However, still their energies have to be equalized when they are in contact. Therefore electrons in the material with higher Fermi level have to transfer to material with lower Fermi level even these particles are in nano-scale. The Fermi level of SnO₂ is high compared to the gold (Figure 5.4a). Therefore, electrons in the CB of SnO₂ transfer to gold to gain an equilibrium energy state. Since the particles are in nano-range the potential of the conduction band edge of SnO₂ rises up together with the shallow traps [44] and the upper most electrons occupied energy level of the conduction band called quasi-Fermi level (QFL) of the Au/SnO₂ composite (Figure 5.4c). As a consequence the photovoltage of the cell increases because the conduction band edge of SnO₂ is now at a higher level. And also, the shift of the flat band potential which decides the conduction band position of semiconductor nano-particles have been observed due to strong absorption of negative counter ions on the surface of a semiconductor by electron accepting
surface modifier molecules [44-47]. Since the gold nano–particles are good electron acceptors, one can interpret this result even as a surface modification process to describe the shift of the CB when gold particles are in contact with SnO2.

![Figure 5.4](image)

Figure 5.4 Band diagram of (a) SnO2 and Schottky junction of (b) SnO2 and gold (c) SnO2 and gold nano–particle contact.

The shift of the conduction band edge due to the addition of gold to the Au/SnO2 composite is calculated with Mott–Schottky measurements. Figure 5.5 shows the mott–schottky plots of bare SnO2 film and Au/SnO2 film deposited on FTO glass. It clearly indicates that the potential of conduction band edge of the Au/SnO2 film shifts up by ~ 0.34 eV.
Figure 5.5 Mott–Schottky plots of (a) Au/SnO₂ composite and (b) SnO₂ films, respectively.

When electrons are injected to the Au/SnO₂ film by excitation of the dye molecules they travel across SnO₂ and Au nano–particles in the composite film. The band structure of the Au/SnO₂ film is depicted schematically in Figure 5.6. Here electrons suppose to transport ballistically across the gold nano–particles in between two SnO₂ particles when the particle size of gold is comparatively small [48]. But when the gold particles grew bigger, the structure become more alike a multiple quantum well where electrons possibly fall or trapped in the quantum wells. This is attributed to the retardation of photocurrent of the cells when the gold content in the film is increased. But this will not effect on the photovoltage which is decided by the conduction band position of the Au/SnO₂ composite
relative to the energy position of the redox–couple \( (I_1/I_3) \), so that the photovoltage of the cell remains further at the maximum value.

Figure 5.6  Schematic band diagrams of Au/SnO$_2$ composite to illustrate the electron transportation through the film.

5.4 Conclusions
The present study shows that DSSCs made of composite films of metals and semiconductors of nanometer size particles enhance the charge separation and transportation when the work function of the metal is greater than that of the semiconductor. In this study we have taken gold as the metal and SnO$_2$ as the semiconductor considering potentials of those materials. According to our investigation it is clearly seen that the conduction band edge of the semiconductor move to a higher potential when the Fermi level of the contact metal particle lies below the Fermi level of the
semiconductor though the band bending at the semiconductor metal interface would not appear in particles of nano-range. Since SnO$_2$ has high density of shallow traps near the conduction band edge, their potential also moves up to a higher energy with the shift of the conduction band edge. This will result to suppress the recombination of germinated electrons with acceptors in electrolyte which increases the photocurrent. The shift of the conduction band edge to a higher level attributes to higher photovoltage and photocurrent of the cell. I–V characteristics and Mott–Schottky measurements provided sufficient evidences to support this idea. Previously we have shown that composite films made combining different types of semiconductors and semiconductors with insulators improve the performance of DSSCs. With this issue it will open up the field to construct films of DSSC with composites of semiconductors and metals to enhance the performance of DSSC that operate in a different way.
CHAPTER 6

SUPPRESSION OF RECOMBINATION CHANNELS OF DYE–SENSITIZED PHOTO–ELECTROCHEMICAL SOLAR CELLS MADE FROM SnO₂ FILMS BY INCORPORATION OF ZrO₂

6.1 Introduction

At present, the field of dye–sensitized (DS) solar devices based on nano–crystalline films of high band gap semiconductors [49–50] is an attractive field of research that is being carried out by scientists all over the world. The reason for this is that photovoltaic conversion of solar energy at low cost appears to be one of the most promising avenues to meet the increasing energy demands of the future, when conventional sources of energy are being rapidly depleted. Of the many semiconductor materials utilized for conversion of solar energy, SnO₂ is a high band gap semiconductor that has been freed for this purpose. However, its performance is inferior when compared to other semiconductor materials such as TiO₂ working under similar circumstances (similar film thickness and morphology, same level of loading, same electrolyte etc.). Previous reports have indicated that the high recombination of injected electrons in a DS device through the shallow trap levels of SnO₂ [51–52] is the prime factor for their inferior behaviour.

The efficiency of solar cells could be enhanced by controlling recombination in such devices which could undergo through four distinct channels, i.e. (1) germinate electron, e⁻ recombination with the dye cations D⁺; (2) non-germinate electron, e⁻ recombination with the dye cations D⁺; (3) recombination of injected electron, e⁻ with an acceptor in the electrolyte at
the semiconductor/electrolyte interface; and (4) recombination of injected electron, $e^-$ with an acceptor in the electrolyte at the exposed conducting glass/electrolyte interface. Of these four channels, channel (1) can be neglected because of the rapidity of electron injection [53–54] and slowness of the back reaction [55–57]. Since quickness of hole transportation to the electrolyte, the recombination through channel (2) could also be ignored. As the conducting fluorine doped tin oxide (FTO) glass surface is about nearly three hundred orders of magnitude smaller than that of the rough nano-crystalline $\text{SnO}_2$ surface, voids in this conducting film accounts only for a small fraction, and the rate of channel (4) similarly could be negligible. Therefore, channel (3) becomes the most significant process in the recombination mode.

Electrons injected to a semiconductor from the excited dye molecule could transport directly via conduction band or traps in shallow levels. The electrons in traps diffuse towards the counter electrode by hoping from trap to trap. Because of the high existence of trap levels in $\text{SnO}_2$, it is obvious that recombination of injected electrons through mode (3) in trap-to-trap hoping is the major reason for the inferior performance in $\text{SnO}_2$ films. The delay time $\tau_D$ of electrons to the back contact can be expressed as $\tau_D = \frac{d^2}{4D_n}$, where $D_n$ and $d$ are respectively, the diffusion coefficient, and the thickness of the film. As the diffusion coefficients of electrons associated with trap-to-trap hopping are smaller than those corresponding to transport in the conduction band, the recombination of electrons with acceptors in the electrolyte is favorable in trap-to-trap hopping since such electrons takes a longer time to reach the back contact.
In dye-sensitized electrochemical solar cells (DSECSCs), open-circuit photovoltage is theoretically determined by means of the difference between the energy positions of the redox-couple (I\(^{-}/I_3^+\)) and the conduction band edge of n-type semiconductor material. Since the trap-to-trap transport is favorable in DS solar devices based on nano-crystalline films of SnO\(_2\), open-circuit photovoltage is decided by the difference between the energy positions of the redox-couple (I\(^{-}/I_3^+\)) and the trap levels of SnO\(_2\), which is situated below the conduction band edge of SnO\(_2\). And therefore the value of open-circuit photovoltage is below that of the theoretical upper limit. Besides, recombination via traps reduces short-circuit photocurrent. However, there are many articles in literature that have reported higher efficiencies of DSECSCs of which SnO\(_2\) crystallites in the film are coated with an ultra-thin outer shell of insulators such as MgO, Al\(_2\)O\(_3\) (we denote such films by the symbol [X]Y, where X and Y are core and shell materials, respectively) [58–59]. And also, it has been reported that the enhancement of photocurrent is only possible by the formation of an ultra-thin outer shell of insulators around the crystallites of high band gap semiconductor in composite semiconductor insulator films (capped type heterostructures).

ZrO\(_2\) is an insulating material with its energy gap in between 5–7 eV. It has the monoclinic crystal structure at room temperature and converts in to the cubic or the tetragonal structure at higher temperature. The pressure which is exerted with the accumulation of tetragonal forms at higher temperatures could cause again to convert the tetragonal form into monoclinic form with the retardation of further growth accompanied by volume expansion. This would enhance the fracture toughness of the material and significantly extends the reliability and lifetime of the device made by this stabilized ZrO\(_2\).
This chapter describes the improvement of both the photovoltage and photocurrent of DSECS cells constructed by SnO$_2$ crystallites coated with an ultra-thin outer shell of insulator ZrO$_2$ abbreviated by [SnO$_2$]ZrO$_2$ compared to bare SnO$_2$ films based on the experimental results.

### 6.2 Experimental Details

The performance of the DSECS cells constructed by [SnO$_2$]ZrO$_2$ films was compared with that made by bare SnO$_2$ films in this study. In the preparation of the [SnO$_2$]ZrO$_2$ films, 1 ml of SnO$_2$ colloidal solution (Alfa chemicals, 15 \% SnO$_2$ colloidal in H$_2$O), few drops of glacial acetic acid and sufficient amount of ethanol were added together in to an agate mortar and mixed well. Known weight of zirconyl chloride (ZrOCl$_2$) dissolved thoroughly in glacial acetic acid was added to the above mixture. The mixture was dispersed in 30 ml of ethanol and ultrasonically agitated for several minutes. The solution was sprayed onto 0.5x1.0 cm$^2$ conducting fluorine doped tin oxide (FTO) glass plates (sheet resistance 13 $\Omega$/sq) heated to 150 $^\circ$C and then sintered at 550 $^\circ$C ($\text{ZrOCl}_2$ decompose in to ZrO$_2$ at 400 $^\circ$C) in a furnace for 30 minutes. The size of SnO$_2$ particles in the film was around 100 nm and the thickness was maintained at $\approx$ 10$\mu$m. The film area was determined by adsorption of monolayer of dye on mesoporous film. Bare SnO$_2$ films were prepared by the same method adopted above without incorporation of ZrOCl$_2$. Indoline D-149 dye was coated on surface of the electrode by soaking plates in the dye solution (1.5x10$^{-4}$ M in $t$-butyl alcohol+acetonitrile, 1:1 by volume) for 1.5 hours. Photo-electrochemical cells (PECs) were fabricated by clamping a Pt sputtered FTO glass plate onto the dyed surface and filling the capillary space with the electrolyte (0.5 M tetrapropyl ammonium iodide + 0.05 M iodine
in 1:4 by volume mixture of acetonitrile + ethylene carbonate). I–V characteristics of the
cells were recorded using a Keithley 2420-3A source meter and a 1.5 AM, 1000 Wm$^{-2}$ solar
simulator lamp. Photocurrent action spectra were recorded with a monochromator (Nikon
Monochromator Autoscanner). An Eko pyranometer (MS 80) measured the light intensities.
Absorption spectra of the dye solution were recorded with a Shimadzu UV-1600
Spectrophotometer. SpectroFluorophotometer (Shimadzu RF-5000) was utilized to obtain
emission spectra of the relevant sample. The flat band potential of SnO$_2$ and [SnO$_2$]ZrO$_2$
electrodes were measured by Mott–Schottky measurements. 0.5 M Na$_2$SO$_4$ solution was
used as the electrolyte and voltage is measured with respect to a standard calomel electrode
(SCE).

6.3 Results and Discussion

When SnO$_2$ and ZrO$_2$ particles are in nano scales, SnO$_2$ crystallites in the film are assumed
to be coated with an ultra–thin over–layer of insulating material ZrO$_2$ which acts as a
barrier against recombination of photo generated electrons.

The thickness $T$ of the shell material ZrO$_2$ in [SnO$_2$]ZrO$_2$, with SnO$_2$ as the core
material is estimated using the formula,

$$T = \frac{r}{3} \frac{W_{ZrO_2}}{W_{SnO_2}} \frac{\rho_{SnO_2}}{\rho_{ZrO_2}}$$  \hspace{1cm} (6.1)

Where, $r$ is the median radius of SnO$_2$. $W_{ZrO_2}$ and $W_{SnO_2}$ are weights and $\rho_{ZrO_2}$ and
$\rho_{SnO_2}$ are densities of ZrO$_2$ and SnO$_2$, respectively.
The DSECSCs constructed utilizing composite [SnO₂]ZrO₂ films produce high efficiency which is accompanied by the development of both photocurrent as well as photovoltage compared to bare SnO₂ films. Figure 6.1 has shown the IV characteristics of indoline D-149 sensitized solar cells made of (a) composite [SnO₂]ZrO₂ and (b) bare SnO₂ electrodes. Introduction of ZrO₂ to the composite film gradually increases both the photocurrent and the photovoltage of the cell and reaches their maximum when the contents of ZrO₂ in the [SnO₂]ZrO₂ film is 0.9 % by weight. At that optimum point, the efficiency of the ZrO₂ doped cell reaches 3.8 % compared to 2.2 % for an equivalent cell with bare SnO₂ film.

Figure 6.1 I-V characteristic curves of dye-sensitized electrochemical solar cells made of (a) [SnO₂]ZrO₂ composite (ZrO₂, 0.9 % by weight) and (b) bare SnO₂ films, respectively.
And also the capping has enhanced fill factor as well. Table 6.1 illustrate the improvement of all IV parameters abbreviated by $I_{sc} =$ short-circuit photocurrent, $V_{oc} =$ open-circuit voltage, $\eta =$ efficiency, FF = fill factor of the cells with the introduction of ZrO$_2$ in [SnO$_2$] ZrO$_2$ film. Further increment of ZrO$_2$ in the composite film decreases the photocurrent where as increases the photovoltage slightly of the cell. Indoline D–149 dye is well adsorbed on films made only with ZrO$_2$. This is confirmed by showing the photocurrent (even very small) and the photovoltage of the DSECSCs made of ZrO$_2$ films only (Table 6.1).

<table>
<thead>
<tr>
<th>Cell configuration</th>
<th>ZrO$_2$ by weight (%)</th>
<th>$I_{sc}(mA/cm^2)$</th>
<th>$V_{oc}(mV)$</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.0</td>
<td>9.3</td>
<td>524.4</td>
<td>49.5</td>
<td>2.22</td>
</tr>
<tr>
<td>b</td>
<td>0.7</td>
<td>9.9</td>
<td>558.3</td>
<td>61.8</td>
<td>3.53</td>
</tr>
<tr>
<td>c</td>
<td>0.9</td>
<td><strong>10.5</strong></td>
<td><strong>562.7</strong></td>
<td><strong>63.8</strong></td>
<td><strong>3.77</strong></td>
</tr>
<tr>
<td>d</td>
<td>1.1</td>
<td>10.3</td>
<td>566.7</td>
<td>62.8</td>
<td>3.65</td>
</tr>
<tr>
<td>e</td>
<td>2.2</td>
<td>8.8</td>
<td>576.0</td>
<td>64.6</td>
<td>3.27</td>
</tr>
<tr>
<td>f</td>
<td>4.2</td>
<td>7.4</td>
<td>588.9</td>
<td>67.2</td>
<td>2.95</td>
</tr>
<tr>
<td>g</td>
<td>6.2</td>
<td>6.5</td>
<td>595.2</td>
<td>67.3</td>
<td>2.60</td>
</tr>
<tr>
<td>h</td>
<td>8.2</td>
<td>5.6</td>
<td>595.2</td>
<td>66.9</td>
<td>2.22</td>
</tr>
<tr>
<td>i</td>
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<td>0.1</td>
<td>390.6</td>
<td>31.1</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 6.1 I–V parameters ($I_{sc} =$ short-circuit photocurrent, $V_{oc} =$ open-circuit voltage, $\eta =$ efficiency, FF = fill-factor) of different systems sensitized with indoline D–149. (a) bare SnO$_2$ and capped SnO$_2$ of (b) 0.7 (c) 0.9 (d) 1.1 (e) 2.2 (f) 4.2 (g) 6.2 (h) 8.2 of ZrO$_2$ by weight and (i) bare ZrO$_2$ films, respectively.
When SnO$_2$ and ZrO$_2$ particles are in nano scales, the formation of ultra-thin over-layer of ZrO$_2$ around SnO$_2$ crystallites could be expected and the dye is almost entirely adsorbed onto the ZrO$_2$ surface. Further, the introduction of ZrO$_2$ to the composite film increases the thickness of this shell which acts as a quantum barrier to suppress recombination of photo-generated electrons. High energetic electrons (hot electrons) generated by the excitation of the indoline D-149, inject through this barrier and relax to the CB or shallow traps of the SnO$_2$ particles (Figure 6.2). These electrons are not allowed to penetrate through the barrier again because of the diminishing of their energy. Thus it suppresses

![Diagram](attachment:figure6_2.png)

**Figure 6.2**  Schematic band diagrams of [SnO$_2$]ZrO$_2$ composite to illustrate the electron transportation through the thin barrier film of ZrO$_2$ towards the FTO back contact with the rising up of QFL (For thin ZrO$_2$ layer).
recombination of these electrons with acceptors in the electrolyte at the semiconductor/electrolyte interface or with the dye cations $D^+$ again. However, further injection of these hot electrons fills the shallow traps as well as CB of SnO$_2$ particles. Under these circumstances, upper most electrons occupied energy level of the CB called quasi—fermi level (QFL) which in turn, determines the value of $V_{OC}$ with respect to the energy position of the redox—couple ($I^+/I^{-}$), gradually increases. When the barrier width is narrow, newly generated hot electrons have enough energy to penetrate through the narrow barrier and transport towards FTO back contact (Figure 6.2). At the optimum point of the cell, the thickness of the ZrO$_2$ shell calculated by equation 6.1 is about 0.2 nm.

The shift of the flat band potential which decides the QFL (under these circumstances) of SnO$_2$ nano—particles due to the addition of ZrO$_2$ in [SnO$_2$]ZrO$_2$ composite film was calculated with Mott-Schottky measurements. Figure 6.3 shows the mott–schottky plots of bare SnO$_2$ film and [SnO$_2$] ZrO$_2$ film deposited on FTO glass. It clearly indicates that the potential of the [SnO$_2$] ZrO$_2$ film shifts up by $\sim 0.48$ eV at the utmost point of the cell. Thus, rising up of QFL increases the photovoltage whereas suppression of recombination increases the photocurrent of the cell.
However, thicker shell of ZrO$_2$ decreases the photocurrent of the cell whereas as increases the photovoltage slightly of the cell (Table 6.1). When the thickness of the shell is high, the width of the barrier increases preventing further penetration of photo-excited electrons through it. However, further rising of QFL due to gathering of injected electrons, increases the photovoltage of the cell. Broad barrier width of ZrO$_2$ confines these electrons to SnO$_2$ particles. In this case, the suggestion is that the electron is transferred to a trap state of ZrO$_2$ shell [60]. The existence of trap states acting as an intermediate in the tunneling of the electron to the next SnO$_2$ particle cannot be ruled out (Figure 6.4 and Figure 6.5a). When the ZrO$_2$ layer is made thicker and thicker the electrons hop from one trap state to another.
Figure 6.4  Schematic band diagrams of [SnO₂]ZrO₂ composite to illustrate the electron transportation through the thick barrier film of ZrO₂ by hopping electrons over the trap states of ZrO₂ towards the FTO back contact with the rising up of QFL (For thick ZrO₂ layer).

The thermal excitation of electrons causes the de-trapping and putting them back to the CB of some other SnO₂ particle [61]. Therefore when the thickness of ZrO₂ layer increases, a drastic drop in photocurrent could be observed.
Figure 6.5  Tunneling of electron from one SnO$_2$ particle to another SnO$_2$ particle through (a) a single trap state of thick ZrO$_2$ layer (b) multiple trap states of very thick ZrO$_2$ layer.

The transportation of photo-excited electrons through the trap states of ZrO$_2$ is reported in many literature articles too [62–64]. DSECSCs constructed utilizing bare ZrO$_2$ film has given photovoltage and low photocurrent (Table 6.1). The transportation of these electrons through CB of ZrO$_2$ can not be expected [64–65]. However, certain photo-generated current was experimentally observed. The hopping of these electrons from one trap state to another trap state of some other ZrO$_2$ particle following a trapping and
de-trapping mechanism, could produce low photocurrent which is agreeable with the experimental results.

Figure 6.6 shows the emission spectra of (a) Mercurochrome in ethanol (10 μM) and (b) ZrO₂ suspended Mercurochrome in ethanol (10 μM) excited at 400 nm. In obtaining the emission spectra to confirm the existence of the trap levels belonging to ZrO₂, mercurochrome was utilized as the dye because it shows the fluorescence effect well. Mercurochrome emitted intense fluorescence peak at 535 nm. When ZrO₂ powder ground well is suspended in the above dye solution, in addition to the emission at 535 nm, new broad peak emitted at 455 nm which is suggested due to the existence of trap states.
belonging to ZrO$_2$. Even by changing the excitation wavelength, the peak positions (535 nm and 455 nm) remained unchanged while its intensity changed.

Figure 6.7  Schematic diagram illustrating band positions of SnO$_2$ and ZrO$_2$, excited and ground levels of indoline and mercurochrome dyes and redox level of electrolyte.
As mentioned earlier, the transportation of photo-excited electrons through the trap states of ZrO$_2$ is reported in many literature articles [62, 64]. The existence of these trap states were further confirmed with the results obtained using emission spectra (Figure 6.6). In concerning the data of emission spectra (Figure 6.6), the path of electrons in trap states of ZrO$_2$ may happen in two different ways. It has possibility to jump into to the VB of ZrO$_2$ or ground state level of mercurochrome, respectively. However, as far as, the calculated energy value of this transition is concerned; the former path (to jump into to the VB of ZrO$_2$) is most feasible. On this based, the position of these trap states were calculated (Figure 6.7). And these positions were well agreeable with the mechanism of electron transportation through the thick barrier film of ZrO$_2$ by hopping electrons over the trap states of ZrO$_2$ towards the FTO back contact (Figure 6.4). In obtaining the emission spectra, the above results were confirmed with the using of indoline D–149 dye too. However, mercurochrome exhibits noticeable observation as compared with indoline D–149 dye.

6.4 Conclusions

The above investigation has shown that the inferior performance of DSECSCs made from SnO$_2$ may be due to the recombination of electrons injected into SnO$_2$ with acceptors in the electrolyte at the semiconductor/electrolyte interface. Suppression of recombination processes through the incorporation of the insulating material ZrO$_2$ improved cell performance significantly. The formation of ZrO$_2$ shell around the SnO$_2$ crystallites in the [SnO$_2$] ZrO$_2$ is thought to enhance both the photovoltage as well as the photocurrent of the cell. SEM images did not support the above argument due to invisibility of ZrO$_2$ nano
particles in the [SnO₂] ZrO₂ film. However, according to the other experimental evidences including shell thickness calculation and also the reported data in many literature articles, the formation of ZrO₂ shell around the SnO₂ crystallites in the [SnO₂] ZrO₂ can not be ruled out.
SUMMARY AND SUGGESTIONS FOR FUTURE WORK

7.1 Summary

Of the many semiconductor materials utilized for conversion of solar energy into electricity in dye-sensitized solar cells, SnO$_2$ is a high band gap semiconductor that has been freed for this purpose. However, its performance is inferior when compared to other semiconductor materials such as TiO$_2$ and ZnO working under similar circumstances (similar film thickness and morphology, same level of loading, same electrolyte etc.). Utilization of composite systems in this type of solar cells improved the efficiency by suppressing the recombination processes. The incorporation of certain stable metals as well as insulating materials into SnO$_2$ was well examined.

Depositing nano particles of gold on to SnO$_2$ shows enhancement of photo responses in visible region. Many articles in literature revealed that this improvement is mainly based on the surface plasmon resonance of the gold particles in which it emphasis the increment of photocurrent only. However, it improves photovoltage as well. Alternatively, the mechanism of operation of these devices can be proposed to explain as stated below. Since the particles are in nano range, to achieve the equalization of Fermi–levels of gold and SnO$_2$ particles, the potential of the conduction band edge of SnO$_2$ rises up together with the shallow traps. This will result to suppress the recombination of germinated electrons with acceptors in electrolyte which increases the photocurrent. The shift of the conduction band edge to a higher level attributes to higher photovoltage and
photocurrent of the cell. I–V characteristics and Mott-Schottky measurements provided sufficient evidences to support this idea.

ZrO$_2$ is an insulating material with its energy gap in between 5-7 eV. Suppression of recombination processes through the incorporation of the insulating material ZrO$_2$ improved cell performance significantly. The formation of ZrO$_2$ shell around the SnO$_2$ crystallites in the [SnO$_2$] ZrO$_2$ is thought to enhance both the photovoltage as well as the photocurrent of the cell. SEM images did not support the above argument due to invisibility of ZrO$_2$ nano particles in the [SnO$_2$] ZrO$_2$ film. However, according to the other experimental evidences including shell thickness calculation and also the reported data in many literature articles, the formation of ZrO$_2$ shell around the SnO$_2$ crystallites in the [SnO$_2$] ZrO$_2$ can not be ruled out. This ZrO$_2$ shell coated around SnO$_2$ prevents the recombination of germinated electrons with acceptors in electrolyte. And gathering of these electrons in SnO$_2$ particles rises up quasi-fermi level (QFL) of the [SnO$_2$] ZrO$_2$ composite. This will attributes to higher photovoltage and photocurrent of the cell. I–V characteristics, Mott-Schottky measurements and other experimental data provided sufficient evidences to support the above argument.

As mentioned above, performance of dye–sensitized solar cells based on SnO$_2$ film is inferior due to existing of shallow trap levels belong to it. On the other hand, the existing of these defects on TiO$_2$ film is minimum and hence, improvement of cell performance based on composite systems become marginal for TiO$_2$ semiconductor. However, the efficiency of indoline D–149 sensitized photoelectrochemical solar cells increases significantly when the nanocrystalline TiO$_2$ is surface doped with Cu to a concentration similar to the dye concentration. Indoline D–149 possesses sulfur in rhodanine rings in addition to
carboxylate ligand. Therefore, sulfur in rhodanine rings of indoline D-149 too could coordinate with copper in TiO$_2$ in addition to the anchoring of this dye to TiO$_2$ surface via the carboxylate ligand. And hence it suppresses the aggregation of the dye molecules. The exact mode of coordination of the dye to copper sites in the TiO$_2$ surface is not clear. As the surface concentration of Cu on TiO$_2$ is very low, the resolution of the FTIR measurements is not sufficient to obtain any clues to support the mode of coordination of indoline D-149 dye to the copper doped TiO$_2$ surface. However, other experimental data such as photocurrent action spectrum, dark I–V measurement, photovoltage transient, I–V characteristic and relevant calculation made throughout, support the above argument. The firm bonding of the indoline D-149 molecule to the TiO$_2$ surface at two points (i.e., carboxylate link to TiO$_2$ and coordination of sulfur in the rhodanine rings to Cu atoms) covers TiO$_2$ surface without leaving any voids. Therefore, suppression of recombination through these voids may increase both photovoltage as well as photocurrent.

7.2 Suggestions for Future Work

Previously we have shown that composite films made combining different types of semiconductors and semiconductors with insulators improve the performance of DSSCs. However, in our experiments, DSSCs made of Au/SnO$_2$ films showed better performance of the devices. With this issue it will open up the field to construct films of DSSC with composites of semiconductors and metals to enhance the performance of DSSC that operate in a different way.
The prescription adopted to prepare TiO₂ films with Cu in the investigation is not optimized standard procedure. However, the efficiency increased from 5.8 to 8.1% on doping the TiO₂ film with Cu. We believe that the efficiency can be further improved by optimization of the TiO₂ film casting procedure.
REFERENCES


APPENDIX 1

LIST OF PUBLICATIONS AND COMMUNICATIONS FROM THESIS

Publications


Abstracts