

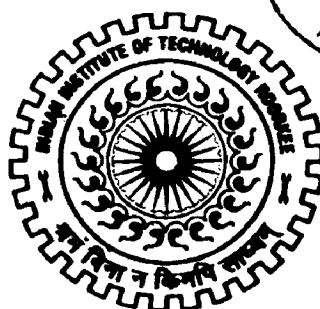
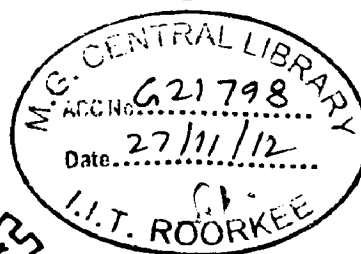
APPLICATION OF GRAPHENE OXIDE AND TiO_2 IN THE FABRICATION OF SOLAR CELL MODULE BY ELECTRODE MODIFICATION

A DISSERTATION

*Submitted in partial fulfillment of the
requirements for the award of the degree*
of
MASTER OF TECHNOLOGY
in
NANOTECHNOLOGY

By

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CANDIDATE'S DECLARATION

I hereby certify that the work being presented in dissertation entitled '**Application of Graphene Oxide and TiO₂ in the fabrication of Solar Cell module by electrodes modification**' submitted in partial fulfillment of the requirement for the award of degree of **Master of Technology in Nanotechnology**, submitted in the **Centre of Nanotechnology, Indian Institute of Technology Roorkee**, is an authentic record of my own work carried out in Centre of Nanotechnology, Indian Institute of Technology Roorkee for a period from June 2011 to June 2012 under the supervision of **Dr. B.S.S. Daniel**, Associate Professor, Department of Metallurgical and Materials Engineering and **Dr. Sanjeev Manhas**, Assistant Professor, Department of Electronics and Computer Engineering, Indian Institute of Technology Roorkee, Roorkee.



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This is to certify that the above declaration made by the candidate is correct to the best of my knowledge and belief.



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Date: 12 June 2012

Place: Roorkee



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ABSTRACT

The use of graphene oxide nanosheets as a counter-electrode material substituting platinum in dye-sensitized solar cells (DSSC) shows the cheap way of fabricating DSSC and also shows highly increase in conversion efficiency. Graphene oxide nanoparticles were synthesized by Hummer's method and were applied on conducting glass slides by drop casting method. The DSSC Active electrode composed of graphene oxide-P25 and for comparison cell using P25 only as an active electrode also fabricated.

The incorporation of graphene oxide in active electrode was increased the conversion efficiency of DSSC significantly. The DSSC was fabricated, consists of graphene-TiO₂ as an active electrode and compared to cell only consist of TiO₂ as an active electrode, while using carbon as a counter electrode. The doctor blade method was used to fabricate the active electrodes, where TiO₂ nanoparticles were synthesized by sol-gel method. Then whole DSSC was fabricated with electrolyte solution containing 0.5M Potassium iodide mixed with 0.05M iodine in water free ethylene glycol and organic dye, and then they were tested for their characterization (XRD, FT-IR, SEM and UV Absorbance) and performance (I-V characterization).

Contents

Candidate's Declaration	2
Acknowledgement	3
Abstract	4
Contents	5
List of Figures	7
1 Introduction	9
1.1 Literature review	15
1.2 Aim	22
2 Materials and equipments	25
3 Procedural details	28
3.1 Preparation of graphene oxide	28
3.2 TiO ₂ Formation	29
3.3 Prepare active electrode of DSSC	29
3.4 Stain the GO/Titanium Dioxide with the Dye	30
3.5 Prepare the Carbon-Coated Counter Electrode	31
3.6 Prepare the graphene oxide Counter Electrode	31
3.7 Assemble Device and Determine Output Characteristics	31
3.8 Characterization	32
3.9 Measurement for photoelectrochemical performance	33
4 Results and Discussions	34
4.1 Characterization of TiO ₂ nanoparticles	34
4.2 Characterization of graphene oxide nanoparticles	35
4.3 UV- vis Absorbance study	38
4.4 Properties of Graphene oxide -Modified TiO ₂ Films	41

4.5 FTIR Analysis of graphene oxide	42
4.6 Counter electrode	44
4.7 Photocurrent-Voltage (I-V) Characteristics of Different Electrodes	46
5 Conclusion and Future work	51
6 Bibliography	53
7 Conference proceedings	56

List of Figures

1.1	A photochemical cell is a device in which a photo-driven reaction induces electrons to travel from one substance to another.	10
1.2	Typical Silicon Solar cell.	11
1.3	A layer of dye (shown as black dots) adsorbing to the TiO ₂ nanocrystals.	12
1.4	Energy Diagram for the dye sensitized solar cell.	14
1.5	Graphene Oxide Structure and TEM image [17].	18
1.6	Picture of single layer graphene oxide.	22
1.7	Schematic diagram of GO incorporated in both Active electrode and Counter electrode of Dye Sensitized Solar Cell.	23
3.1	Deposition and distribution of the TiO ₂ solution on the conductive glass. A rapid horizontal motion of the glass rod will coat the masked glass plate with a uniform layer of TiO ₂ nanoparticles.	30
3.2	Assembled solar cell or detector showing offset glass plates, clips, and electrical contact points. The stained TiO ₂ layer is in contact with the carbon-coated conductive layer. Light enters the sandwich through the TiO ₂ -coated glass plate, which is the anode of the electrochemical device.	32
3.3	Photographs of instruments at Photovoltaic laboratory, Centre of Energy Studies, IIT Delhi.	33
4.1	XRD pattern of TiO ₂ nanoparticles.	34
4.2	Photograph showing synthesized TiO ₂ by sol gel method.	35
4.3	Photographs of graphene oxide and natural graphite powder.	35
4.4	a) XRD pattern of natural graphite and b) XRD pattern of GO.	36
4.5	a) Photograph of GO dispersed in D/W and b) SEM image of Bulk graphene	

oxide.	37
4.6 FE-SEM image of GO.	38
4.7 UV-vis Absorbance of natural graphite and graphene oxide.	38
4.8 a) UV Absorbance of GO/ TiO ₂ composite at various concentration of GO and b) Enlarge portion of UV Absorbance of GO/TiO ₂ composite at various concentration of GO.	39
4.9 a) Photographs of graphene oxide/ TiO ₂ thin films and b) SEM images of graphene oxide/ TiO ₂ .	41
4.10 FT-IR spectrum of graphene oxide.	42
4.11 Photograph showing conducting glasses with active layer dipped into organic dye.	43
4.12 Photographs of fabricated carbon and graphene oxide counter electrodes for Dye Sensitized Solar Cell.	44
4.13 Mechanism of in-situ photoelectrochemical reduction of GO in a DSSC assembly.	44
4.14 a) Photograph of Dye sensitized solar cell fabricated in lab and b) Photograph of solar cell testing in sunlight.	46
4.15 a) Photocurrent J–V characteristics of DSSCs with TiO ₂ and b) TiO ₂ -Graphene oxide electrodes with carbon as counter electrode.	47
4.16 a) Photocurrent J–V characteristics of DSSCs with P25 electrode and b) P25-Graphene oxide electrodes with graphene oxide as counter electrode.	49
5.1 Operational principle of the device: the introduced 2D graphene oxide bridges perform as an electron acceptor and transfer the electrons quickly. Hence, the recombination and back reaction are suppressed.	52

Chapter 1

Introduction

The story of the nanocrystalline solar cell starts in the late 19th century within the principles of photography [2-5]. It was discovered that certain colored organic dye molecules allowed silver chloride based photographic film to respond to a wider range of visible wavelengths than it otherwise could. Modern photography is based on sensitized silver halides using dyes. The mechanism for this sensitization in modern photography involves the electron transfer from the organic molecules to the semiconducting silver halides particles in the photographic film a process known as electron injection.

The first photovoltaic cell, measured by Becquerel in 1839, used copper oxide or silver halide coated metal electrodes immersed in an electrolyte solution. To observe this photoelectrochemical effects, one can place two copper sheets vertically in a glass and half immerse them in copper sulfate solution. Like the acid in car battery, this liquid solution is called an electrolyte. After few days, an oxide will form on the copper, and the illumination of one plate in this solution will produce a small voltage that can be measured by using a sensitive volt meter connected to each plate via alligator clips.

Modern solar cells, other hand, are not wet photoelectrocheimal cells such as those described above. They were first developed over forty years ago by Bell Labs and are essential for us today since they power satellites and provide reliable electricity in remote locations. In the most common solar cells (formed from thin silicon wafers),

electrons and holes are created by the absorption of light with in silicon (the semiconductor).

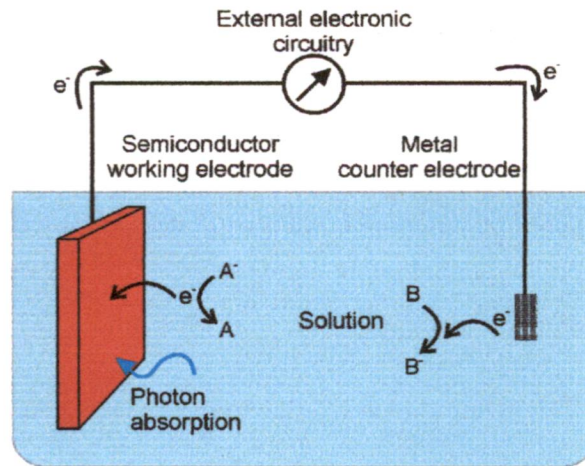


Figure 1.1: A photochemical cell is a device in which a photo-driven reaction induces electrons to travel from one substance to another.

Mobile electrons and holes transport the electrical current through the semiconductor and are thus responsible for the semiconductors conductivity (Figure 1.2). New technologies, which use thin films of semiconductor materials such as amorphous silicon and polycrystalline silicon, are under development and are finding applications in world markets as remote residential and third world village power sources, and in consumer's applications such as watches and calculators [1, 9]. Although over 100 million watts of conventional solar cells are currently produced each year for the application, on solar cell technology has produced an efficient, reliable, and cost-effective solar module that can be widely used to replace fossil fuel energy sources.

In contrast to conventional solar cell, the nanocrystalline dye sensitized solar cell is a photoelectrochemical cell. It resembles natural photosynthesis in two respects: 1) it uses an organic dye like chlorophyll to absorb light and produce a flow of electrons, and 2) it uses multiples layers to enhance both the light absorption and electron collection efficiency [2-5, 8-10]. Like Photosynthesis, it is a molecular machine that is one of the first devices to go beyond microelectronics technology into the realm of what is known as nanotechnology.

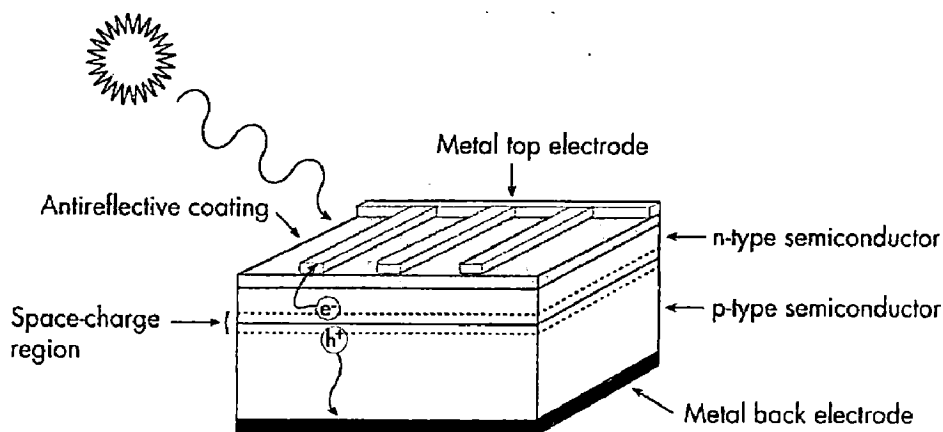


Figure 1.2: Typical Silicon Solar cell.

To create the Nanocrystalline solar cell, a suspension of nanometer size particles of titanium dioxide, TiO_2 , is distributed uniformly on glass, SiO_2 , slides which has previously been coated with thin conductive and transparent layer of tin dioxide, SnO_2 . The TiO_2 film is dried and then heated on the glass to form a porous, high surface area TiO_2 film. When magnified, it looks like a thin sponge or membrane.

The TiO_2 film on the glass slide is dipped into a solution of a dye such as an organometallic complex or green chlorophyll derivative. Many natural dyes can be utilized, but they must possess a chemical group that can attach (absorb) to the TiO_2 surface, and they must have energy levels at the proper positions necessary for electron injection and sensitization. A single layer of dye molecules adsorbs to each particle of the TiO_2 and act as the absorber of the light. To complete the device, a drop of liquid electrolyte containing iodide is placed on the film to percolate into the pores of the film. A counter electrode of conductive glass, which has been coated with a thin catalytic layer of platinum or carbon, is placed on top, and the sandwich is illuminated through the TiO_2 side (Figure 1.3). This Nanocrystalline dye sensitized solar cell was invented at the Swiss Federal Institute of Technology in Lausanne, Switzerland, where it is being actively researched and developed.

Attempts have been made to use thicker coating of organic dyes for solar cells. Electric charges do not move easily within most organic materials, and it was found that

only a very thin layer is active for charge (e.g. electron) injection. Thick organic films therefore do not transfer photo- excited charges as well as thin films. This meant that if a single thick layer of dye were used (so that it would absorb all the light) the solar cell would not be as effective as one made from a series of thin layers that were interconnected. In the nanocrystalline solar cell, each layer of dye does not absorb much light, but the interconnected particles of the porous membrane (or film) can absorb 90% of visible light when added together.

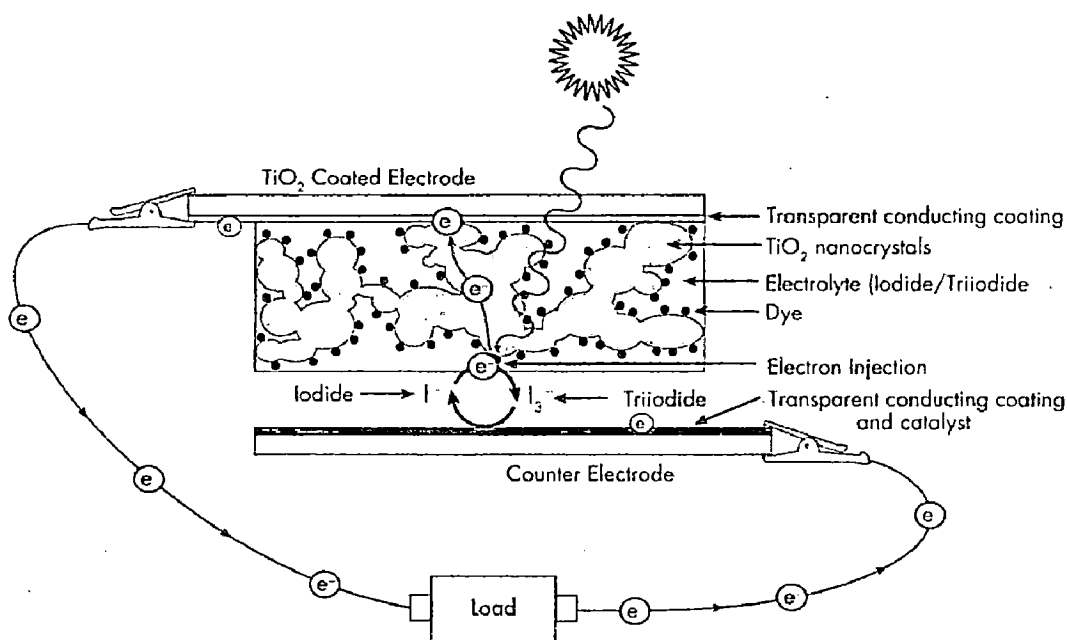
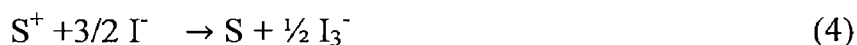
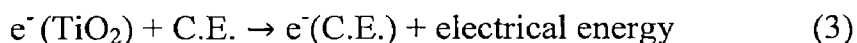


Figure 1.3: A layer of dye (shown as black dots) adsorbing to the TiO₂ nanocrystals.

This aspect of the Nanocrystalline cell involves the use of a rough semiconducting layer to increase the light absorption while allowing for efficient charge collection. Since the dye layer is so thin, almost every excited electron produced by light absorption can rapidly be transferred into the TiO₂. Since the TiO₂ is a semiconductor, this electron transfer is called injection. This sensitizes the TiO₂ to the wide range of wavelengths, or colors, of lights absorbed by the dye. The TiO₂ serves the same role as the silver halide grain in photography except that, in the solar cell, the injected electrons produce electricity instead of forming an image. This is because photographic film does not contain a mediator or a conductive path for the collections of electrons.

In the solar cell, the electrons lost by the dye via light absorption are quickly replaced by the mediator which is the iodide ion in electrolyte solution. The oxidized mediator forms iodine or tri-iodide that, in turn, obtains electrons at the catalyst-coated counter electrode (abbreviated C.E. in the reactions below) after the electron has flowed through the electrical load. If the dye molecule is represented by the symbol S, the sequence of reactions found in the Nanocrystalline dye sensitized solar cell are:



In this model system, the photosynthesis/respiration cycle is replaced by the cyclic flow of electrons and the cyclic oxidation and reduction of the mediator.

If we represent higher electron energy as greater height (on the y axis in Figure 1.4) we can illustrate the energy producing reactions on an energy diagram such as that shown in Figure 1.4. As can be seen in Figure 1.4, and by the equations above, the excited dye, S^* , is oxidized (to S^+) by the TiO_2 and then reduced back to its original state by the mediator, I^- contained in the electrolyte. The catalyst on the counter electrode assists in the rapid completion of the reaction in Equation 5. Since they are not consumed in the net reaction, and they speed up charge transfer, the catalyst coating on the counter electrode, I^- and I_3^- all considered true electrochemical catalysts. The interconnected TiO_2 particles serve as the electron acceptor, the iodide serves as the electron donor, and the dye function as a photochemical “pump” that excites the electrons to higher energy levels by using the energy of the light that is absorbed (Figure 1.4). This energy configuration is like that found in natural photosynthesis in which the electron acceptor is inevitably carbon dioxide, water is the electron donor, and chlorophyll is the photochemical pump.

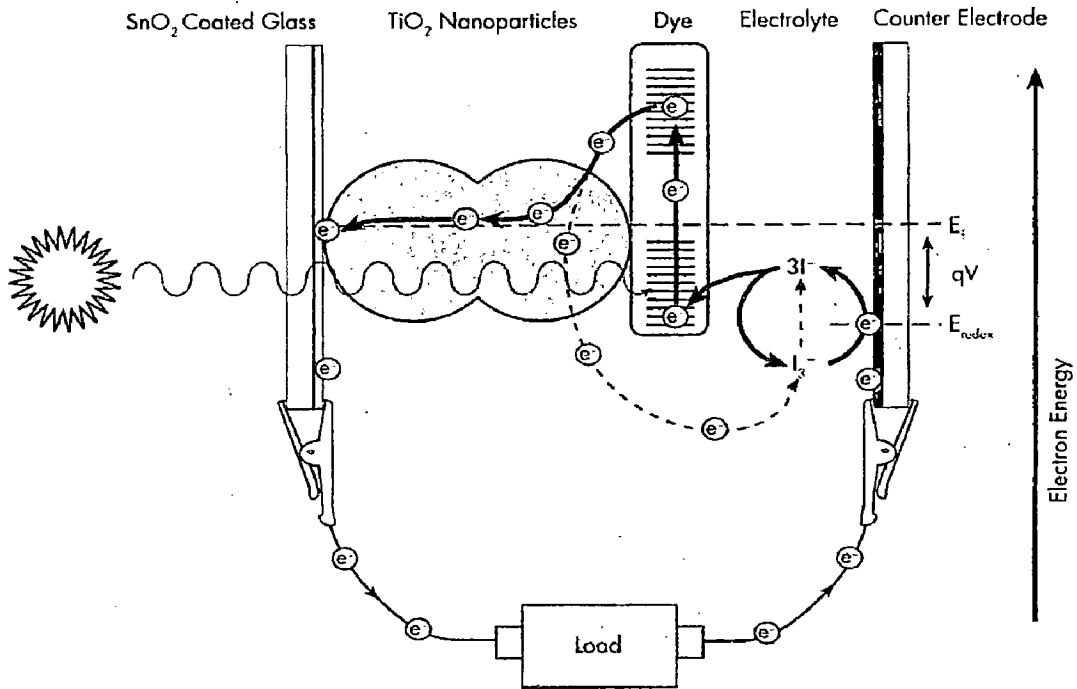
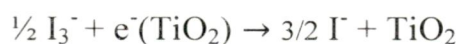


Figure 1.4: Energy Diagram for the dye sensitized solar cell.

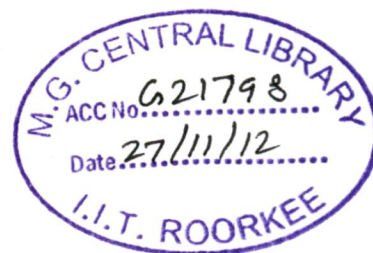
Unlike photosynthesis, the oxidation and reduction process in the dye sensitized solar cell produce electricity in an external electrical circuit. The voltage, V , Produced by the Nanocrystalline solar cell is obtained from the difference in energy levels between the TiO_2 (E_f) and mediator (E_{redox}), and depends. In part on the dye, mediator and liquid electrolyte used as well as the condition of the TiO_2 , and the number of iodide molecules oxidized [2-5]. The charge on the electron, q , multiplied by the voltage converts it to energy so it can be plotted on the diagram in Figure 1.4. The current (in amperes, A) produced by the cell is directly proportional to the amount of light (photons) absorbed by the dye, which itself depends on the intensity of the illumination. This proportionality is true for most solar cells and allows them to be used as a light detector (or a light meter) simply by measuring the current. The current is a measure of the rate of charge transferred through the load. The power output measured in watts, of any solar cell is the product of the voltage and the current flowing through the load.

$$\text{Power} = \frac{\text{energy}}{\text{time}} + V \times A$$

The conversion efficiency of the solar cell is the maximum electrical power output divided by the incoming solar power on the same area. Of course, not all the energy from sunlight can be converted into electrical energy. Some of the sunlight is instead converted into heat. It is a consequence of the second law of thermodynamics that not more than 33% can be converted into electricity for a solar cell with a single type of light absorber that is illuminated by natural day light [6]. The overall sunlight to electrical energy conversion efficiency of a nanocrystalline solar cell using the best dyes currently available is 7-10% under direct sunlight [2-5]. This is to be compared with approximately 0.5% for natural photosynthesis and 12 -20% for commercial silicon solar cell modules [1, 7, 11]. One process that limits the efficiency of the dye sensitized solar cell is transfer of the injected electron to the oxidized mediator before the electron has been collected and passed through the load and counter electrode. This reaction, shown by the dashed electron pathway in Figure 1.4, is represented by



Even with this limitations, calculation that consider the spectrum of the light utilized by the dye indicate that nanocrystalline solar cells of at least 10% efficiency could be realized at a cost of \$0.60/watt, which may be competitive with conventional electricity generation [4]. These cost estimates illustrate the promise of new devices, but further research and development is needed to find ways to seal the cell and allow it to withstand the test of time so that it can be used in large-area commercial solar cells. This is currently being conducted in laboratories around the world.



1.1 Literature review

Great attention has been paid to dye-sensitized solar cells (DSSCs) due to its moderate light-to-electricity conversion efficiency (10.4%), the simple device fabrication process, and low cost [2,3].

The most widely researched structure of the polymer solar cells is a bulk-heterojunction (BHJ), in which a photoactive layer comprises an interpenetrating network

of electron donor and acceptor materials [4]. In this structure, a very large interfacial area between the donor and the acceptor materials can be achieved, leading to the efficient dissociation of excitons into holes and electrons. Recently, it was reported that power conversion efficiency (PCE) as high as 5% has been achieved by the BHJ solar cells fabricated with poly (3-hexylthiophene) (P3HT) and fullerene derivatives [5]. However, BHJ solar cells intrinsically suffer from the charge carrier recombination during the charge transport through the random network of the materials. Electrons or holes inevitably encounter dead ends or islands of a certain phase of materials before they reach the respective electrodes, eventually limiting the PCE. In this regard, ordered heterojunction (OHJ) solar cells were proposed as a promising structure in which the electron donor and acceptor materials were interdigitated within nanometer scale, offering direct pathways for the charge transport [6]. To construct this type of structure, organic/inorganic hybrid solar cells using vertically oriented nanoparticles or nanotubes of inorganic semiconducting materials as an electron acceptor have been preferred due to their structural robustness and electrical properties [7].

TiO₂ is one of the best candidates for electron acceptor materials in solar cells by virtue of high electron mobility and excellent chemical and physical stability. Vertically oriented TiO₂ nanoparticles for this purpose have been developed by various methods including the sol-gel method [8] and direct anodization of titanium(Ti) [9]. However, these methods have limitations in synthesizing an ordered structure of uniform TiO₂ nanoparticles with precise control of dimension and geometry, which influences facile dissociation of excitons, the transport of charge carriers, and consequently high PCE. In addition, the previous studies have experienced difficulties in accomplishing the interdigitated nanostructures of OHJ solar cells [9], because the infiltration of the light harvesting polymers into the nanoparticle arrays is hindered by structural factors of the TiO₂ nanoparticles from such methods, such as inter-tube space and rough surface of sidewalls. Furthermore, incorporation of the polymers into the inorganic nanoporous structures is influenced by complicated factors including pore shape, surface interaction between two materials, spin-coating condition, and so on. Even though a variety of methods has been attempted by many researchers to solve the problem, such as melt-

infiltration, surface treatment, and modification of spin-coating conditions, it could not be a universal solution.

Graphene possesses a range of unusual properties. It can sustain current densities six orders of magnitude higher than that of copper and shows record thermal conductivity, optical transparency, robustness and stiffness. It is impermeable to gases. Individual graphene is also found to have excellent electronic transport properties. So far, graphene has been extensively investigated theoretically with respect to physics and electronic devices. However, the application of graphene in novel devices started. Graphene has been used in transparent conductive films, organic photovoltaic (PV) cells, field-effect transistor devices and ultrasensitive sensors. Moreover, graphene has recently been applied to develop electrodes for capacitive deionization systems, supercapacitors and field emission displays in our group. Following these works, we explored and developed applications of graphene in DSSCs. Besides the single atom thick layer structure feature, the high hole transport mobility, large specific surface area and the inertness against oxygen and water vapor make graphene a promising candidate for photovoltaic application. It was reported that the edge plane sites of graphene exhibit faster electron-transfer kinetics than the basal plane sites, and graphene may offer better electrocatalytic properties than that of CNTs [10, 11].

The increasing demand for energy has motivated us to seek new energy resources. As a renewable and clean energy, solar radiation is the most promising energy source. Therefore, the solar cell for harvesting solar energy has received great attention and various cells have been studied. As well known, semiconductor nanoparticles are attractive candidates for the design of solar cell due to their unique and tunable optoelectronic properties. TiO_2 , as a very important semiconductor material, has been widely studied for the fabrication of solar cell. Unfortunately, the broad bandgap responding only to UV light and invalidated recombination of photogenerated electron with hole hinders its application in light energy conversion. In order to improve the optoelectronic property of TiO_2 , various dye sensitization modes for TiO_2 have been universally studied in constructing solar cells [12–14]. Except for organic dyes, some

narrow bandgap semiconductors which act as the photosensitizers and can absorb visible light, have been coupled with TiO₂ to enhance photovoltaic conversion in solar cells.

Recombination is one of the main issues which hamper photovoltaic conversion in solar cells. To reduce the recombination rate and increase the charge transfer in active electrode some nanoparticles are showing good results. Graphene oxide has great potential, and is commercially available at affordable prices due to the inexpensive methods of production [15]. Graphene oxide is synthesized by simple chemical process so as to explore methods of its production in bulk quantity in an economical ways. Also by just following one more step of thermal treatment of Graphene oxide it forms graphene which will be a major step covered towards making an efficient and viable solar cell.

Graphene oxide (GO), an oxygen-rich carbonaceous layered material, is produced by the controlled oxidation of graphite [16]. Each layer of GO is essentially an oxidized graphene sheet commonly referred to as graphene oxide [17]. Based on recent studies [18, 19, 20] GO consists of intact graphitic regions interspersed with sp³-hybridized carbons containing hydroxyl and epoxide functional groups on the top and bottom surfaces of each sheet and sp²-hybridized carbons containing carboxyl and carbonyl groups mostly at the sheet edges.

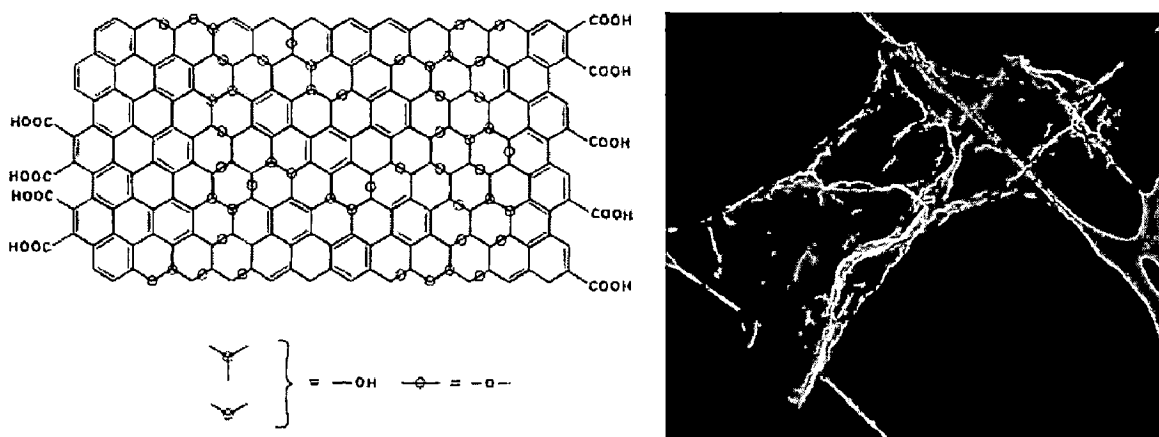


Figure 1.5: Graphene Oxide Structure and TEM image [17]

Study suggests that graphene sheets get oxidized by the formation of epoxy (C-O-C) bonds during oxidation to form graphene oxide. The functionalization of graphene due to bonding of oxygen atoms produces ripples on graphene sheet straining the lattice with C-C bond lengths. The atomic structure suggests that oxygen gets bonded to the graphene sheets through epoxide bonds [31].

Structurally, the GO is similar to a graphene sheet with its base having oxygen-containing groups. Since these groups have a high affinity to water molecules, GO is hydrophilic and can be easily dissolved in water. This property of solubility in water ensures that the thin film deposition of GO is very straightforward. GO is a poor conductor but when it undergoes treatment using heat, light, or chemical reduction, most of graphene's properties are restored. Chemical reduction is normally done using hydrazine. Other green methods are also available to reduce graphene oxide that include introduction of bacteria containing cytochromes.

Graphene sheets stack to form graphite with an inter planar spacing of 0.335 nm, which means that a stack of 3 million sheets would be only one millimeter thick. Graphene is a Zero Gap Semiconductor. So it has high electron mobility at room temperature. It's a Superconductor. Electron transfer is 100 times faster than Silicon. Graphene has a record breaking strength of 200 times greater than steel, with a tensile strength of 130GPa. Graphene can be used to create circuits that are almost superconducting, potentially speeding electronic components by as much as 1000 times. Graphene electrodes used in lithium-ion batteries could reduce recharge times from two hours to about 10 minutes.

Graphene oxide finds application in the following fields:

Transparent Conductive Films – GO finds application mainly in the fabrication of transparent conductive films. It is possible to deposit GO films on any substrate, and then convert it into a conductor. These coatings may be used in solar cells, flexible electronics, chemical sensors, liquid crystal devices, and as an indium tin-oxide (ITO) replacement. ITO is the present material of choice for touch screen devices.

Composites and Paper-like Materials – GO can blend easily with a number of polymers, forming nanocomposites, and greatly improves the characteristics such as tensile strength, elastic modulus, thermal stability and electrical conductivity of the original polymer. GO flakes in its solid state may affix to each other forming highly stable and thin paper-like structures that can be wrinkled, folded and stretched. Such free-standing GO films are considered for applications such as ion conductors, hydrogen storage applications, and nanofiltration membranes.

Energy-Related Materials – GO and its reduced forms have a very high surface area. This high surface area enables these materials to be used as electrode materials in double-layered capacitors and batteries as well as solar cells and fuel cells. GO manufacture can be easily done in bulk quantities when compared to other graphene materials, and hence may soon be utilized for energy-related purposes. Its hydrogen-storage ability may in the future find application in hydrogen fuel storage in hybrid cars. Graphene Supermarket offers Reduced GO with Brunauer-Emmett-Teller (BET) with a surface area of around 833 m²/g.

Applications in Biology and Medicine – GO has been discovered to be fluorescent and hence can be used in biosensing, assisting in finding cure for cancer, early detection of disease. GO has also been used in fluorescent-based biosensors in order to detect proteins and DNA, with a promise of better HIV diagnostics. Additionally, GO is tested as a drug carrier. It is superior to several other anticancer drugs since it does not target healthy cells, only tumors, and has a low toxicity.

Antibacterial Materials - The growth of E. Coli bacteria may be reduced when disrupted by GO. Since GO fabrication is inexpensive, it may be produced in bulk when its applications become commercial. This will enable more opportunities for developing antibacterial materials, and may help in healing wounds by destroying bacteria. These materials can also be made into a thin paper used for packaging meats, which will be more sanitary than present packaging techniques.

Surfactant – GO can also act as a surfactant, similar to how soap or shampoo can make a stain disperse in water. This characteristic can be used as an agent for dispersion of insoluble materials such as carbon nanotubes [15].

Counter-electrode plays a key role by catalyzing the reduction of the redox species in DSSCs. It serves to transfer electrons from external circuit to tri-iodide and iodine in the redox electrolyte. A high-performance DSSC requires the counter-electrode to be highly catalytic and high conductive. Hence, platinum, which is a good catalyst for the reduction of the redox species, such as tri-iodide/iodide, is usually used as the counter electrode of the DSSC. The best platinum counter electrode of the DSSC is produced by a high-temperature hydrolysis process. However, the noble platinum remarkably increases the cost of the DSSC. Thus, many alternative cheap materials have been investigated as the counter-electrodes for DSSC. Carbonaceous materials are quite attractive to replace platinum due to their high electronic conductivity, corrosion resistance towards I_2 , high reactivity for tri-iodide reduction and low cost [21]. Under simulated sunlight (AM 1.5 at 100mWcm^{-2}), graphite, activated carbon [22], single walled carbon nanotubes (SWCNTs) [23], double-walled carbon nanotubes (DWCNTs) [24] and multi-walled carbon nanotubes (MWCNTs) [25] showed conversion efficiency (g) of 6.67% (active area 0.40 cm^2), 3.9% (0.05 cm^2), 4.5% (0.25 cm^2), 6.07% (0.25 cm^2) and 3.06% (0.25 cm^2), respectively.

Graphene oxide [GO], produced by exfoliation of graphite oxide, has been traditionally considered to be a precursor for graphene [26]. GO has recently attracted research interest due to its good solubility in water and other solvents, which allows it to be easily deposited onto a wide range of substrates [27, 28]. Besides, GO has variable optical, mechanical, and electronic properties that can be tuned by controlling the degree of oxidation [29, 30].

1.2 Aim

This study is aimed at using graphene oxide and TiO_2 nanoparticles for making electrodes of solar cell module and thus attempting to improve efficiency of solar cell by using conducting and transparent property of graphene oxide.

Within the photoanode of a solar cell, photo-induced electrons must overcome grain boundaries to be collected by a conductive glass. The low transfer efficiency of photo-induced electrons across a TiO_2 matrix represents a major limitation of such nanostructured photoanodes. The inefficient charge transfer paths cause photo-induced electrons to recombine with the oxidizing species or tri-iodide ions present in the electrolyte, resulting in a decrease in photocurrent and photoconversion efficiency. Preventing charge recombination can therefore improve the photo-induced transfer of electrons. Study, study also show that the introduction of TiO_2 matrix of the photoanode of solar cells can improve the performance of the cell by improving the electron conduction paths and distribution of the pores.

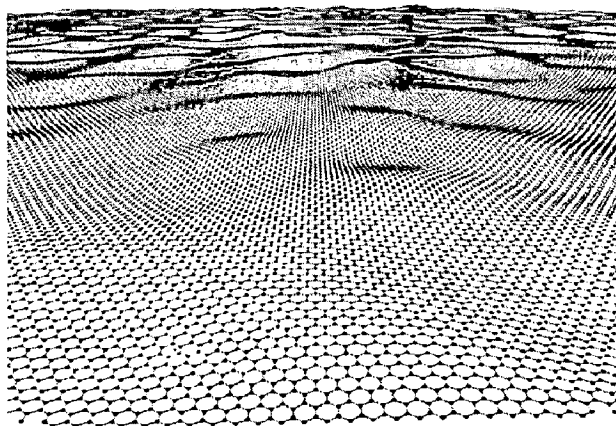


Figure 1.6: Picture of single layer graphene oxide

Recently, two-dimensional (2-D) structured graphene/GO has emerged as a conductive nanomaterial showing considerable promise for use in organic solar cells. Graphene has been progressively developing in the application of photoanodes. Now graphene introduced into a TiO_2 matrix as a 2-D bridge for the photoanode of solar cells. They demonstrated lower recombination rates, increased efficiency in electron transport, and enhanced light scattering through the incorporation of graphene oxide into the

photoanode, contributing to improved cell performance. They demonstrated that the introduction of graphene to TiO_2 -based working electrodes improves in both dye adsorption and electron lifetime. The preparation of a photoanode in which chemically synthesized graphene oxide will be incorporated into a TiO_2 matrix. Studies also determine that the implantation of graphene oxide provided additional transport pathways for photo-induced carriers, leading to an increase in photocurrent.

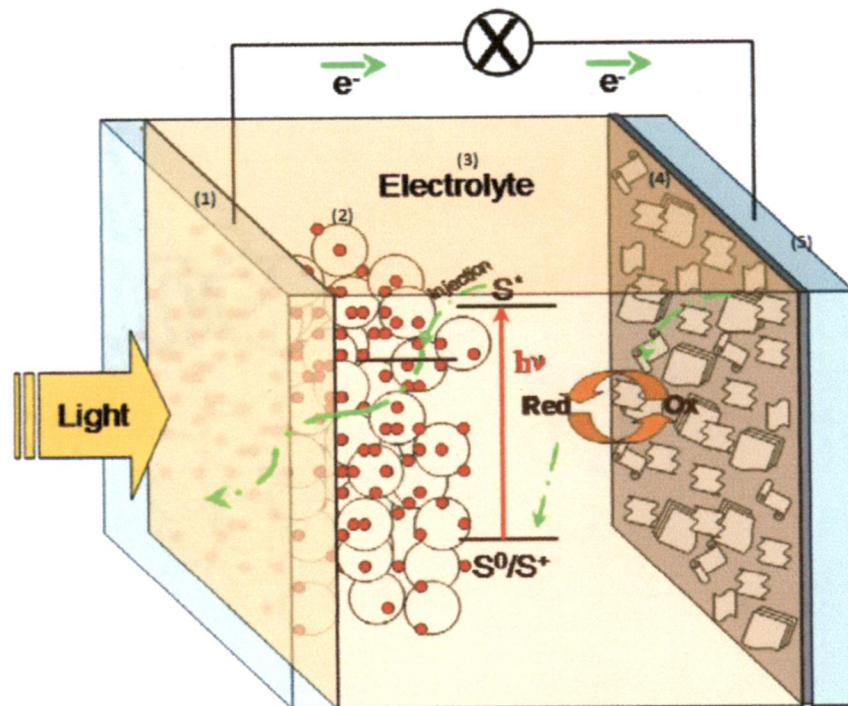


Figure 1.6: Schematic diagram of GO incorporated in both Active electrode and Counter electrode of Dye Sensitized Solar Cell

Where,

- (1) Conducting glass -tin dioxide glass plate
- (2) Complex containing TiO_2 highly porous nanocrystalline layer, GO transparent layer and Dye (organic)
- (3) Electrolyte solution
- (4) Graphene oxide based counter electrode
- (5) Conducting glass

We aim to prepare dye sensitized solar cell represented by figure above, containing the graphene oxide/TiO₂ composite for stationary energy storage device and subsequently we will study the graphene oxide used as a counter electrode. The active layer consists of a highly porous nanocrystalline graphene oxide/titanium oxide deposited on a transparent electrically conducting substrate (tin dioxide glass plate). Layers of a sensitizing dye on the composite GO/TiO₂ surface absorb the incoming light. The device is completed by a counter-electrode and an organic solvent based electrolyte containing the redox-couple iodide/triiodide. We shall attempt to investigate 2D graphene oxide as an efficient catalyst for tri-iodide reduction in DSSC. GO will be synthesized by modified Hummer's method, and will be applied to prepare the counter-electrodes for DSSC. We shall finally check the solar cell (as active electrode GO/TiO₂) performance of graphene oxide based counter electrode to that of carbon based DSSCs fabricated in the same condition.

Chapter 2

Materials and equipments

- Conductive (tin dioxide coated) transparent glass

Two pieces of glasses were used per solar cell. Pre cut commercial (2.5cm × 2.5cm) TEC 10 glass purchased from: Harford Glass Co., P.O. Box 613, Hartford City, IN 47348; 765/346-1282; fax: 765/346-54 35; email: hartlgass@netusal.net.

- Colloidal titanium dioxide powder

AEROXIDE TiO₂ P 25 (20 g included) was used in few DSSC for comparison. P25 purchased from Evonik Degussa Corporation, 379 Interpace Parkway, Parsippany, NJ 07054; 973/541-8106.

- Copper foil tape (3M No.1181 with pressure sensitive conductive adhesive)

Two 1-cm long pieces are used per solar cell. Copper foil tape purchased from ICE

- Iodide electrolyte solution

0.5M Potassium iodide mixed with 0.05M iodine in water free ethylene glycol (not very stable in sunlight without a UV filter)

The calculations for making the electrolyte solution are as follows

Potassium Iodide, KI:

$(0.5 \text{ mol/L}) \times (0.01 \text{ L}) \times (166.01 \text{ g/mol}) = 0.83 \text{ g}$ in 10 mL of solvent

Iodine, I₂:

$(0.05 \text{ mol/L}) \times (0.01 \text{ L}) \times (253.81 \text{ g/mol}) = 0.127 \text{ g}$ in 10 mL of solvent

- Soft graphite pencil (HB woodless graphite pencil)

Graphite pencil purchased from local art supply store.

- Binder clips

Two clips were used per cell. The binder clips should be bent so that the pressure they exert is not too great. The jaws should be partially opened.

- Organic dye

Dye was prepared from pomegranate seeds.

- Dropper bottle

Used for storing and dispensing the TiO₂ suspension.

- H₂SO₄ 35.4% (1.18) AR, SDFCL.
- Absolute ethanol AR, Changsho yangyuan chemical china.
- HNO₃ LR, Fisher scientific.
- Polyethylene glycol (8000) LR, Himedia.
- Natural graphite LR, sd fine – CHEM Limited.
- NaNO₃ LR, RANKEN.
- KMnO₄ LR, RANKEN.
- H₂O₂ 30% LR.
- TTIP 98%, AVRA.
- Magnetic stirrer.
- Centrifuge, REMI CPR-30.

Centrifugation was carried out in 3000 to 5000 RPM range.

- Heat source

Ceramic top hotplate (able to reach 450^oc), TRANSONS.

- Ultrasonication Equipment
- Ethanol and deionized water in wash bottles.
- Multimeter, capable of measuring volts and ohms.
- Pipettes.
- Mortar and pestle.
- Tweezers.
- Tongs.
- Transparent tae.
- Glass stirring rod.
- Absorbent tissue paper.
- Cotton swabs.
- Filter paper, glassware.
- Safety goggles.
- Protective gloves.

Chapter 3

Procedural details

3.1 Preparation of graphene oxide

Graphene oxide was synthesized from natural graphite by a Hummers method [16]. In a typical experiment, the graphite powder (1 g) and NaNO_3 (1 g) were introduced into concentrated H_2SO_4 (46 ml) in an ice bath. The KMnO_4 (6 g) was added gradually under stirring to prevent rapid temperature rise, and the temperature of the mixture was kept below 20°C . The mixture was then stirred at 35°C for 30 minutes. Then, deionized water (300 ml) was slowly added to the solution. Finally, the mixture solution was stirred at 98°C for about 1 h until the color changed from brown to yellow. After the residual KMnO_4 was removed by adding 30% H_2O_2 (10 ml), the precipitate was separated by centrifugation and washed with warm water repeatedly.

For purification, the solid product as-obtained was fully dispersed in water under ultrasonication at room temperature for 30 min. After ultrasonication, centrifugation at 3,000 rpm for 5 min was carried out. GO powder was obtained by drying the GO suspension.

3.2 TiO₂ Formation

In the preparation of Ti-precursor sol, (30 ml) TTIP was mixed with (15 ml) absolute ethanol. Then the mixture was slowly added into a de-ionized water-ethanol solution (water: absolute ethanol =12:1, v/v). After stirring vigorously for 1 min, (1.2 ml) HNO₃ was slowly added into mixture. The final solution was stirred vigorously for 24 h until the Ti- precursor sol formed. Then Ti- precursor sol was dehydrated and the alcohol removed in evaporator (31).

3.3 Prepare active electrode of DSSC

Preparation of active electrode that is GO/TiO₂ thin film was done using conventional Doctor-Blade method. For the Doctor-Blade method, a dense GO/TiO₂ paste was prepared as following:

TiO₂ powder/GO (1:0, v/v) was blended with a mixture of polyethylene glycol (PEG, MW of 20,000, 0.5 g) and de-ionized water (1.5 ml) in a plastic bag under rolling of a steel pipe for 10 min.

Various composites were prepared on the basis of % GO amount in composite with TiO₂ like 0%, 0.03%, 0.05%, 0.1%, and 0.13%. After UV-vis absorption study best composite was selected for further study, and then the resulting GO/TiO₂ paste was coated on conducting glass to make a thin film using the Doctor-Blade method.

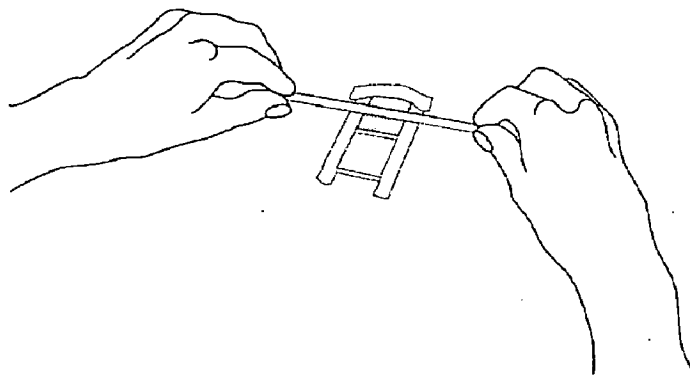


Figure 3.1: Deposition and distribution of the TiO_2 solution on the conductive glass. A rapid horizontal motion of the glass rod will coat the masked glass plate with a uniform layer of TiO_2 nanoparticles.

The obtained GO/ TiO_2 thin film was then dried in air for 30 min. The derived GO/ TiO_2 thin film was calcined at 450°C for 2 h.

3.4 Stain the GO/Titanium Dioxide with the Dye

Organic dye (anthocyanins) from fresh pomegranate seeds was used in DSSC. Fresh or frozen blackberries, raspberries, or pomegranate seeds are crushed with 3–4 drops (1/2 mL) of water, filtered, and used as a crude dye solution. Conducting glass containing active layer were deep in freshly squeezed Pomegranate seeds for 30 min [11]. Alternatively, the film can simply be placed on top of crushed berries to which a small amount of water has been added.

Several fruits and leaves contain anthocyanins that, although colored, may not chelate to the TiO_2 surface (e.g., strawberries). These pigments are not suitable for the dye sensitized solar cell. A requirement for the dye structure is that it possess several =O or –OH groups capable of chelating to the Ti-IV sites on the titanium dioxide surface. A mixture of cyanin 3-glycoside and cyanin 3-rutinoside are the main (sugar-bound) anthocyanin pigments from California blackberries (*Rubus ursinus*) and are excellent natural dyes for sensitization (13).

3.5 Prepare the Carbon-Coated Counter Electrode

The GO/TiO₂ electrode is being stained in the pomegranate seeds juice or chlorophyll solution, mean while the counter electrode can be made from another (2.5 × 2.5 cm) piece of conductive SnO₂-coated glass. A graphite soft pencil “lead” is used to apply a light carbon film to the entire conductive side of the plate. This thin carbon layer serves as a catalyst for the tri-iodide to iodide regeneration reaction. No masking or tape is required for this electrode, and thus the whole surface is catalyst coated.

3.6 Prepare the graphene oxide Counter electrode

To realize the in-situ photoelectrochemical reduction, graphene oxide counter electrode was used for DSSCs. The graphene oxide electrode was prepared by Drop casting the graphene oxide solution of 1 mg/ml on a clean tin dioxide glass substrate and dried in room temperature.

3.7 Assemble Device and Determine Output Characteristics

The cyanin-stained active electrode is carefully removed from the staining solution and rinsed with water. It is important to dry the stained electrode and to remove the water from within the porous GO/TiO₂ film before the iodide electrolyte is applied to the film. Then active electrode was dried at 80°C for 10 min. The dried electrode is then placed on the table so that the film side is face up, and the catalyst-coated counter electrode is placed on top so that the conductive side of the counter electrode faces the GO/TiO₂ film. The two opposing glass plates are offset so that all of the GO/TiO₂ is covered by the counter electrode, and the 4mm strip of glass not coated by GO/TiO₂ is exposed (see Figure 3.2).

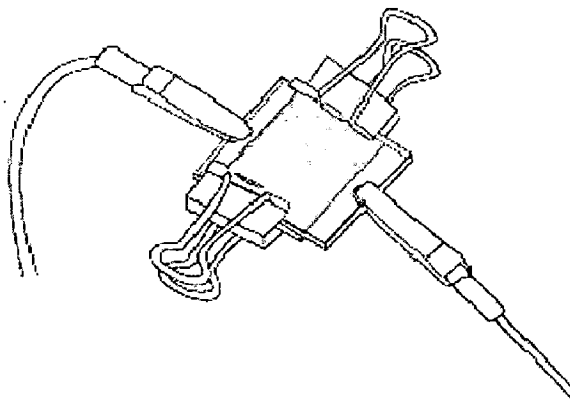


Figure 3.2: Assembled solar cell or detector showing offset glass plates, clips, and electrical contact points. The stained TiO_2 layer is in contact with the carbon-coated conductive layer. Light enters the sandwich through the TiO_2 -coated glass plate, which is the anode of the electrochemical device.

The two exposed sides of the device will be the contact points for the negative and positive electrodes so that electricity can be extracted to test the cell. Two binder clips are used to hold the plates together loosely at the other edges. The cell had an active area of 1 cm^2 . One or two drops of the electrolyte solution containing 0.5M Potassium iodide mixed with 0.05M iodine in water free ethylene glycol can then be placed at the edges of the plates and the two binder clips are alternately opened and closed while in place. The liquid is drawn into the space between the electrodes by capillary action, and can be seen to “wet” the stained GO/ TiO_2 film.

3.8 Characterization

The films as-prepared were characterized by a scanning electron microscope (SEM, LEO 435 VP) and X-ray diffractometer (XRD, D8 advance Bruker axs, graphite monochromatized CuK radiation, wavelength = 0.15406 nm). The UV-vis absorption spectrum was recorded on a UV spectrometer (5000 UV-vis-NIR-spectrophotometer, Varian). The FTIR analysis (Nexus-FT-IR Thermo-Nicolet) was carried out.

3.9 Measurement for photoelectrochemical performance

The measurement of solar cell efficiency was performed at the IIT Delhi Photovoltaic lab.

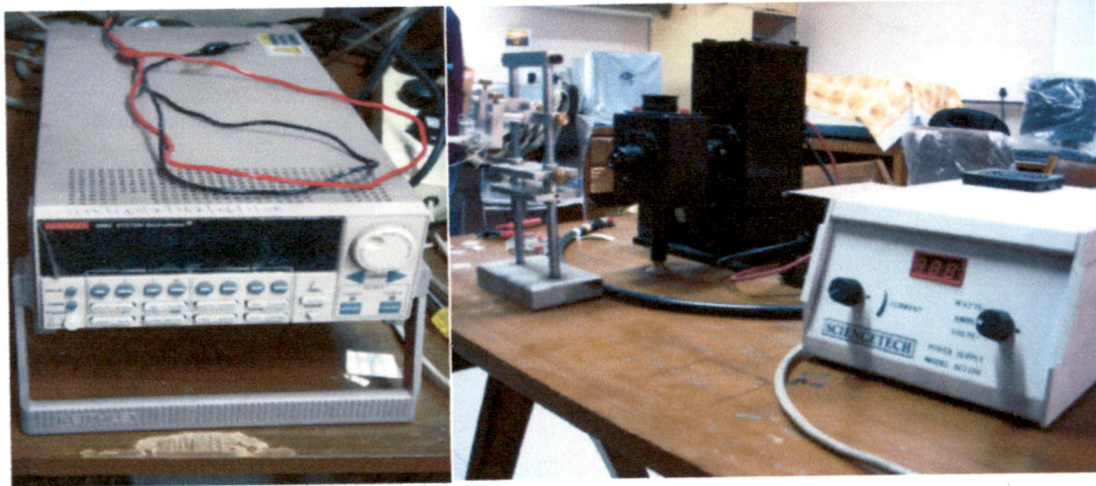


Figure 3.3: Photographs of instruments at Photovoltaic laboratory, Centre of Energy Studies, IIT Delhi

Chapter 4

Results and discussion

4.1 Characterization of TiO₂ nanoparticles

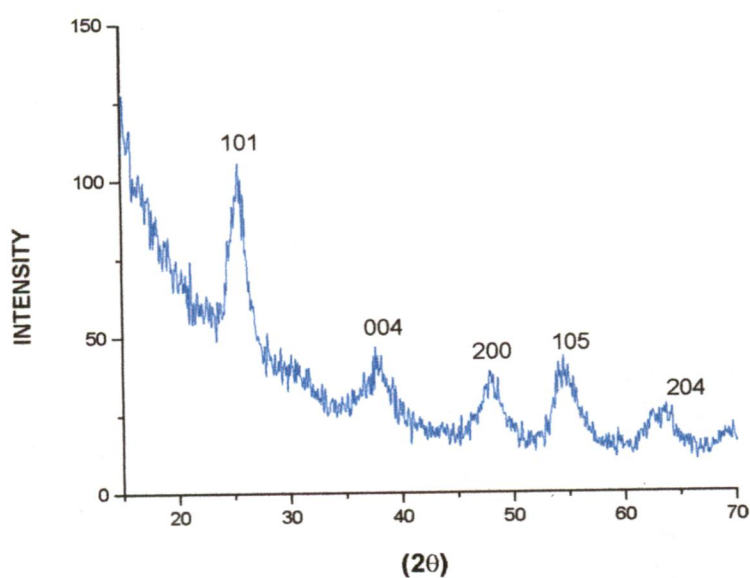


Figure 4.1: XRD pattern of TiO₂ nanoparticles

Structural characterization of the TiO₂ powder was performed by X-ray diffraction patterns (XRD). Figure 4.1 displays the data for the XRD pattern of TiO₂ nanoparticles synthesized from TTIP as main precursor by sol gel method. It can be concluded that the TiO₂ layer is made up of crystalline structure, since all the peaks in

XRD pattern can be attributed to the anatase phase by comparing with that in JCPDS (83-2243) file.

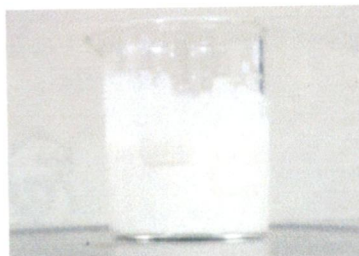


Figure 4.2: Photograph showing synthesized TiO_2 by sol gel method

TiO_2 nanoparticles (average particle size 95nm) were synthesized by sol gel method. Titanium tetra isopropoxide (TTIP) was used as Ti-precursor in the process of TiO_2 preparation.

4.2 Characterization of graphene oxide nanoparticles



Figure 4.3: photographs of graphene oxide and natural graphite powder

In Figure 4.3 is the black product graphene oxide? To investigate its chemical information XRD study was carried out at Institute Instrumentation Centre of IIT Roorkee.

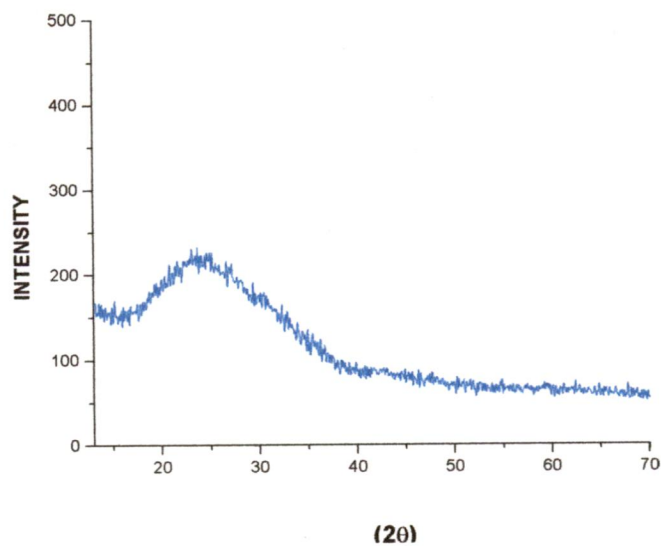
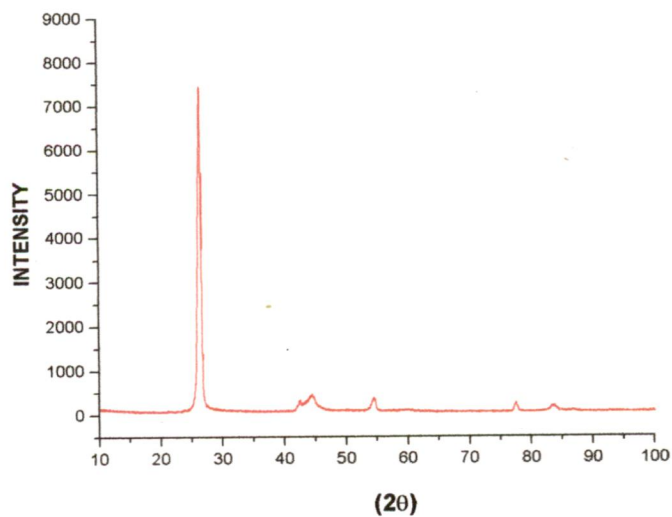


Figure 4.4: a) XRD pattern of natural graphite and b) XRD pattern of GO

Graphene oxide was synthesized by reduction of natural graphite powder. From Figures 4.4 a) and b) it can be concluded that the reduction of natural graphite takes place, simultaneously graphene oxide nanoparticles 90nm in size were synthesized. Comparison between XRD pattern of graphite and graphene oxide resolved the structural change and formation of graphene oxide nanoparticles.

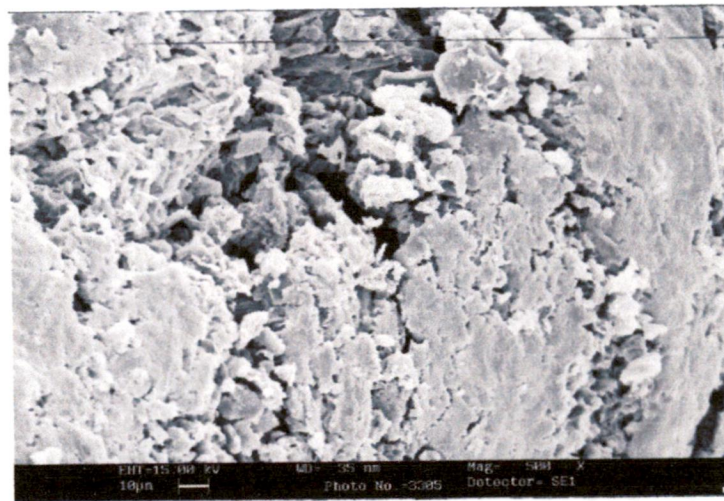
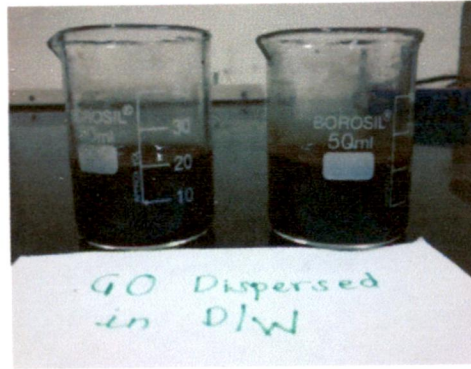


Figure 4.5: a) Photograph of GO dispersed in D/W and b) SEM image of Bulk graphene oxide

Synthesized graphene oxide of average particle size 90nm dispersed into deionized water or D/W. To disperse graphene oxide in water it takes prolong sonication process. Water as a dispersion media has many advantages like reduce process cost by replacing costly solvents, easy to fabricate electrodes etc.

Also in comparison to the natural graphite, a very wide peak is observed for GO, and it clearly indicates the damage of the regular crystalline of pattern graphite during the oxidation. The presence of broader diffraction peaks in the diffraction pattern indicates very short range atomic coherence. There is a loss of coherence between graphene-like layers. However, in plane peaks are sharper, showing larger in plane structural coherence.

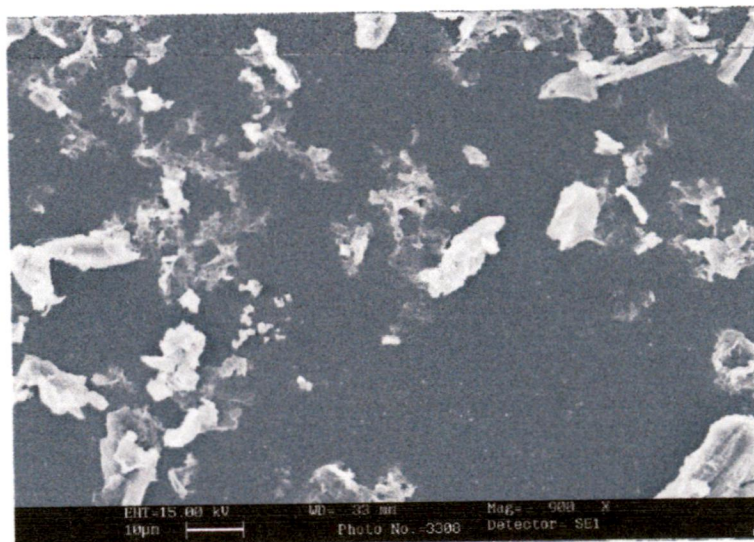


Figure 4.6: FE-SEM image of GO

The morphology of graphene oxide nanosheets was examined by a LEO 435 VP field emission scanning electron microscope (SEM). A powder sample of the graphene nanosheets was used for SEM characterization. The Figure 4.6 reveals the randomly formed networks of graphene oxide nanosheets.

4.3 UV-vis Absorption study

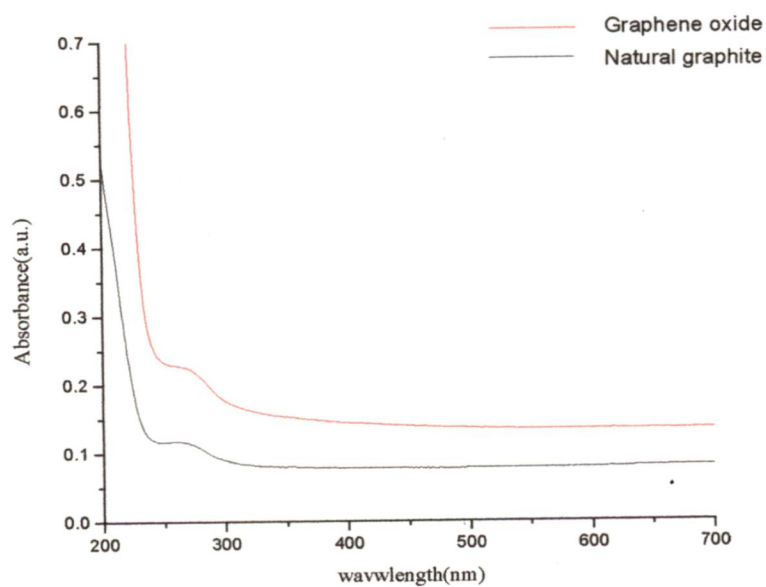


Figure 4.7: UV-vis Absorbance of natural graphite and graphene oxide

The UV-vis absorption study of samples was analyzed by VARIAN 5000 UV-vis-NIR spectrophotometer. From Figure 4.7 we now state that the graphene oxide shows increase in absorbance in visible range of light compared to natural graphite, also the absorption across the entire UV-visible range increased significantly.

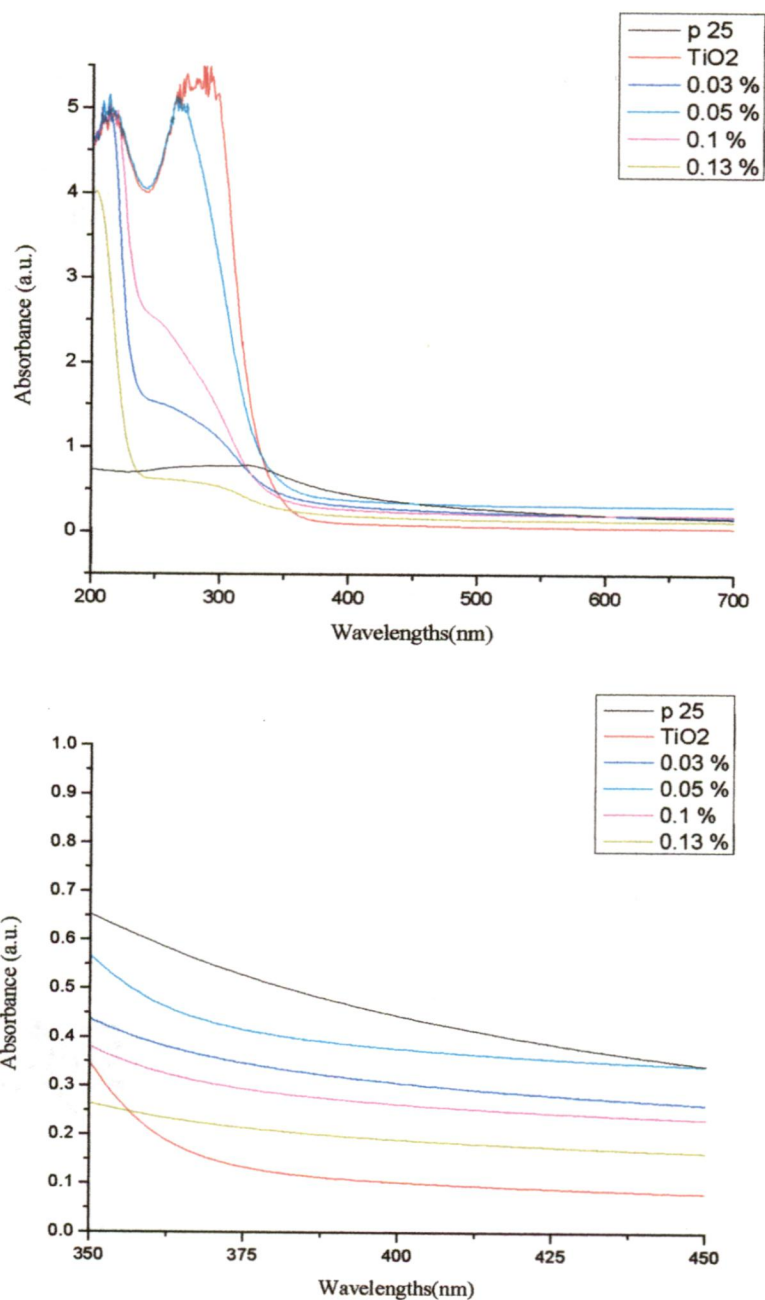


Figure 4.8: a) UV-vis Absorbance of GO/TiO₂ composite at various concentration of GO and b) Enlarge portion of UV-vis Absorbance of GO/TiO₂ composite at various concentration of GO.

The UV–vis absorption study of graphene oxide supports the incorporation of graphene oxide into active electrode of DSSC. This modification i.e. graphene oxide/TiO₂ as an active electrode in DSSC can increase the absorbance in visible range of light. Also has a good potential to increase efficiency of DSSC.

It is proved that amount of graphene oxide affects the light absorption for graphene oxide/ TiO₂ composites dramatically. To examine the role of graphene oxide in photoelectrochemical performance of TiO₂ composite, we varied the loading amount of graphene oxide in the thin composites. The graphene oxide/TiO₂ composite can be obtained by a simple mechanical mixing of graphene oxide and TiO₂ nanoparticles. The concentration of TiO₂ was kept constant at 1 g while various composites were prepared on the basis of % GO amount in composite with TiO₂ like 0%, 0.03%, 0.05%, 0.1%, and 0.13%.

The UV-vis absorption spectra of the films are shown in Figure 4.8 a). The UV region absorption of the composites can be assigned to the absorption caused by the excitation of electrons from the band-to-band or band-defect transitions. From the curve in Figure 4.8, it can be seen that the pure TiO₂ film shows a weak absorption in the UV–visible region, and has an absorption onset at 380nm.

By doping with the graphene oxide nanoparticles, the graphene oxide/TiO₂ film as-formed shows an intense absorption comparing with both TiO₂ film and graphene oxide/TiO₂ film as shown in Figure 4.8 a). The phenomenon results from the conductivity and structural property of graphene oxide that can facilitate separation of photogenerated charges, and will show increase in DSSC photo-conversion efficiency. Because in the way, the introduced 2D graphene bridges increase the charge transport and suppress the electrons in TiO₂ to recombine with the dye and redox species, and hence the Voc will not be decreased.

The enlarged portion of Figure 4.8 a) is shown in the Figure 4.8 b). From Figure 4.8 b), it can be concluded that the 0.03% graphene oxide containing composite shows increase in absorbance in UV-visible region comparing to 0%, 0.05%, 0.1% and 0.13%

graphene oxide/TiO₂ composite. By using UV-vis absorbance study we choose 0.03% graphene oxide containing composite for further study.

4.4 Properties of Graphene oxide -Modified TiO₂ Films

The Doctor-Blade method was used to prepare graphene-TiO₂ thin films on tin dioxide coated glass. A suspension of known-amount of TiO₂ and graphene oxide in PEG and deionized water was deposited to the tin dioxide coated glass.

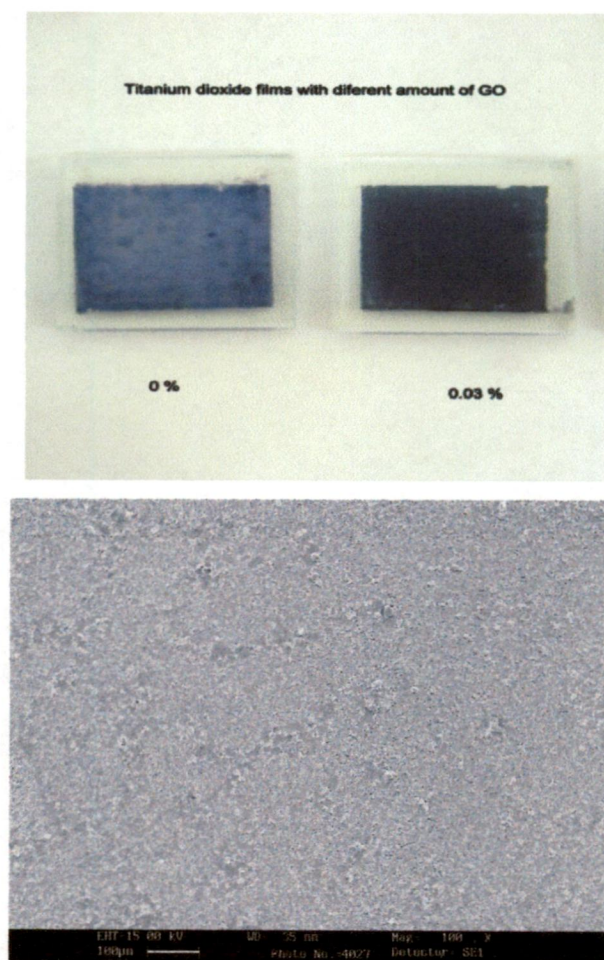


Figure 4.9: a) Photographs of graphene oxide/TiO₂ thin films and b) SEM images of graphene oxide/TiO₂

Careful deposition of the suspension on tin dioxide coated glass results in the formation of homogeneous tin dioxide coated glass/Graphene oxide-TiO₂ thin films after absorption of dye as shown in Figure 4.9 a). While pure TiO₂ thin film indicates uniform white color, addition of small amount of graphene gradually modify the color of thin films to light and dark-gray. Purple color indicates adsorption of dye on both the slides. The tin dioxide coated glass/Graphene oxide-TiO₂ turns black when graphene oxide is added, i.e. color of graphene oxide becomes dominant.

Figure 4.9 b) shows surface morphology of graphene oxide-TiO₂ electrode after annealing. Surface morphology shows a compact and uniform porous surface, which increase the surface area for dye adsorption. It demonstrates that the graphene oxide nanosheets act as dispersing agent in the graphene oxide/TiO₂ composites paste, preventing aggregation of TiO₂ nanoparticles.

4.5 FT-IR Analysis of graphene oxide

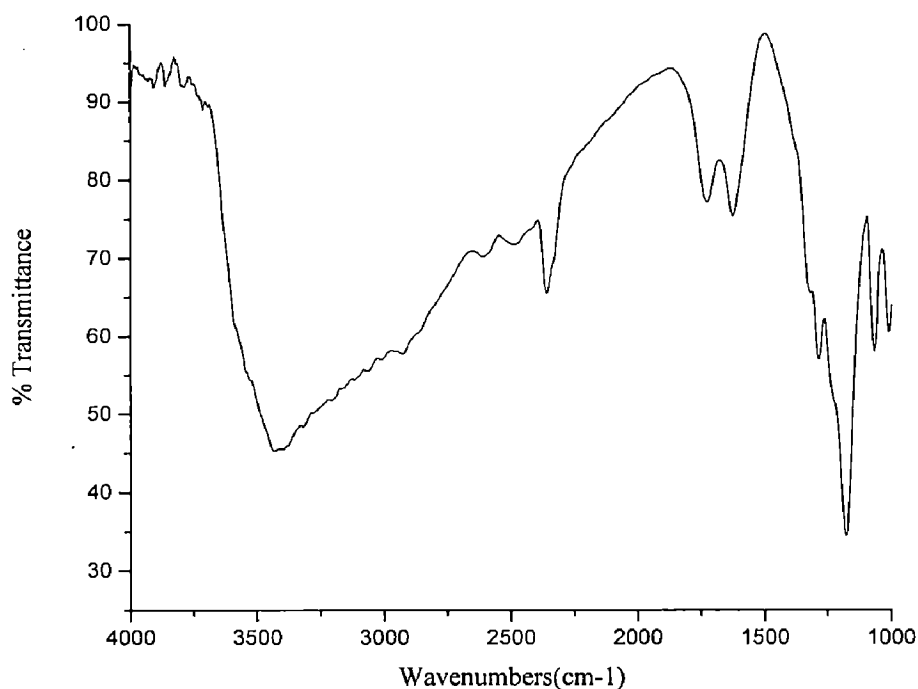


Figure 4.10: FT-IR spectrum of graphene oxide.

FT-IR spectroscopy was used to indicate the reduction of oxygen-containing groups of GO. FT-IR study was carried out by NEXUS FT-IR Thermo Nicolet, where study confirms that the graphene oxide has potential to act as counter electrode in DSSC.

Figure 4.10 shows the characteristic bands of graphene oxide. The FT-IR spectrum of graphene oxide showed a broad band between 3000 and 3700 cm^{-1} that was associated with the hydroxyl groups of graphene oxide. The shoulder band at 1730 cm^{-1} was related to the C=O stretching motions of COOH groups at the edges of the graphene oxide nanosheets. The peak at 1621 cm^{-1} contained a peak corresponding to aromatic C=C bonds and was assigned to the stretching and deformation vibrations of absorbed water. Finally, the peaks at 1285 and 1177 cm^{-1} were assigned to the vibrations of C-O-C and C-O (alkoxy and epoxy), respectively.

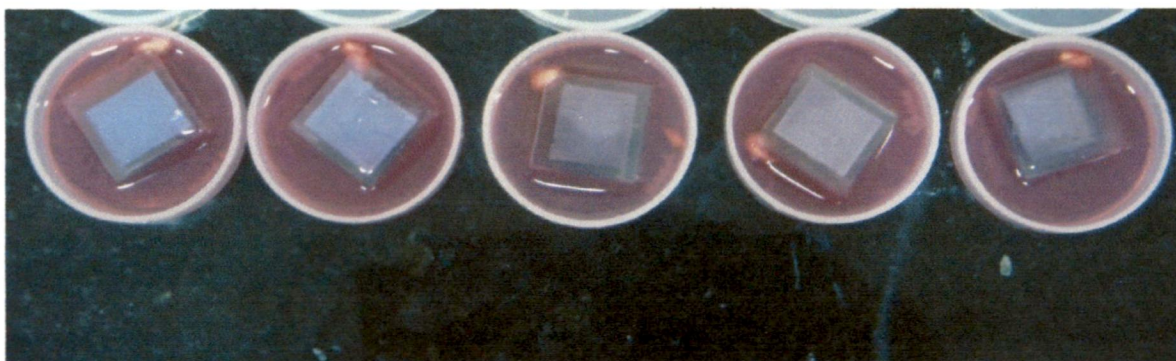


Figure 4.11: Photograph showing conducting glasses with active layer dipped into organic dye

Figure 4.11 shows the various active electrodes were fabricated and they were ready to use as active electrode only after TiO_2 molecules absorbed dye molecules on them. Above Figure confirmed the color change, all active electrodes were became purple in color.

4.5 Counter electrode

For substituting expensive platinum counter electrode in DSSC, platinum was replaced with graphene oxide as cost effective counter electrode. The graphene oxide electrode is fabricated by Drop-casting method, also traditional carbon electrode was fabricated for comparison as shown in Figure 4.12.

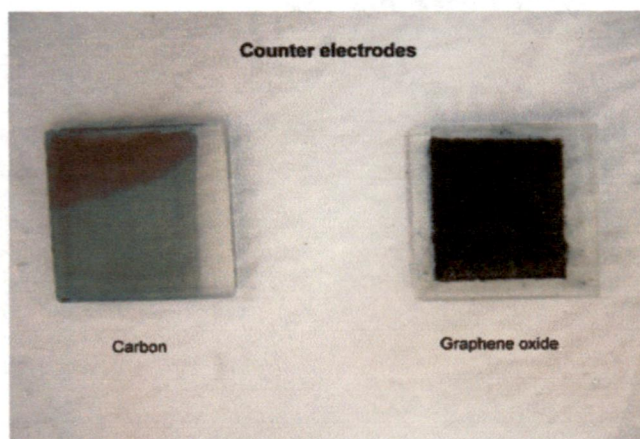


Figure 4.12: Photographs of fabricated carbon and graphene oxide counter electrodes for Dye Sensitized Solar Cell.

The dye molecular was photo-excited and then injected an electron into the conduction band of the TiO_2 . The original state of the dye was subsequently restored by electron donation from the iodide/tri-iodide redox couple.

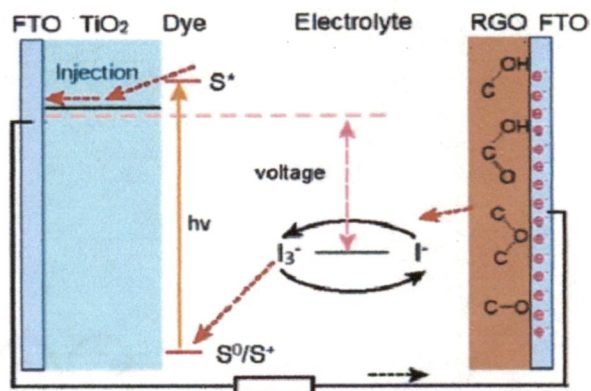


Figure 4.13: Mechanism of in-situ photoelectrochemical reduction of GO in a DSSC assembly

The electrons transported to the counter-electrode via electron migration through the external load. The iodide was regenerated in turn by the reduction of tri-iodide at the counter-electrode. Thus, the counter-electrode serves to inject charge into the electrolyte and catalyzes the reduction of tri-iodide in DSSCs. At the counter electrode of energy efficient DSSC tri-iodide should be efficiently reduced to iodide. The counter electrode must be catalytically active to ensure rapid reaction. It also has to be well conducting and exhibit a low over potential for the rapid reduction of the redox couple in order to carry the photocurrent across the width of each solar cell. Hence, besides the specific surface areas, the adhesion between the counter electrode layer and the FTO substrate, the work function and electron binding energy of graphene oxide nanosheets exert their influence on the PV performance.

4.6 Photocurrent-Voltage ($I-V$) Characteristics of Different Electrodes:

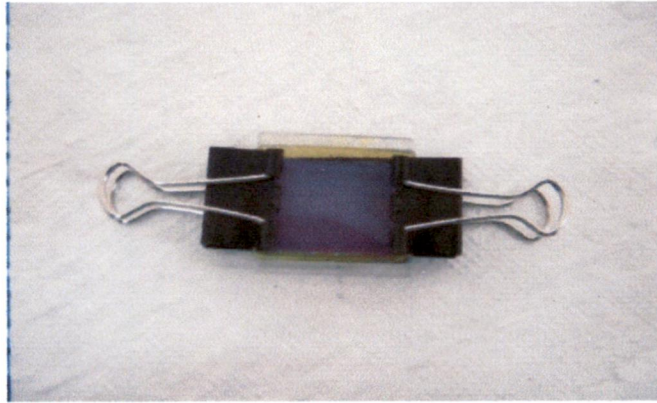


Figure 4.14: a) Photograph of Dye sensitized solar cell fabricated in lab and b) Photograph of solar cell testing in sunlight.

As discussed in UV-vis Absorption study, 0.03 % GO amount in active layer with TiO_2 was showing an increased absorption in visible light and was also showing good stability in UV-vis region as compared to other composites. The thickness of all of the different electrodes is assumed to be same and the efficient area of the device is 1cm^2 .

The concentration of TiO_2 was kept constant at 1 mg/cm^2 while amount of graphene was varied.

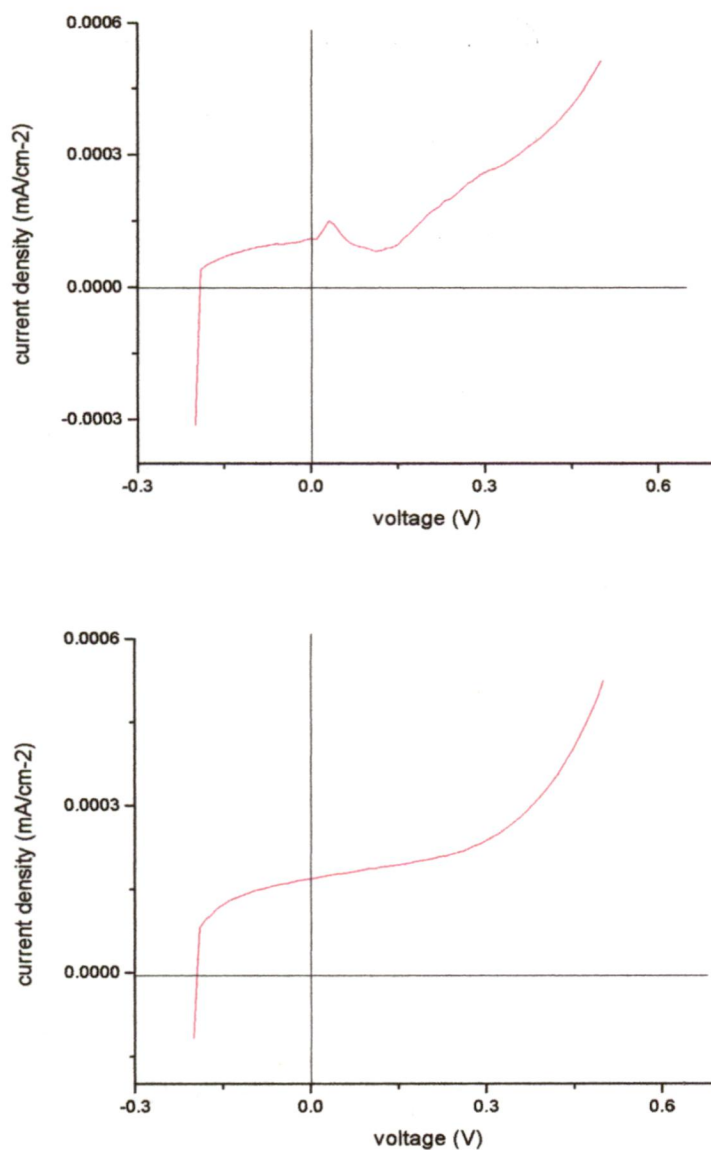


Figure 4.15: a) Photocurrent J–V characteristics of DSSCs with TiO_2 and b) TiO_2 -Graphene oxide electrodes with carbon as counter electrode.

We probed the photocurrent generation of tin dioxide coated glass/Graphene oxide- TiO_2 thin films by employing the films as the photoanodes in the operation of a photoelectrochemical cell. Photocurrent measurements were performed with 0.5M

Potassium iodide mixed with 0.05M iodine in water free ethylene glycol as the electrolyte and traditional carbon electrode as counter electrode was fabricated.

The photocurrent action spectra recorded on the tin dioxide coated glass /Graphene oxide-TiO₂ is shown in Figure 4.15. Upon irradiation with UV light, TiO₂ particles undergo charge separation to yield electrons (e⁻) and holes (h⁺). Without anodic bias introduced to the system, these electrons are collected by the electrode and flow through the circuit generating photocurrent. Photocurrent of 0.5 μA was obtained on the pure TiO₂ thin films. The photocurrent response was rapid and reproducible during repeated on/off cycles of illumination. Interestingly, we observed a significant increase in photocurrent generation to achieve 1.0 μA while 0.03 % of graphene oxide was added to the TiO₂ thin films. Although increasing the loading of graphene to the TiO₂ thin films gradually decrease the photocurrent, existence of graphene in overall enhances the photocurrent generation. As shown in earlier study, the electrons generated in excited TiO₂ nanoparticles are conveniently transferred to graphene oxide to induce the reduction of graphene oxide to reduced graphene sheets. Owing to the restoration of π network within the carbon structure by the reduction reaction, electrons stored in graphene sheets are greatly mobile leading to the acceleration of the charge transportation from graphene oxide-TiO₂ nanocomposites to the collecting electrode surface.

However, at higher loading of graphene as the color of thin films turns darker, light harvesting of TiO₂ is obstructed by graphene. Therefore, increasing graphene oxide content in the thin films gradually decreases the photocurrent generation.

Photoelectrochemical performance measurement was carried out, where the loading amount of graphene oxide is 0.03 % with P25 in the thin films as active electrode and graphene oxide as counter electrode in DSSC was fabricated for comparison.

Previous studies have shown that a counter-electrode usually affects the performance of cell in three aspects. The first is the electrical property or sheet resistance. The second is the electrochemical property or catalysis efficiency, which is usually determined by the inverse of charge transfer resistance. The last, is the optical property or reflection of illumination.

The tin dioxide coated base cell containing P25 as active electrode and graphene oxide as counter electrode gave an (I_{sc}) of $0.5 \mu A$ and a voltage (V_{oc}) of $0.16 V$, as shown in Figure 4.16 a). As shown in Figure 4.16 b), a short-circuit current density of (I_{sc}) $1.9 \mu A$ and an open-circuit voltage of (V_{oc}) $0.3 V$ were obtained for cell module containing graphene oxide-P25 as active electrode and graphene oxide as counter electrode.

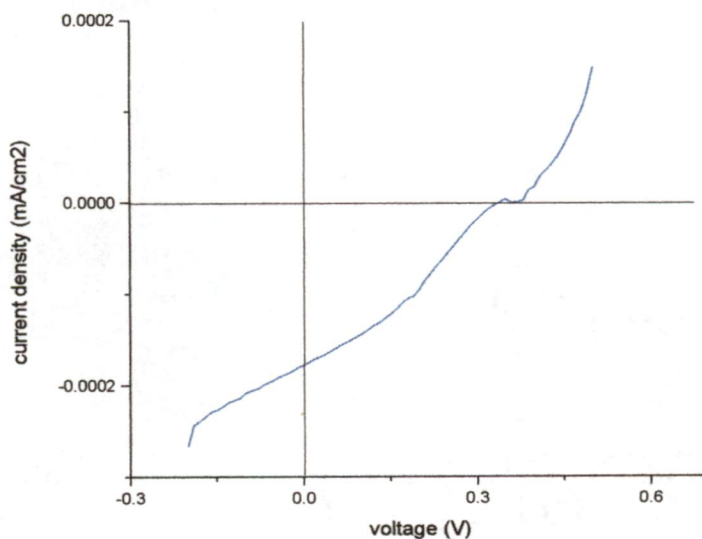
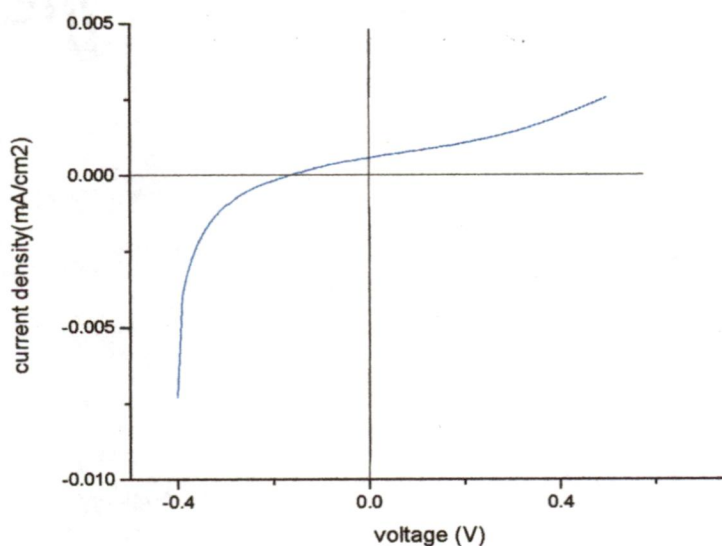


Figure 4.16: a) Photocurrent J–V characteristics of DSSCs with P25 electrode and b) P25-Graphene oxide electrodes with graphene oxide as counter electrode.

Both devices showed very comparable performance. Our work demonstrated that graphene oxide nanosheets are a very promising counter-electrode material for DSSC. Nevertheless, the preparation of graphene oxide involves simple and less no of processing steps. The fabrication of photovoltaic cells is also a multistage process. Thus it is very important to eliminate as many sources of potential contamination as possible during these multi-step processes. Impurities or defects would act as the recombination centers, which might increase the dark current so as to decrease the fill factor of the device. Moreover, it was found that graphene oxide nanosheets easily aggregated due to their nanometer thicknesses. The aggregation would reduce the electrochemical catalytic activity towards reduction of tri-iodide ions, resulting in the increase of the dark current too. The improved purity and dispersion ability of graphene oxide materials can expect to increase the fill factor. Enhancing fill factor can significantly increase the efficiency of graphene oxide based DSSC. On the other hand, the efficiency of graphene oxide based DSSC can be improved further by raising the purity of other raw materials, substituting GO as graphene and optimizing device architectures that enhance light absorption and facilitate electron transport.

Chapter 5

Conclusions and Future works

In summary, 2D graphene oxide has good potential, and we introduced it into both nanocrystalline anode and cathode of DSSC successfully.

- Incorporation of Graphene oxide in active electrode with TiO_2

After introducing GO in fabrication of active electrode, the conversion efficiency of DSSC increases significantly in comparison to the cell using TiO_2 alone as an active electrode, while using carbon as a counter electrode.

- Graphene oxide as a counter electrode

The conversion efficiency of DSSC increases highly when active electrode consisted of graphene oxide-P25 in comparison to the cell using P25 only as active electrode, while graphene oxide was used for making counter electrode in both the cells.

This may be due to a lower recombination and a faster electron transport with the introduction of graphene oxide chiefly. Also, the higher light scattering is a benefit to a certain extent. This study proved that the 2D charge carriers have more advantages than the 1D material, such as compactly an anchoring and homogeneous dispersion. The incorporation of 2D nanomaterial with 0D nanoparticles can also be extended to other

electronic devices, especially using graphene oxide as an electron acceptor and charge transfer medium.

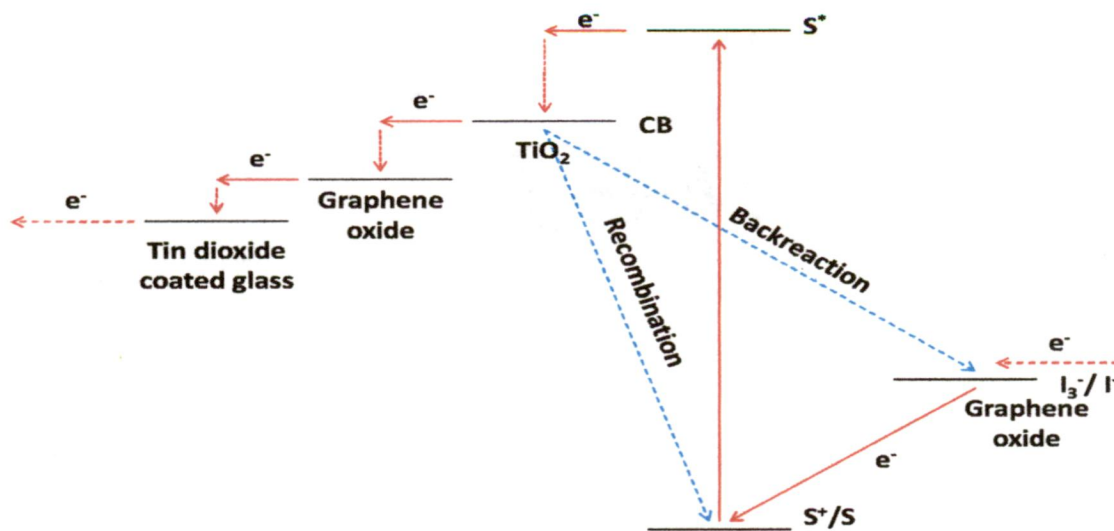


Figure 5.1: Operational principle of the device: the introduced 2D graphene oxide bridges perform as an electron acceptor and transfer the electrons quickly. Hence, the recombination and back reaction are suppressed.

In further works DSSC is very likely to show increment in photo-conversion efficiency when we introduce highly conducting graphene as an active electrode and also as a counter electrode, in conjunction with more efficient commercial Dyes like N719 and better electrolyte solution.

TiO₂ costs around \$2.20 for a kg. The same amount of silicon costs around \$60. Graphene oxide when introduced in the both photoanode and counter electrode, can aid large scale production at low cost. It may help in remarkable reduction of prize in DSSC, while not compromising on efficiency. The advantages of our approach include cheap, abundant carbon resources and simple fabrication procedures.

Bibliography

1. K. Zweibel, *Harnessing Solar Power, The Photovoltaic Challenge*, Plenum Press, New York, (1990).
2. B. O'Regan and M. Gratzel, A Low Cost, High-efficiency Solar Cell Based on Dye Sensitized Colloidal TiO₂ Films, *Nature*, 353, 737 (1991).
3. M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphrybaker, E. Mueller, P. Liska, N. Vlachopoulos and M. Gratzel, Conversion of Light to Electricity by cis-X₂ Bis(2, 2 bipyridyl-4, 4 dicarboxylate) ruthenium (II) Charge Transfer Sensitizers (K=Cl⁻, Br⁻, I⁻, CN⁻, and SCN⁻) on Nanocrystalline TiO₂ Electrodes, *J. Amer. Chem. Soc.*, 115, 6382 (1993).
4. G. P. Smestad, C. Bignozzi and R. Argazzi, Testing of Dye Sensitized TiO₂ Solar Cells I & II, *Solar Energy Materials and Solar Cells*, 32, 259-273 (1994).
5. A. Hagfeldt and M. Gratzel, Light-Induced Redox Reactions in Nanocrystalline Systems, *Chem. Rev.*, 95, 49 (1995).
6. A. De Vos, *Endoreversible Thermodynamics of Solar Energy Conversion*, Oxford Science Publishers, Oxford, P. 90-104, P. 150-160 (1992).
7. L. Schipper, S. Meyer, R. Howarth and R. Steiner, *Energy Efficiency and Human Activity: Past Trends, Future Prospects*, Cambridge University Press., Cambridge, 7-35 (1997).
8. G. Meyers, Efficient Light to Electrical Energy Conversion, Nanocrystalline TiO₂ Films Modified with Inorganic Sensitizers, *J. Chem. Educ.*, 74, 652 (1997).
9. P. Ball, *Made to Measure, New Materials for the 21st Century*, Princeton University Press, Princeton, NJ, 244-281 (1997).
10. N. Cherepy, G. P. Smestad and M. Gratzel and J. Z. Zhang, Ultrafast Electron Injection: Implications for a Photochemical Cell Utilizing an Anthocyanin Dye-Sensitized TiO₂ Nanocrystalline Electrode, *J. Phys. Chem. B.*, 101, 9342 (1997).
11. G. P. Smestad and M. Gratzel, Demonstrating Electron Transfer and Nanotechnology, A Natural Dye Sensitized Nanocrystalline Energy Converter, *J. Chem. Educ.*, 75, 752 (1998).

12. E. Thimsen, N. Rastgar, P. Biswas, Nanostructured TiO₂ films with controlled morphology synthesized in a single step process: performance of dye-sensitized solar cells and photo watersplitting, *J. Phys. Chem.*, 112, 4134 (2008).
13. K.M. Lee, C.Y. Hsu, W.H. Chiu, M.C. Tsui, Y.L. Tung, S.Y. Tsai, K.C. Ho, Dye sensitized solar cells with a micro-porous TiO₂ electrode and gel polymer electrolytes prepared by in situ cross-link reaction, *Sol. Energy Mater. Sol. Cells*, 93, 2003 (2009).
14. G.D. Sharma, P. Suresh, M.S. Roy, Effect of surface modification of TiO₂ on the photovoltaic performance of the quasi solid state dye sensitized solar cells using a benzothiadiazole-based dye, *J. Power Sources*, 195, 3011 (2010).
15. AZoNano, Graphene Oxide – Properties and Practical Applications, (2011)
16. W. Hummers and R. Offema, Preparation of graphitic oxide, *J. Am. Chem. Soc.*, 80(6), 1339 (1958).
17. M. Hirata, T. Gotou and M. Ohba, Thin-film particles of graphite oxide, Preliminary studies for internal micro fabrication of single particle and carbonaceous electronic circuits. *Carbon*, 43(3), 503-510 (2005).
18. T. Szabo, O. Berkesi and I. Dekany, DRIFT study of deuterium-exchanged graphite oxide, *Carbon*, 43(15), 3186-3189 (2005).
19. A. Lerf, H. He, M. Forster and J. Klinowski, Structure of graphite oxide revisited. *J Phys Chem B*, 102(23), 4477-4482 (1998).
20. A. Lerf, H. He, T. Riedl, M. Forster and J. Klinowski, ¹³C and ¹H MAS NMR studies of graphite oxide and its chemically modified derivatives, *Solid State Ionics*, Pt. 2, 857-862 (1997).
21. M. R. Tarasevich, E. I. Khrushcheva, *Modern aspects of electrochemistry*, 2nd ed., New York, Plenum, 19, (1989).
22. K. Imoto, K. Takahashi, T. Yamaguchi, T. Komura, J. Nakamura, K. Murata, High-performance carbon counter electrode for dye-sensitized solar cells, *Sol. Energ. Mat. Sol.*, 79, 459-469 (2003).
23. K. Suzuki, M. Yamaguchi, M. Kumagai, S. Yanagida, Application of carbon nanotubes to counter electrodes of dye-sensitized solar cells, *Chem. Lett.*, 32, 28-29 (2003).

24. D. W. Zhang, X. D. Li, S. Chen, F. Tao, Z. Sun, X. J. Yin, Fabrication of double-walled carbon nanotube counter electrodes for dye-sensitized solar cell, *J. Solid State Electrochem.*, 14(9), 1541-1546 (2010).
25. K. Lee, S. H. Hwang, J. H. Moon, K.S. Noh, D. Y. Lee, D. H. Kim, Multi-walled carbon nanotubes as a counter electrode of dye sensitized solar cells, *Technical Digest of the International PVSEC-17, Fukuoka, Japan*, 6P, 6-11 (2007).
26. S. S. Stankovich, D. A. Dikin, R.D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T.Nguyen, R. S. Ruoff, Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide, *Carbon*, 45, 1558-1565 (2007).
27. H. Yamaguchi, G. Eda, C. Mattevi, H. Kim, M. Chhowalla, Highly uniform 300mm wafer-scale deposition of single and multilayered chemically derived graphene thin films, *ACS., Nano.*, 4, 524-528 (2010).
28. G. Eda, G. Fanchini, M. Chhowalla, Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material, *Nature Nanotech*, 3, 270-274 (2008).
29. R. J. W. E. Lahaye, H. K. Jeong, C. Y. Park, Y. H. Lee, Density functional theory study of graphite oxide for different oxidation levels, *Phys., Rev. B*, 79 (2009).
30. S. Saxena, T. A. Tyson, E. Negusset, Investigation of the local structure of graphene oxide, *J. Phys. Chem. Lett.*, 1, 3433-3437 (2010).
31. W. C. Hung, Y. C. Chen, H. Chu, T. K. Tseng, Synthesis and characterization of TiO₂ and Fe/TiO₂ nanoparticles and their performance for photocatalytic degradation of 1,2-dichloroethane, *Applied Surface Science*, 255, 2205-2213 (2008).

Conference proceedings:

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4. **Attended International conference and workshop** on nanostructured ceramics and other nanomaterials at DU, Delhi during 13-16 March 2012.