

Some Studies On Cost Efficient Solar Cells

Thesis submitted in partial fulfilment of the requirements for the award of the degree
of

Master of Technology in VLSI Design & Microelectronics Technology

by

Anubhujyoti Dey

Examination Roll No: M6VLS22018

Class Roll No: 001910703019

Registration No.: 150146 of 2019-2020

Under the Esteemed Guidance of

Prof. Subir kumar Sarkar

DEPARTMENT OF ELECTRONICS AND TELE-COMMUNICATION ENGINEERING

JADAVPUR UNIVERSITY, KOLKATA - 700032, WEST BENGAL, INDIA

June 2022

DECLARATION OF ORIGINALITY AND COMPLIANCE **OF ACADEMIC ETHICS**

I hereby declare that the thesis entitled “ **Some Studies On Cost Efficient Solar Cells**” Submitted by me, for the award of the degree of Master of Technology in VLSI and Microelectronics to Jadavpur University is a record of bonafide work carried out by me under the supervision of guide Professor. Subir kumar Sarkar.

I further declare that the work reported in this thesis has not been submitted and will not be submitted, either in part or in full, for the award of any other degree or diploma in this institute or any other institute or university.

Place: Kolkata

Date: 28/6/2022

Anubhujyoti Dey

Signature of the candidate

Faculty of Engineering and Technology,
Jadavpur University
CERTIFICATE

This is to certify that the work contained in this thesis entitled "**Some Studies On Cost Efficient Solar Cells** " is a bonafide work of **Anubhujyoti Dey (Exam Roll No: M6VLS22018; Class Roll No: 001910703019; Registration No.: 150146 of 2019-2020)**, carried out in the Department of Electronics and Telecommunication Engineering, Jadavpur University, Kolkata under my supervision and that it has not been else where for a degree.

GUIDE

Prof. Subir kumar Sarkar
Jadavpur University, Kol-700032

Prof. Ananda Shankar Chowdhury

Head of the Department

Department of ETCE,
Jadavpur University, Kol-700032

Prof. Chandan Majumdar

Dean

Faculty Council of Engg. & Tech. (FET),
Jadavpur University, Kol-700032

**Faculty of Engineering and Technology,
Jadavpur University**

CERTIFICATE OF APPROVAL*

*This is to certify that the Master Thesis entitled " **Some Studies On Cost Efficient Solar Cells** " is hereby approved as a creditable study of an engineering subject carried out and presented in a manner satisfactory to warrant its acceptance as pre-requisite to the degree for which it has been submitted. It is understood that by this approval the undersigned do not necessarily endorse or accept every statement made, opinion expressed, or conclusion drawn therein but approve the thesis only for the purpose for which it has been submitted.*

**Committee on Final
Examination for Evaluation of
the Thesis**

Examiners

*Only in case the thesis is approved

ABSTRACT

Dye sensitized solar cells are well known as a cost-effective photovoltaic device because of inexpensive materials and simple fabrication process. Dye-sensitized solar cells are composed of titanium oxide (TiO_2) semiconductor which is commonly used as a paint base in pigment industry, and the dye sensitizer that can be extracted from a variety of natural resources with minimum costs. In addition, carbonaceous materials could be used to replace platinum catalyst which can further reduce the material cost. As such, DSSCs are easy to fabricate since they are insensitive to environment contaminants and process able at ambient temperature. These unique features are favoured in roll-to-roll process which is a continuous, low-cost manufacturing method to print dye-sensitized solar cells on flexible substrates. Furthermore, DSSCs work better even during darker conditions, such as in the dawn and dusk or in cloudy weather. Such capability of effectively utilizing diffused light makes DSSCs an excellent choice for indoor applications like windows and sunroof. In my project I have prepared solar cells using three different dye extracted from flower of colour red blue and 3rd is combination of both colour. I have studied all electrical parameter like current, voltage, Fill factor and efficiency of the prepared sample

ACKNOWLEDGEMENT

I would like to profusely thank my guidance Prof. Subir Kumar Sarkar for his patience , enthusiasm, motivation and guidance . I attribute the level of my Masters degree to his encouragement and without his guidance with immense knowledge and experience in research, my thesis would not have been completed or written .

CONTENT

1. CHAPTER 1: Introduction to dye sensitized solar cell

1.1 Background

1.2 Dye Sensitized Solar Cell

2. CHAPTER 2: Literature Review

2.1 Review of Dye sensitized solar cell

3. CHAPTER 3: Theory

3.1 General theory of solar cell.

3.2 Power conversion efficiency of photovoltaic devices

3.3 Theory of dye sensitized solar cell

3.3.1 Function of dye

3.3.2 Function of MOS

3.3.3 Function of electrolyte

3.3.4 Function of electrodes

3.4 Working principle of dye sensitized solar cell

3.5 Trap state

4. CHAPTER 4: Fabrication and characterization of Dye sensitized solar cell.

4.1 Dye preparation

4.1.2 Dye from hibiscus and Clitoria ternetia

4.2 Result of fabricated dye sensitized solar cell.

5. CHAPTER 5: Conclusion

Future Scope

Reference

CHAPTER 1

Introduction

1.1 Background

The future supply of fossil fuels won't be enough to meet the rapidly rising global energy demand [1]. As sediment and rock layers accumulated throughout time, fossilised plants and animals were compacted into fuels like coal and oil. These energy sources have an impact on the environment since they produce pollution. The carbon dioxide that is released into the atmosphere when fossil fuels are burned causes the ozone layer, a layer of greenhouse gases that covers the whole planet, to expand [2]. This ozone layer absorbs heat from the sun to keep the world from freezing over. The ozone layer will trap too much heat if it thickens too much, which will lead to droughts and extremely hot weather. The biggest issue in solar power is its power conversion efficiency to cost ratio for bigger area PV. The theoretical maximum efficiency which is also known as Shockley-Queasier limit. For a single junction mono crystalline silicon cell found to be 32.9% [4]. But when practical efficiency is taken into consideration it is only 25%, due to practical losses like junction loss, contact loss, recombination loss and near band gap absorption losses [5]. The cost of extraction of crystalline silicon, and wafer processing are also not economical when compared to grid based energy source. Crystalline silicone solar cells need great purity silicon as substrate and which require many refined vacuum processing stages for manufacture. It also requires high temperature for doping impurities which limit their application in low cost solar cells.[6]. Now a day PV production is divided into mono crystalline and poly crystalline silicon cells[7].Photovoltaic technologies have also matured to the stage of elaboration and implementation of the 3rd generation solar cells based on “high performance and low cost” products.

The biggest issue in solar power is its power conversion efficiency to cost ratio for bigger area PV. The theoretical maximum efficiency which is also known as Shockley-Queasier limit. For a single junction mono crystalline silicon cell found to be 32.9% [4]. But when practical efficiency is taken into consideration it is only 25%, due to practical losses like junction loss, contact loss, recombination loss and near band gap absorption losses [5]. The cost of extraction of crystalline silicon, and wafer processing are also not economical when compared to grid

based energy source. Crystalline silicon solar cells need great purity silicon as substrate and which require many refined vacuum processing stages for manufacture. It also requires high temperature for doping impurities which limit their application in low cost solar cells.[6]. Now a day PV production is divided into mono crystalline and poly crystalline silicon cells[7].Photovoltaic technologies have also matured to the stage of elaboration and implementation of the 3rd generation solar cells based on “high performance and low cost” products.

1.2 Dye Sensitized Solar Cell

In comparison with high-cost conventional silicon solar cells, dye sensitized solar cells are well known as a cost-effective photovoltaic device because of inexpensive materials and simple fabrication process. Dye-sensitized solar cells are composed of titanium oxide (TiO₂) semiconductor which is commonly used as a paint base in pigment industry, and the dye sensitizer that can be extracted from a variety of natural resources with minimum costs. In addition, carbonaceous materials could be used to replace platinum catalyst which can further reduce the material cost. As such, DSSCs are easy to fabricate since they are insensitive to environment contaminants and processable at ambient temperature. These unique features are favored in roll-to-roll process which is a continuous, low-cost manufacturing method to print dye-sensitized solar cells on flexible substrates. Furthermore, DSSCs work better even during darker conditions, such as in the dawn and dusk or in cloudy weather. Such capability of effectively utilizing diffused light makes DSSCs an excellent choice for indoor applications like windows and sun roof.

The advantages of dye-sensitized solar cells paved the way for intensive research interest, which had reflected a tremendous increase in the number of publications in the past decade. Though the seminal work on dye-sensitized solar cells (DSSCs) was initiated in 1991 by O'Regan and Grätzel, the research has advanced at a rapid pace and a considerable amount of work has been made to improve the device efficiency from 7.1% in 1991 to 13% in 2014, a level deemed as necessary for commercial use. In this work, the current state-of-art on DSSCs including modeling, and critical technologies are reviewed. The interested readers could also refer to our previous review on fundamental concepts and novel materials used in DSSCs including panchromatic dyes, semiconductor photo anode, counter electrode, and electrolyte

development for a complete understanding of the processes and parameters controlling their photovoltaic operation. Besides, recent reviews detailing material development on all key components in DSSC have provided important pathways towards better device performance. A brand-new technology that has garnered a lot of interest recently is the dye-sensitized solar cell. The only solar cell that replicates the charge separation process in photosynthesis is a dye-sensitized solar cell, which is the first photovoltaic device to use a three-dimensional junction to convert sunlight to energy. The green leaf, which stacks its thylakoids membranes so that the light can reach many molar layers of chlorophyll before it is extinguished, served as inspiration for the development of the dye-sensitized solar cell. In this solar cell, a similar trick is employed, but instead of stacking thylakoids, we are using nano-sized titanium particles. Solar cells with dye-sensitization.

Dye has a significant role in absorbing sunlight and turning it into electricity among all the essential components used in dye-sensitized solar cells. Because the manufacture of the ruthenium (Ru) complexes utilised in the majority of industries is difficult, natural dye is employed in DSSC. An excellent dye must be able to inject electrons into semiconductor materials and have a wide absorption spectrum. Anthocyanin and chlorophyll, two types of natural pigment obtained from flowers, have the aforementioned outstanding characteristics [26]. Chlorophyll absorbs light in the range of 430–662 nm, whereas anthocyanin does so in the range of 450–600 nm [26]. The hydroxyl group acts as an anchoring agent in anthocyanin and carbonyl, allowing the pigment to adhere to TiO_2 nanostructures [27].

Summary of literature review

A perfect solar cell material must have strong and broad optical absorption, quick charge carrier transit, little energy needed for exciton separation, and low recombination rates.

Making efficient and affordable photovoltaic systems is possible by studying the qualities of the solar cell material and using advanced engineering to regulate those properties.

CHAPTER 2

Literature Review

Review of Dye sensitized solar cell

Because of its record cell efficiency of above 10%, the dye-sensitized solar cell, created in the 1990s, is a novel solar electric technology that has received a lot of interest. The technology is reviewed, new research findings and methodologies are discussed, and the dye-sensitized solar cell is evaluated in comparison to current conventional solar electric technologies. This thesis also discusses a recent symposium attended by many of the world's leading experts on dye solar cells. The dye solar cell has the potential to compete with current conventional power technologies and accessible solar electric technologies as a low-cost method of generating electricity. But because it is a relatively new technology, there are several obstacles in the way of becoming commercially viable. This evaluation suggests because of its potential. Current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF), and energy conversion efficiency are some of the measures used to evaluate a solar cell's electrical performance. In a photochemical cell, the principles of solar cell operation were initially uncovered. When the solar electric effect was discovered in the 1830s by the French scientist Becquerel, he referred to his invention as a "pile" or "cell" that generated an electric current when exposed to sun rays [2]. With two electrodes submerged in an electrolyte, Becquerel's solar cell was an electrolytic device whose current increased in response to light exposure. In order to separate this solar cell's behaviour from that of a thermocouple, Becquerel noted that solar radiation, not solar heating, caused

However, photovoltaics, or PV, is the term used for many years by technologists in the field. In either case, PV or solar electricity is one of the renewable energy technologies because the sun is a non depletable resource. Yet PV is not the best name for the technology, especially when describing it to the general public. There are even some technical inaccuracies with the term. While photo refers to light, volt ignores the fact that amperes are also part of electricity. Strictly speaking, it is the sunlight that produces the amperes of electric current. Also, power in watts is the product of voltage and amperes, so solar power is technically very accurate. Most of this paper will refer to solar electricity, solar electric technologies, solar electric power,

or solar power rather than PV. Photosynthesis, one of the most crucial and vital process of plants is carried out by Chlorophyll. It has ability to absorb sunlight and convert it into energy. It is green pigment that is present in all leaves of plants and absorption range of chlorophyll is within 430- 662 nm range. It has been widely studied by many researcher. Studies involve extraction of chlorophyll pigment from figs leaves and apricot leaves with highest absorption peak 413 nm and 394 nm, with short circuit current and open circuit voltage as $J_{sc}=2.09$ mA/cm², $V_{oc}=0.60$ V and $J_{sc}=0.52$ mA/cm², $V_{oc}=0.62$ V and efficiency of 0.64%., 0.26% respectively. Cream leaves chlorophyll were also extracted for research and got the electrical performance as the $J_{sc}=2.28$ mA/cm², $V_{oc}=0.61$ V, FF=0.44 and energy conversion efficiency of 0.64%. [35]. Leaves of *Zizyphus* and *Azadirachta indica* were experimented for pigment extraction and tested as dye sensitizer, they showed J_{sc} , V_{oc} FF as $J_{sc}=1.50$ mA/cm², $V_{oc}=0.68$ V, FF =0.40 and $J_{sc}=0.43$ mA/cm², $V_{oc}=0.40$ V, FF=0.40. The energy conversion efficiency of *Zizyphus* leaves was recoded as 0.40% and the energy conversion efficiency of *Zizyphus* leaves was recoded as 0.72%. The highest absorption peak of *Zizyphus* leaves was at 432 nm and 664 nm whereas the highest absorption peak of *Azadirachta indica* leaves 471 nm and 662 nm.[35]. General presentation of chlorophyll pigments the dye extracted from leaves of *Azadirachta indica* showed good performance when compared with others with power conversion efficiency of 0.72%. Beside anthocyanin and chlorophyll, betalain pigments are also one of the most favorable dye sensitizer in DSSC. Betalain have favorable light absorption and have the carboxylic (COOH) functional group that allows it to bind with TiO₂ as shown in Fig. 4. Additionally, betalain has a larger oxidation potential, which improves its ability to interact with the iodine/iodide redox pair. Another kind of dye sensitizer utilised in DSSC is betalain. This is another worthy contender for a dye sensitizer, in addition to anthocyanin and chlorophyll. The carboxylic group acts as an anchoring agent to connect the dye molecule to the semiconductor, and its absorption peak is within the region of 450 to 650 nm. It has a higher oxidation potential than anthocyanin and chlorophyll, and as a result, it forms a strong network with electrolyte. This pigment has a strong absorption range between 400 and 600 nm. According to studies, the betalain pigment that was derived from purple wild Sicilian displayed the greatest results, with an energy conversion efficiency of 2.06 percent. Other electrical performance included short circuit current, open circuit voltage, and fill factor, which were computed as $J_{sc}=8.80$ mA/cm², $V_{oc}=0.39$ V, and FF=0.60 [50]. The 450 nm range was the absorption peak. The red bougainvillea glabra bloom displayed an absorption peak in the 480–650 nm range[36], with a 0.98 percent energy conversion efficiency. While the open circuit voltage and short circuit current are 3.72 mA/cm² and 0.44 V, respectively, with a 0.59 fill factor. The

efficiency of the red turnip plant, which was also tested for DDSC, was 1.7 percent, which was fairly high. More than a dozen of the most renowned scientists and creators of the dye-sensitized solar cell presented their work at the symposium. Finding research organisations that have advanced the technology is one part of a technology assessment from the standpoint of a government programme. The possibility for advancement through additional research is another factor. The vital dye solar cell research being conducted throughout the world was highlighted at the ECS conference, which was cosponsored by DOE and NREL. From among more than 70 presenters at the Thirteenth International Conference on Photochemical Conversion and Storage of Solar Energy, which took place in Snowmass, Colorado, in August 2000, the researchers who were invited to the dye-cell session of the ECS symposium were chosen.. Of the more than 300 presentations at the conference, the dye-sensitized solar cell presentations made up a sizable chunk. The discussion of research findings from the ECS conference that follows is organised by group rather than by technical concerns. The most well-known research team at the symposium is EPFL, which is based in Lausanne, Switzerland. It has roughly 20 researchers under the direction of Michael Grätzel. The United States Air Force Research Laboratory is one of the financing sources for EPFL. The ground-breaking dye-sensitized solar cell study was first published in 1991 by Grätzel and O'Regan, as was previously reported. Their early research was inspired by a fascination in synthetic photosynthesis or biomimicry. Chlorophyll, a molecule with a core magnesium atom encircled by a nitrogen-containing porphyrin ring, serves as the model for an energy-absorbing pigment that is produced by nature. A similar structure in blood, haemoglobin, an iron-containing oxygen-carrying molecule, serves to highlight the significance of the chlorophyll structure in nature. Although the main pigments found in nature are limited to magnesium and iron, other metallic elements can be added to manufactured porphyrin colours. In order to sensitise titanium dioxide, Clark and Suttin utilised a tripyridyl ruthenium complex in 1977, but because the dye was in solution, charge transfer was incredibly ineffective [7]. The concept of using an acid carboxylate group to attach the dye to the metal oxide surface first surfaced in 1980 [7]. By injecting electrons, this bonding promoted charge transfer. In contrast to competing recombination processes, it is now understood that an electron moves from the dye molecule through the bridge carboxylate group to the semiconductor substrate within picoseconds. $\text{RuL}_2(\text{NCS})_2$ (L=bipyridyl), sometimes known as "N3" since it was Nazeeruddin's third dye experiment at EPFL, is one of the most successful dye compounds studied over the previous ten years. According to NREL testing in air-mass (AM) 1.5 sunlight, EPFL has the highest dye cell efficiency record (10.4 percent) [7]. It also led to the creation of the most advanced black

dye, L2, which adds a thiocyanate group and reduces the bis-bi-pyridyl ligand system to ter-pyridyl. The infrared and visible regions of the black dye's spectral sensitivity are both close to the ideal absorption edge position (1.4 eV) for optimum solar energy conversion. By using an appropriate salt, the bonding of the Ti ion to the carboxylate group of the dye has also been improved, enabling higher temperature thermal treatments during manufacture for ensuing bonding, sealing, and curing procedures. Recent research from EPFL investigates a novel configuration known as a sensitised nanostructured heterojunction, in which n-type nano crystalline titanium dioxide is in contact with an organic p-type semiconductor. Due to the electric field of the heterojunction, this novel configuration might improve electron transit and even electron injection. And the liquid electrolyte's role as a positive charge conductor is taken up by the organic semiconductor. The group has licenced their technology to at least eight businesses and is therefore aware of its potential for commercialization. The device's lifetime is a significant commercialization concern. The long-term stability of the gadget has been studied and improved by the EPFL group. The system has been able to pass required stability certification tests for outdoor applications, including thermal stress for 1000 hours at 85°C, with adequate cell sealing and the addition of suitable solvents in the electrolyte formulation. For a relatively new solar electric technology, the predicted lifetime is currently greater than 10, which is fairly respectable.

Lawrence Peter is in charge of the University of Bath's research project. The peculiar transport characteristics that set dye cells apart from traditional solid-state devices were fully covered in their presentation [9]. For instance, ion transport, a somewhat slow mechanism that results in ionic diffusion transit times of the order of 0.1 s, is used to move charge in the electrolyte phase. To develop more effective dye cells, this research, however, relies on understanding electron charge transit, trapping, and recombination. The University of Bath research discovered that at AM 1.5 illumination, the diffusional transit time for electrons in a typical 10-m thick titanium dioxide layer is of the order of milliseconds due to remarkably small electron diffusion coefficients, but 100 s at seven orders of magnitude lower light intensity. It is astonishing, as they point out in their study, that an effective solar cell can be built on a system with such slow charge transfer. A decrease in cell efficiency that is considerably smaller than may be anticipated at low light intensities is partially explained by the fact that electron lifespan increases with decreasing light intensity. From a different angle, the dye cell operates well in low light conditions, opening doors for the development of indoor applications.

This study of photo voltage decay followed by short-circuit extraction of remaining electron charge permits the derivation of information about trapped electron charge and its

corresponding trap distribution. Electrons are evidently trapped at levels in the bandgap, and the assumption is that these levels are associated with surface states present at the high internal surface area of the nano crystalline oxide ($\approx 100 \text{ m}^2/\text{g}$). These levels are responsible for the retardation of electron transport that is characteristic of dye cells in that diffusion takes place through electron trapping and de trapping processes. In two types of sensitive nano crystalline films, interfacial charge separation and charge recombination have been studied experimentally, according to a team from Emory University led by Professor Tianquan Lian [10]. The National Science Foundation and the DOE's Office of Science provided funding for their studies (NSF). One class consists of the nanocrystalline dye-sensitized wide-bandgap semiconductor films utilised in Grätzel solar cells. For fully solid-state cells, the second one includes conjugated polymer/nanocrystalline thin-film composites (the MEH-PPV is also the hole transporter). They conducted tests on their own samples of MEH-PPV/SnO₂ and compared the results with those performed on their TiO₂, SnO₂, and ZnO dye-sensitized nanocrystalline thin films. Their experimental results show that for both systems, charge separation can be very rapid and efficient (some 300 ps), whereas charge recombination is much slower (microseconds). For example, for MEH-PPV/TiO₂, the electron transfer is believed to be substantially faster than the rate of polymer exciton decay because transfer has been demonstrated and the polymer photoluminescence is quenched. The Emory technique, using femtosecond mid-infrared (IR) spectroscopy, leads to direct monitoring of injected electrons and substantiates this belief. The comparison is intriguing because they have shown that subpicosecond electron injection from dye to semiconductor is possible with a favorable electronic coupling of the electron-donating and -accepting orbitals and/or a large density of accepting states. But for the MEH-PPV nanocrystalline films, the electron injection is just as fast, yet there are no covalent linkages between MEH-PPV and the SnO₂. The fast charge separation and slow recombination results, like those in dye-sensitized nanoporous films, show that conjugated polymer/inorganic semiconductor nanoporous film composites have promise for solar electricity production.

Chem Motif, a small business headed by Mark Spitler in Concord, Massachusetts, has been funded by the DOE's Small Business Innovative Research program for research and development of dyes for the dye-sensitized solar cell. The company explored the use of different cyanine dyes and made devices with higher short-circuit photocurrents than those of cells using the well-known N3 dye [11]. The trade-off between broad-band absorption and extinction coefficient for a single dye like N3 leads to slightly thicker titanium dioxide films (10 μm) than could be achieved with aggregates of dyes needing only a 4- μm film thickness.

High extinction coefficients for monomer dyes, such as rhodamine, oxazine, thiazine, and cyanine, are associated with very narrow absorption bandwidths. ChemMotif tried to circumvent this obstacle by using aggregates of organic dyes with high absorption over a greater portion of the spectrum. Their work focused on the use of different carboxylated cyanine dyes. They measured absorbance versus wavelength for 14 dyes and their combinations by exploring the structure of the tether of the dye to the titanium dioxide, the terminal heterocycle on the chromophore, the length of the methine bridge, and substituents on the molecule. Some dye pairs did not mix and appeared to collect in different regions on the nanocrystalline surface. They observed the degree of aggregation of the cyanine dyes on the surface to be highly dependent on the procedure for attaching the dyes to the titanium dioxide. An enlightening observation in their work is that some of their heterogeneous collections of dye molecules are used in photography in panchromatic films. This presentation hinted at the large number of dye molecules possibly beneficial to the dye solar cell concept and suggested that dye aggregates may be even more important.

The NREL group, under the leadership of both Arthur Nozik and Arthur Frank, is probably the strongest in the US. NREL presented three papers at the ECS symposium, two on electron transport and one on a new family of dyes [12], [13], [14]. The NREL team recently measured a preliminary 9.18% efficiency for a dye cell using a titanium dioxide film deposited by screen printing, possibly the highest efficiency by any group for films prepared by screen printing. This group has been jointly funded by DOE's Office of Science and Office of Energy Efficiency and Renewable Energy.

The NREL group has modeled electron transport using a random walk analysis [12]. In their introduction, they state that the reason transport of photo injected electrons in the TiO₂ occurs by diffusion is because of the absence of any electric field across the film due to screening by the electrolyte. The collection time for electrons is on the order of milliseconds, much slower than collection times in single-crystal titanium dioxide. The slow collection time is attributed to electrons undergoing many trapping–detrapping events in trap states believed to be on the surface, although the trap states could just as well be inside the nanoparticles. Another attribute of the dye cell system is the coupled motion of electrons and ions moving in opposite directions — ambipolar diffusion. A consequence of ambipolar diffusion is that a current can only be measured in the external circuit upon the arrival of charge carriers at the electrode; this is called an arrival current. Their modeling and corresponding experimental results support the concept of an arrival current, as well as multiple trap states with an exponential distribution [13]. This

experimental agreement suggests that even shallow traps, owing to their relative abundance, can contribute significantly to the overall transport kinetics.

Another NREL study described a new generation of perylene-based dyes that may make excellent photosensitizers of nano crystalline titanium dioxide [14]. Although the perylene dye cell efficiencies are low — about 1% — they are reported for the first time in this paper. Perylenes are inexpensive and durable dyes, which is important because the widely used N3 dye is presently quite expensive, more expensive per square meter than glass. Its high price is a consequence of its limited use only in the dye solar cell.

Caltech's group, led by Nathan Lewis, has been funded by the DOE's Office of Basic Energy Sciences, the NSF, and DuPont. They were recently awarded funding under NREL's Photovoltaics Beyond the Horizon program. Their presentation focused on electron-transfer dynamics using different transition elements, either Os or Ru, in the dye [15]. The dynamics in the dye cell span many orders of magnitude, from tens of femtoseconds to milliseconds, and require a combination of different techniques to study them. The group studied electron injection, charge recombination, and iodide oxidation for different Ru and Os sensitizers. Absorption involves promotion of an electron from the metal-based d orbitals to the bipyridyl-based π^* orbitals. Their work substituted different types of ligands for five sensitizers to explore the electron donation process, charge recombination, and sensitizer regeneration. They looked at oxidized sensitizer regeneration rates for different electrolytes. Charge recombination had higher rate constants for sensitizers having more negative M(III)/M(II) ground-state reduction potentials. Their study concludes that overlap between the solar spectrum and sensitizer absorption spectrum, although clearly important, needs to be considered in light of the importance to optimize sensitizer regeneration dynamics with respect to charge recombination when charge recombination is limiting cell performance.

The Imperial College group, under the direction of Professor James Durrant, reported on new measurements of recombination of photoinjected electrons directly with oxidized species in the redox electrolyte [16]. This work supplements their previous studies of recombination of the injected electrons directly with dye cations prior to their re-reduction by I^- . They measured the transient change of light absorption by their samples in response to a laser excitation source (337 nm) and under the varying experimental conditions. Their recent results show an influence of trapping and detrapping of electrons within the titanium dioxide particles on the kinetics of this recombination path between the photoinjected electrons and the electrolyte. Other studies have shown that electron transport in the nanocrystalline titanium dioxide is mediated by trapping in intraband defect states. The Imperial researchers observe two types of

recombination behavior, depending on the iodine concentration. In the low I_2 limit, they observe single-exponential kinetics, consistent with a scarcity of holes in the electrolyte. In the high concentration limit, they observe stretched-exponential behavior consistent with trap-limited electron diffusion within the titanium dioxide becoming the rate-limiting step.

STI, whose president and CEO is Gavin Tulloch, has worked with the EPFL group for several years and has licensed the EPFL technology. At the ECS symposium, STI announced construction of the world's first dye cell manufacturing facilities, funded mainly by private investors but partly by the Australian government [17]. Testing procedures are critical to the successful technology development of crystalline silicon modules, and STI wants to identify critical failure mechanisms pertinent to the dye cell. The STI presentation focused on the development of accelerated ultraviolet (UV) testing procedures for dye-sensitized solar cells for an initial product with a minimum warranty of 7 years. Their first product is expected to be an exterior building panel marketed as a solar wall panel. They identified UV radiation and elevated temperatures as the dominant stress factors for dye-sensitized cells and modules. They began tests with areas of 1 cm² and described plans for future testing of 100 m² panels. They found good solar cell durability with appropriate concentrations of iodine and lithium iodide in the electrolyte. Their 600-h temperature studies showed a surprising increase in dye cell performance with temperature. Specifically, they measured a 25% power increase between 30 and 65°C, with 80°C power still 15% higher than the baseline temperature power.

Johns Hopkins University group was funded by NREL for dye solar cell research soon after the 1991 discovery of the concept. Their recent work was funded by DOE's Office of Science and the NSF. They were recently awarded funding under NREL's Photovoltaics Beyond the Horizon program for a new solar cell concept based on molecular chromophores, antenna-like sensitizer molecules. Their ECS presentation described new approaches to increase the efficiency of the dye solar cell to 15%.

The Johns Hopkins group points out that if the spectral response of the dye solar cell can be increased to 1100nm, an efficiency of 20% has been predicted [18]. They discussed two approaches for optimizing the photocurrent by tuning the chromophoric ligands and/or the nonchromophoric ligands in the Ru(II) dye molecule (sensitizer) used in the most successful dye solar cells. The current state-of-the-art dye solar cell is composed of the coordination compound $\text{cis-Ru}(\text{dcbH}_2)_2(\text{NCS})_2$, where dcbH₂ is 4,4'-(CO₂H)₂-2,2'-bipyridine. This is the compound called N3. They point out that the metal-to-ligand charge-transfer (MLCT) absorption can be extended to longer wavelengths by appropriate substituent changes on chromophoric ligands. But moving the carboxylic acid groups from the 4 and 4' positions led

to some spectral enhancement, but also to a lower efficiency than N3. The group referenced the EPFL work whereby a novel Ru(II) complex increased the spectral sensitivity to about 920 nm, but the benefits of increased spectral sensitivity were offset somewhat by the lower extinction coefficient of the dye. Nevertheless, this dye resulted in the record 10.4% efficiency solar cell. Nonchromophoric ligands are not directly involved in the MLCT absorption but can be used to change the color of the compounds. Drawbacks in different ligands can include poor electron injection yields and sluggish iodide oxidation rates.

The group observes that the open-circuit voltage is determined by the energetic difference between the Fermi levels of the illuminated transparent conducting oxide contact to the nano crystalline titanium dioxide film and the platinum counter electrode where the iodide is regenerated. The platinum electrode's Fermi level is expected to be close to the energy of the redox couple in the solution. An interesting possibility is to select a redox couple with a more positive equilibrium potential. This will decrease the energy loss associated with dye regeneration and may increase the open-circuit voltage. They propose a thiocyanate/thiocyanogen couple to replace the iodide/triiodide electrolyte, which could lead to 16% efficiency if the fill factor and current remain unchanged. They discuss other possible ways to increase the photovoltage, including Fermi-level tuning by adsorption of cations, inhibiting charge recombination of injected electrons with iodide oxidation products at the TiO₂ electrode, reduced sensitizers that are stronger reductants than their excited states, and the possible use of sensitizer-antenna molecular devices. Their experiments with a branched antennae sensitizer on TiO₂ in aqueous solution at pH 3.5 resulted in significant photocurrents. Subsequent experiments on this complex anchored to nano crystalline TiO₂ gave a global conversion efficiency of about 7%. They conclude that, unlike the photocurrent, the open-circuit photo voltage and thermodynamics are not optimized because only about one third of the free energy stored in the molecular excited state of the sensitizer is captured in the operational cell. They believe there are several approaches to extend the efficiency of the dye-sensitized cells to beyond 15%.

The Ångström Solar Center (ASC) in Uppsala, Sweden, described a new method for manufacturing the dye-sensitized solar cell using only room-temperature processing [19]. The ASC group began work on the dye cell in 1996 with the goal of developing the technology so that it would be better than competing thin-film technologies, like amorphous silicon or copper indium diselenide. They chose a very ambitious goal of manufacturing the dye cell on a flexible plastic substrate at room temperature. They started with glass substrates, but reported in their

ECS paper on a process using plastic substrates that reproducibly led to 4.1%-efficient solar cells (at 0.1 sun). A key process step is the fabrication of the titanium dioxide porous matrix. Instead of sintering, the titanium dioxide nanoparticles are compressed on the plastic substrate using static pressure. They conclude that it is quite plausible for a roll press to be integrated into a continuous room-temperature production line for dye-sensitized solar cells. Since the vacuum processes of today's thin-film solar cell technologies require major investments for their production facilities, the development of non vacuum processes for the dye solar cell can lead to substantially lower manufacturing investment costs and subsequently lower technology costs.

The research project proposed by Caltech is titled 'Efficiency Improvements of Dye-Sensitized Nano crystalline TiO₂ Solar Cells' [20]. The researchers will try to better understand how to alter or replace the existing molecular components of the cell with alternatives that will simultaneously provide higher photo voltages, while retaining the high photocurrents exhibited by the present system. The goal is to develop alternative material combinations to the well-studied nanocrystalline titanium dioxide systems based on a Ru(II) dye, a non aqueous electrolyte, and the I³-/I⁻ redox couple. This combination of materials results in a thermodynamic limitation on the photovoltage, due to a less-than-optimal separation between the Fermi level of the redox electrolyte and the conduction band of the titanium dioxide.

The Caltech group will explore two strategies to improve efficiency of the cell. In one approach, they will try nano crystalline semiconductors with a more negative conduction band energy along with appropriately modified sensitizers. The second strategy will use redox mediators with more positive Fermi levels. In implementing this work, they will focus on three areas: (1) understanding the role of the energetics of the semiconductor and dye around the I³-/I⁻ redox couple, (2) determining the mechanism of the I³-/I⁻ couple, and (3) determining the role of injection and recombination on performance. The goal of Professor Nathan Lewis, the principal investigator, is to more than double the efficiency of the dye-sensitized solar cell, while maintaining the stability achieved in its current configuration.

The proposal from Johns Hopkins, jointly with North Carolina State University, is entitled 'Solar Energy Conversion with Ordered, Molecular, Light-Harvesting Arrays'. The proposal describes a new molecular approach in which prefabricated chromophore arrays will be organized on electrode surfaces for use in regenerative solar cells [21]. The approach is new, but borrows from lessons learned in dye-sensitized and organic solar cells. The technique takes advantage of recent advances in synthetic chemistry that allow the rational construction of

linear chromophore arrays. Professor Gerald Meyer is the principal investigator and will be working with NCSU's Professor Jonathan Lindsey. NREL funded Meyer and Peter Searson in the 1990s to study the dye-sensitized solar cell. The project's specific objectives are to (1) use porphyrins, phthalocyanines, chlorins, and derivatives of these compounds in linear, rigid, chromophore arrays; (2) identify linkers and surface binding groups for the chromophores; (3) develop an understanding of the steps in the proposed energy conversion process, primarily through electrochemical and spectroscopic studies; and (4) synthesize linear chromophore light-harvesting arrays in solar cell form. The solar cells will be thin (less than a micron thick), flexible, and will not use an electrolyte. They hope their approach will lead to greater than 10% efficiency within their project's time frame of three years.

The DuPont proposal focuses on the 'Development of a Solid-State Electrolyte for Dye-Sensitized Solar Cells' [22]. Led by Thomas Griffin, the research group recognizes that the replacement of the liquid electrolyte in today's highest-performing dye-sensitized solar cells offers several advantages for the technology. But there are major research challenges associated with synthesis, stability, electron-transfer thermodynamics, transport rates and reaction kinetics, compatibility with other anode components, and avoidance of shorting and recombination. Candidate materials include, but are not limited to, gel ionomer systems, polyalkylcarbazoles, polythiophenes, polyanilines, polyalkylthiophenes, and amine hole-transport materials. Part of DuPont's exploration includes electrolyte synthesis through the DuPont 'Building of Materials Library'. Another aspect of this project involves DuPont's collaboration through a subtier contract with Michael Grätzel at EPFL and Gavin Tulloch at STI to conduct an analysis of materials' costs, develop a strategy for cost reduction, and estimate the investment cost for a 100-MW manufacturing plant.

CHAPTER 3

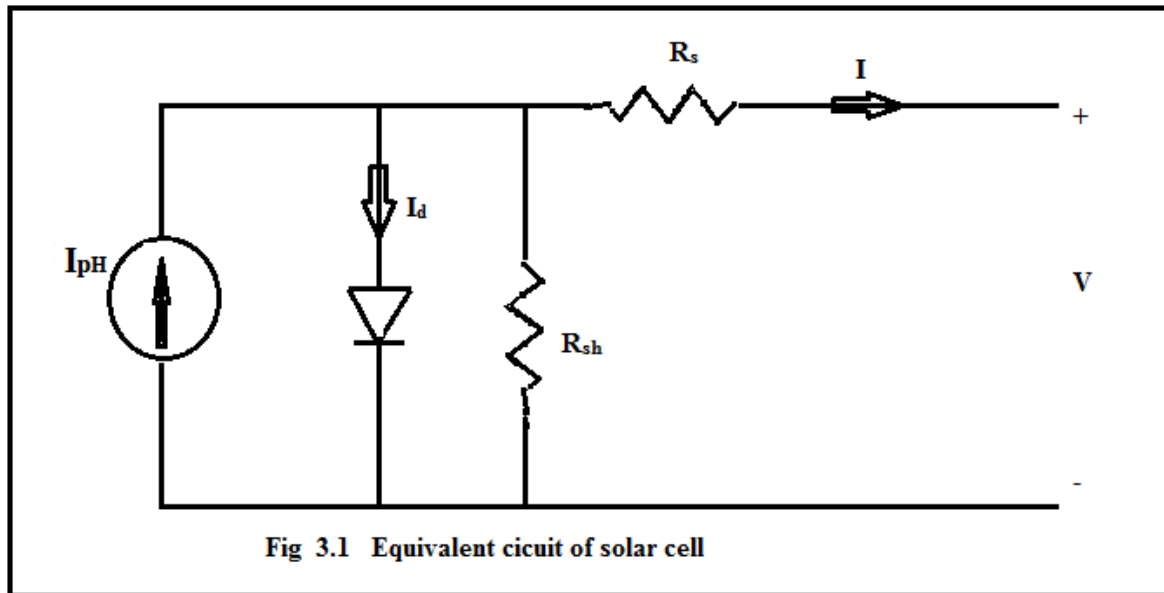
Theory

- 3.1 General theory of solar cell.
 - 3.2 Power conversion efficiency of photovoltaic devices
 - 3.3 Theory of dye sensitized solar cell
 - 3.3.1 Function of dye
 - 3.3.2 Function of MOS
 - 3.3.3 Function of electrolyte
 - 3.3.4 Function of electrodes
 - 3.4 Working principle of dye sensitized solar cell
 - 3.5 Trap state
-

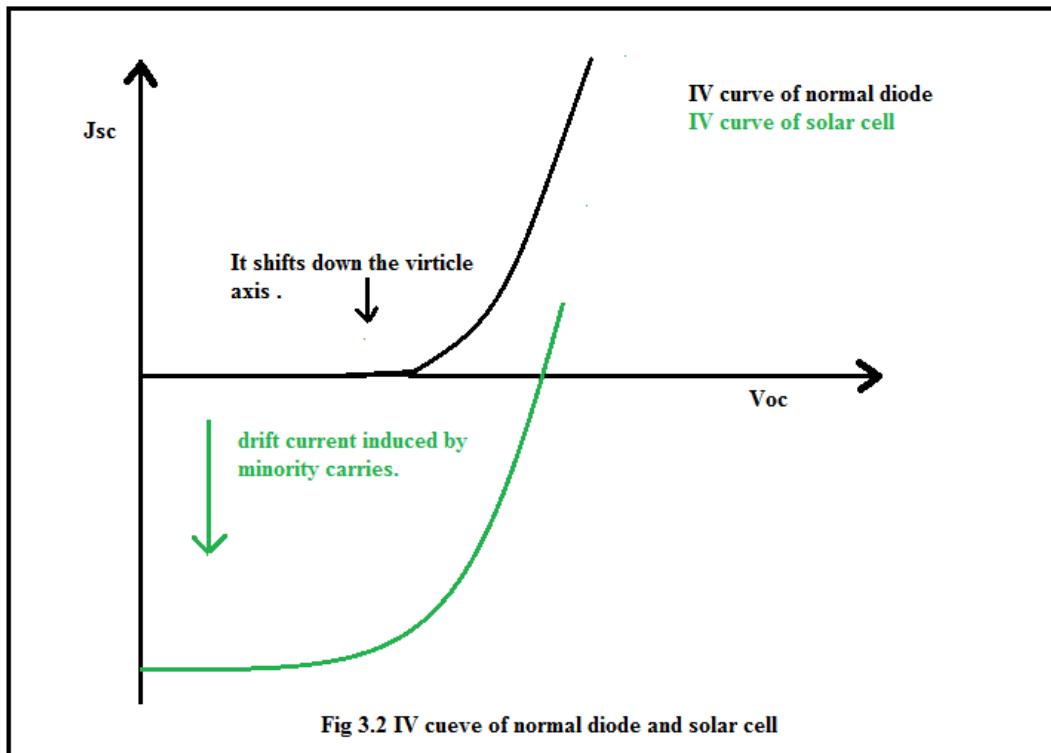
3.1 General Theory of Solar Cell

Simple p-n junction diode that has been lit up is what a solar cell is. When compared to a p-n junction diode, the charge flow mechanism is slightly different. Simple p-n junction diode mechanism must be understood in order to comprehend the mechanism of a simple solar cell. A p-n junction is produced in a semiconductor when one side is doped with n type and the other side with p type. The charge flow in semiconductors is regulated by two distinct mechanisms. Diffusion is the first, whereas drifting is the second. Drift is regulated by the electric field, which is built into the p-n junction, whereas diffusion is controlled by the electric field, which can be applied externally. The space charge region or depletion region at the p-n interface is created in p-n junctions by the diffusion of majority charge carriers through the p-n interface, which is made possible by recombination. In the dark and in thermal equilibrium, drift of minority charge carriers and diffusion of majority charge carriers are in balance. The depletion zone widens, diffusion of the majority charge carrier is separated, and only a very small amount of current associated to drift of the minority charge carrier is produced if reverse bias is applied to such a p-n junction in the dark. The depletion zone's breadth decreases as forward bias is given to the p-n junction in the dark. Minority charge carrier diffusion is greatly increased, outpacing minority charge carrier drift, causing the p-n junction to become conductive and

capable of producing a significant amount of current. When the p-n junction is lighted, the minority charge carrier density increases by many orders of magnitude. As a result, the drift takes over and the p-n junction produces a significant current. The equivalent circuit of a diode is shown in Fig. 3.1. Electrodes made with series and shunt resistance are R_s and R_{sh} .



The current generated by light is I_{ph} where ph stands for photon current it is in the opposite direction of forward current of diode, when photon current is added the typical IV curve of diode is shown in Fig 3.2.



The IV curve of an ideal solar cell can be described by a simple equation

$$I = I_{pH} - I_{dark}$$

$$I = I_{pH} - I_0 \left(\exp \left(\frac{qV}{KpT} \right) - 1 \right)$$

The total current generated by an illuminated p-n junction is the photo current minus current of p-n junction is the photon current of the p-n diode in the dark in the equation. In the above equation electrical losses are not included.

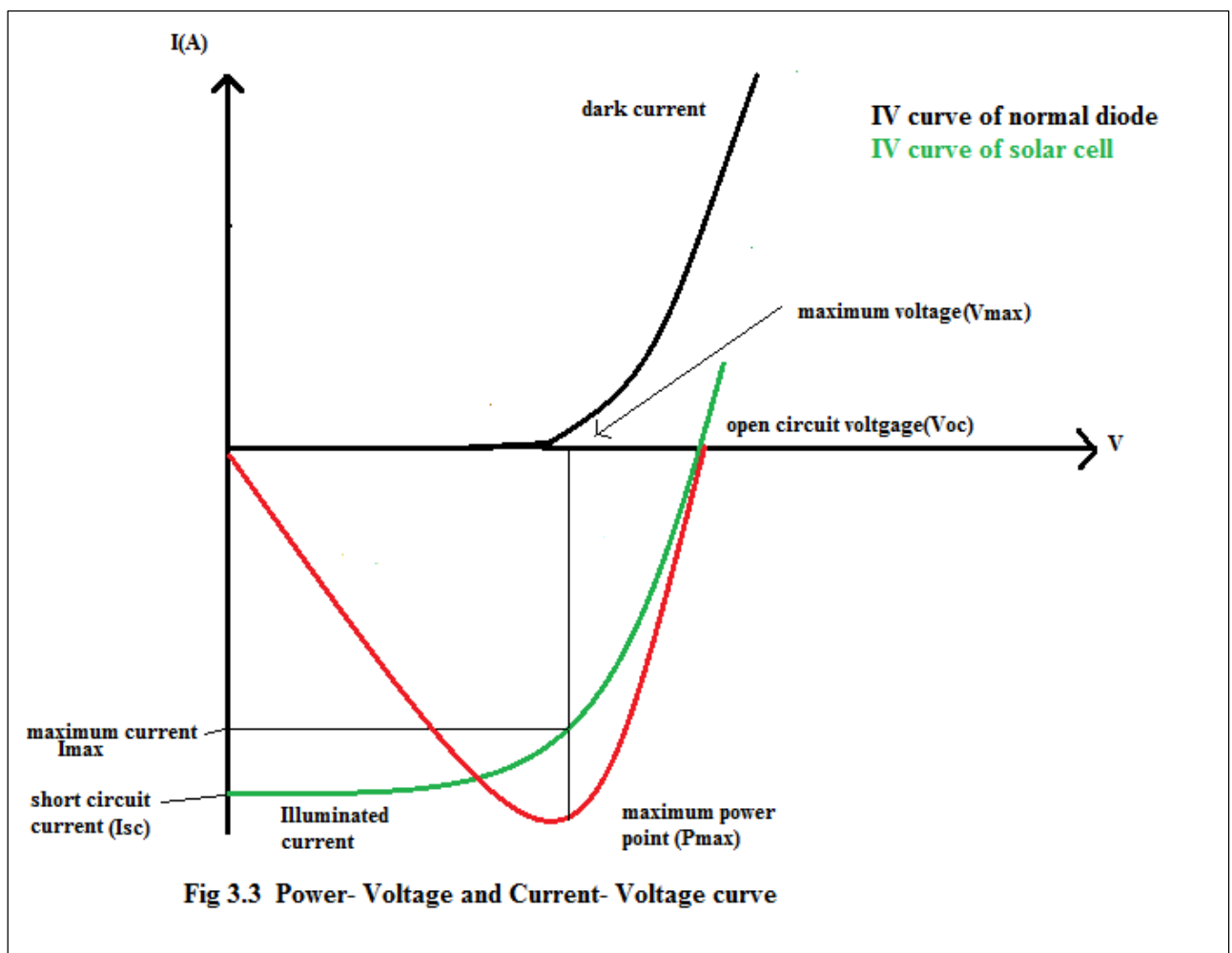
3.2 Power conversion efficiency of photovoltaic devices

The overall sunlight-to-electric-power conversion efficiency, η , of photovoltaic device is the ratio between maximum attainable electric power, P_{max} , at the solar cell electrodes to the input optical power, P_{in} , in Watts incident to the solar cell given by:

$$\eta = \frac{P_{max}}{P_{in}} = \frac{V_{oc} \cdot I_{sc} \cdot FF}{P_{in}}$$

Where, $P_{max} = V_{max} \times I_{max}$

Where I_{max} , the maximum photocurrent, and V_{max} , maximum voltage, are obtained at the maximum power point of a typical photovoltaic device. A typical cell response with I_{max} , V_{max} , and P_{max} is shown in Figure 3.1.



The fill factor, FF , of solar cells is defined as:

$$FF = \frac{P_{max}}{V_{oc} \times I_{sc}}$$

Where V_{oc} is the voltage developed across a cell if the two terminals of the device are open.

I_{sc} is short circuit current delivered by the solar cells device if the value of the load resistance is zero, or if the two terminals of the device are shorted to each other. In open circuit conditions, the photocurrent does not flow through the load; it is redirected through the internal diode. For variety of solar cells, the V_{oc} can be calculated by:

$$V_{oc} = \frac{kT}{q} \ln\left(\frac{I_{sc}}{I_0} + 1\right)$$

Where q is the charge of electron, T is temperature, k is Boltzmann constant, and I_0 is the dark saturation current of the diode. At the voltage range is between 0 and V_{oc} , the photovoltaic device generates power. When the voltage is $V < 0$, the illuminated solar cell consumes power to produce a photocurrent. The diode in this regime operates as a photodetector where its current is linearly sensitive to light intensity and is its value bias independent. At $V > V_{oc}$, the dark current through the diode is larger than the photocurrent developed by the cell hence the solar cell sinks current from the external source. In this regime, the device start to consume power and operates like a light emitting diode, particularly if the solar cell is made of a direct bandgap semiconductor [38].

The efficiency of photovoltaic cell is often expressed in term of short circuit current density, J_{sc} , as:

$$J_{sc} = I_{sc}/A$$

Where A is the active area of the solar cell. Then, the power conversion efficiency, η , of the photovoltaic device can be expressed as:

$$\eta = \frac{FF \times V_{oc} \times J_{sc}}{P_{op}}$$

Where P_{op} is the optical power density incident to the device in W/cm². Under the Standard Test Condition (STC), the solar cell efficiency is measured by an AM 1.5 compatible light with incident power density of 1000 W/m² equivalent to 100 mW/cm² at a temperature of 25 °C.

3.3 Theory of dye sensitized solar cell

Dye sensitized solar was invented by O Regan and Gratzel in 1991, it follows the same process as of photosynthesis in plants. Basic component present in dye sensitized solar are dye, semiconductor material, electrolyte and pair of electrodes. The electrical performance of a solar cell is measured by several parameters which are current density (J_{sc}), open circuit voltage (V_{oc}), and fill factor (FF) and energy conversion efficiency (η).

3.3.1 Function of dye

Among all the basic components, dye plays an important role of absorbing the sun light and converting it into electricity. There is correlation between absorbed light and colour of dye. If dye X absorbs Red light. The colour of dye X will be green. Based on absorption spectra it can be estimated the absorbed light and based on reflectance spectra it can be estimated the reflected light, the colour of dye is based on reflected light. Any material when exposed to sunlight, the sequence of the light is absorption, reflection, and transmission. This is based on wheel of colour if it is absorbed red it will be reflecting green it means it is absorbing 600nm, so if it is absorbing orange colour it will be reflecting green light. Various types of dye consist of various type of functional groups, this is also known as anchoring agent, which acts as syringe to inject electron in metal oxide semiconductor. Dye with more functional group will generate more number of functional group is considered as excellent dye. The dye consists of two energy state LUMO and HUMO i.e. "lowest unoccupied molecular orbital" and "highest occupied molecular orbital", respectively. The difference of energy between HOMO and LUMO is termed the HOMO–LUMO gap. The dye has shorter distance between anchoring H to LUMO. The shorter the distance between the excited state electron density, the more efficient electron could be injected into the MOS.

3.3.2 Function of MOS (metal oxide semiconductor)

TiO₂ is a wide band gap semiconductor that absorbs UV light, it reflects all visible light. The function of TiO₂ is to separate excited electron from hole to prevent recombination with hole, electron will be injected into conduction band of MOS i.e lower energy level than LUMO of

the dye such that the electrons from LUMO of the dye could be injected to the conduction band of TiO_2 . Hole will be injected into higher energy level of oxidation potential of electrolyte.

The efficiency can be increased by making TiO_2 mesoporous, more dye could be adsorbed on the surface of MOS. More excited state electron could be injected into MOS which in turn increases the efficiency. Still number of dye molecules adsorbed to the

Surface of TiO_2 can be increased if the surface can be made nano rods. Hence more surface area could be adsorbed, this solid rod can be made hollow rod, which is known as Nano wire.

3.3.3 Function of electrolyte

Electrolyte is one of the most important ingredients in DSSC, its function is it regenerate electron in the HOMO of dye, hence electrolyte should be higher than HOMO energy level of dye. Electrolyte undergo redox reaction shown below, in working of DSSC.

3.3.4 Function of electrodes

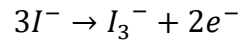
Electrodes are conducting material that is connected to the outer circuit. In this experiment the first electrode is Indium tin oxide and the counter electrode is graphite.

Indium tin oxide is polished on the surface of glass and graphite is fabricated on glass using flame of candle. Electron from TiO_2 goes to ITO coated glass, and then to the outer circuit, does it work i.e and comes back to counter electrode.

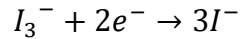
3.4 Working principle of dye sensitizes solar cell

When dye sensitizes solar is exposed to sunlight Light passes through the transparent electrode and excites the electron residing in HOMO of dye molecules to LUMO. From there it goes to the conduction band of the TiO_2 layer which acts as a metal oxide semiconductor (MOS). The electrons flow through the external circuit to the graphite cathode then flow into the iodide electrolyte. The electrolyte then transports the electrons back to HOMO of the dye molecule. In the DSSC, the dye is oxidized (loses an electron). The oxidized dye receives an electron from an iodide ion, which reduces the dye back to its original form.

In this process the iodide ions undergo oxidation.



The electron that returns to the DSSC from the external circuit reduces the I_3^- ion back to $3I^-$.



In this equation we can see the reduction of tri-iodide ions to form iodide ions, the iodide ions can then be oxidized to form tri-iodide ions and electrons. The transparent anode allows sunlight to reach the dye-sensitized TiO_2 nanoparticles. The use of TiO_2 nanoparticles coated with light absorbing dye increases the effective surface area and allows more light over a

wider range of visible spectrum to be absorbed. This allows the DSSC to absorb more light under cloudy conditions than silicon based photo cell.

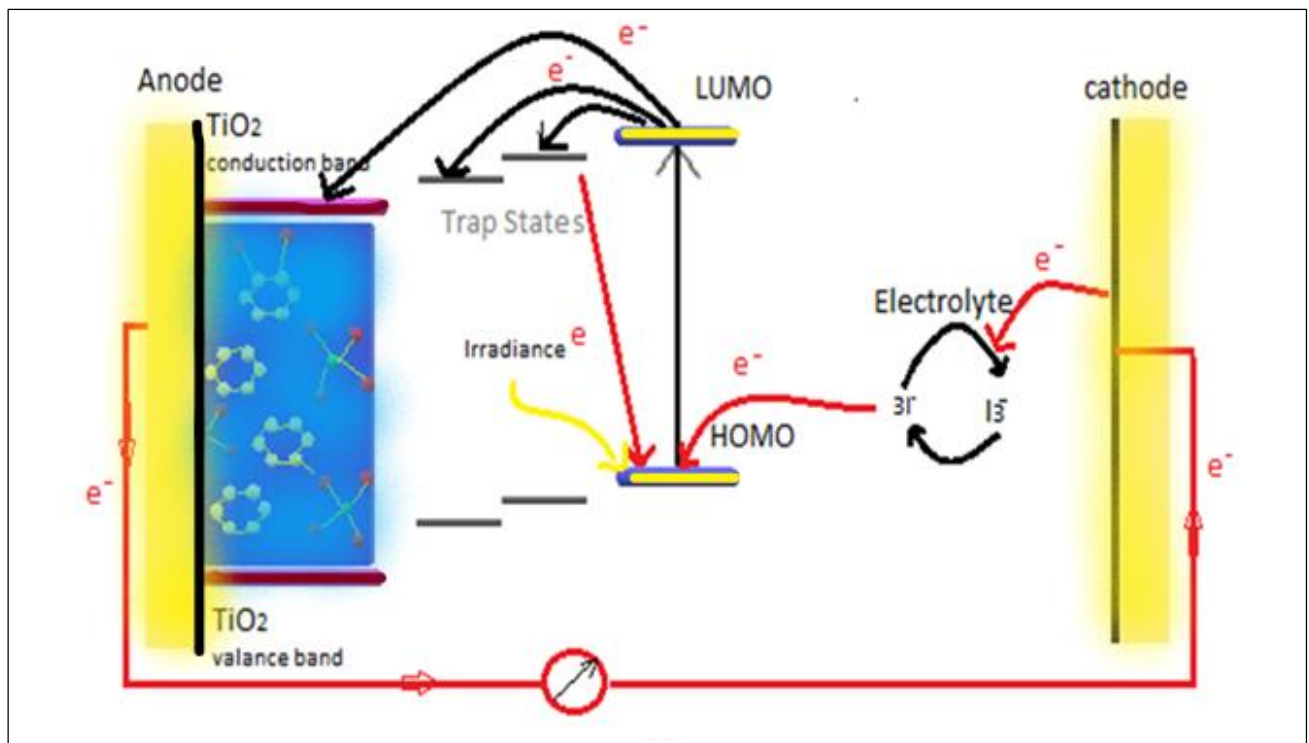


Fig. 3.1 Working principle of dye sensitized solar cell

3.5 Trap State

Model of trap-limited diffusion 3.s shown in Fig. 3, from a physical perspective, TiO_2 nanoparticles experience several trapping-detraping events. During the charge transport process, dye-injected electrons can either be trapped by trap states or thermally released back to conduction [36], [37]. The structural flaws at the surfaces and the grain may be the cause of

the trap states. TiO₂ nanocrystallites' interiors and particle borders both contain oxygen [38]. Defects act as an electron trap state, delaying electron transit and lengthening the distance travelled before recombination [39]. Kopidakis et al. [40] determined the dependency of total trap density on the roughness factor to identify the spatial location of transport-limiting traps. The data's best fit corroborated the relationship between internal surface area and the density of electron traps in the film, showing that the traps are mostly found at the surface of TiO₂ particles as opposed to the inside of the particles or the grain boundaries.

Numerous electronic phenomena are influenced by the energetics of trapped electrons as defined by the density of states (DOS). Since it matches the dynamics of transient photocurrent and photo voltage, Nelson's exponential DOS distribution is widely recognised. Lagemaat et al. correctly interpreted the power-law dependency of the short-circuit current density on the electron concentration in light of the facts that the surface is the primary source of traps and DOS follows an exponential distribution. Recent studies evaluated how shallow and deep traps affected the distribution of DOS. The typical energies of 48 meV () and 765 meV (), respectively, were used by Wang et al. to distinguish between shallow traps (>700 meV) and deep traps (350 meV). It was discovered that the energy of shallow trap states was similar to the energy of the total number of electron trap states (46 meV) and that the quantity of shallow traps was significantly more than the quantity of deep traps.

Similar to this, charge transport and recombination are significantly influenced by the spatial distribution of intra gap trap states. Actually, the photo injected electrons are trapped the majority of the time. Therefore, in the presence of traps, electron transport in nanoparticle films was 103–105 times slower than in the single crystal. As a result, shallow trap states in the bulk dominate the dynamics of electron recombination, which occurs mostly via trap states rather than the conduction band. It is possible that multiple trapping with a wide energy distribution of electron traps is the cause of the sluggish recombination kinetics seen in high-efficiency DSSCs. The characteristics of the electron traps are a function of the carrier density, in contrast to the macroscopic diffusion model, which assumes that the diffusion coefficient is constant (). Ansari-Rad et al. recently discovered that the was independent of nanoparticle size for both surface and volume diffusion and that the trap-filling electronic effect, rather than a geometrical effect, was what caused the to increase with particle size.

CHAPTER 4

Fabrication and characterization of Dye sensitized solar cell

4.1 Dye preparation

4.1.1 Dye from blue Clitoria ternetia

4.1.2 Dye from hibiscus

4.2 Electrolyte preparation

4.3 Preparation of TiO₂ suspension

4.4 Device fabrication

4.5 Result of fabricated dye sensitized solar cell

This chapter contains fabrication and characterisation of dye sensitized solar cell. Three samples of dye have been prepared using seven different flowers. Three samples of dye sensitized solar cell have been fabricated using three samples of dyes. In this session, Short circuit current, Open circuit voltage, Fill Factor and Power Conversion Efficiency are compared. For better understanding of observation, Jsc verses Voc curve has been plotted. Morphology of fabricated cell has been studied using SEM and XRD characterization.

4.1 Dye Preparation

Three different sample of dye sensitizer is prepared for comparative investigation.

4.1.1 Dye from blue Clitoria ternetia:

For preparing dye sample using blue Clitoria ternetia flower are thoroughly washed with ethanol. Blue petals of the flower are carefully separated and grinded in mortar and filtered. The resultant was concentrated to one fourth on a rotatory evaporator at 50°C for few seconds.

8 to 9 drops of Methanol is mixed in the dye and then it was put in storage in the air tight dark bottle.

4.1.2 Dye from Hibiscus:

15 red hibiscus flowers were thoroughly washed with ethanol, its petals were separated leaving behind a sticky portion of flower and then it was crushed in a mortar and filtered using filter paper. The resultant mixture was concentrated to one fourth on a rotatory evaporator at 50°C for few seconds. 7 to 8 drops of Methanol is mixed in the flower juice and then it was stored in the air tight dark bottle.

For the final preparation of Blue Clitoria ternetia and hibiscus were separately washed with ethanol for 15 minutes. Coloured petals of flower were separated carefully, and were individually (flowers of one kind) grinded in mortar. After grinding the paste were filtered and heated at 80°C for few seconds to concentrate it to one fourth, resultant mixture was stored separately. Finally 0.5ml of dye from each sample were mixed together to form mixed dye.

4.2 Electrolyte preparation

For electrolyte preparation 3-ethyl-2-methyl Immidazolium iodide measured 1 Mol/ L was mixed with acetonitrile, the mixture was stirred for 15 min, to make it homogeneous 0.561 Mol/L of KI was dissolved in the above mixture followed by adding 0.13 Mol/L iodine and polyvinyl pyrrolidone to increase conductivity of electrolyte. The mixture was heated at 80°C with dynamic stirring, such that pyrrolidone get dissolved in the mixture. Resultant mixture was cooled down to form gel, and it is stored in air tight container. The resultant electrolyte is now ready for deposition on the top of dye-coated TiO₂ electrode.

4.3 Preparation of TiO₂ suspension

6 g of titanium dioxide powder was unrushed and placed in a mortar. Next, 9 ml of nitric acid was poured into the mortar before crushing the mixture with a crusher until the mixture was consistent. Then, the suspension was kept in a dark container and allowed to equilibrate for 10 minute. In order to break the masses into separate particles, the powder was ground in a ceramic

mortar with a 1 mL of water and 0.1 ml of acetic acid to prevent aggregation of the particles. After the dust had been disseminated by the high shear forces in the viscous paste, it was diluted by slow addition of water (4 mL) under constant grinding. Finally, a detergent was added to smooth the spreading of the colloid on the substrate.

4.4 Device fabrication

ITO glasses were cleaned with deionized water followed by cleaning with Acetone and then it was placed in the ultrasonic bath for almost 15 minutes and dried under nitrogen flow. Its resistance was checked with help of multimeter to find the conductive side and it is of glass conductive side of ITO glass was tested by measuring the resistance of $21\ \Omega$. Generally, it varies from $10\ \Omega$ to $30\ \Omega$. To get the active area on the conductive side of ITO glasses, the transparent tape was used to cover all four edges of the glass, roughly up to 1mm. TiO_2 paste is spread in between the tap, using doctor-blade process ($>10\ \mu\text{m}$). A rose petal was washed with acetone and placed on the surface of TiO_2 , With help of round glass the petal place on the surface of the TiO_2 layer and with help of glass pipe roller it was rolled on to make TiO_2 surface same as petal surface. Rose patterned surface helps in harvesting the good amount of sunlight. After removing the tape, the sample was sintered at 110°C for 25 min. The sample was then immersed in three different dyes(hibiscus(red) dye and clitoria ternetia (and left for 2 hours, its colour changed from white to the colour of respective natural dye sensitizer, and then heated for 10 min at 70°C . The sample was then washed with Deionised water and gently dried with tissue paper. Another electrode was prepared by coating conductive side of cleaned ITO glass with graphite as a counter electrode, it was heated for 15 minutes. Now the cell device was assembled by placing the graphite-coated slide facing down on top of the TiO_2 coated side. The two opposing slides were placed on top of each other with a slight offset to ensure that all of the stained titanium dioxides was covered by the counter electrode and that space was available for connecting the crocodile clips. Next two binder clips were used on opposite edges to gently hold the slides together. Then, two drops of the iodide/iodine electrolyte solution were placed at the edges of the plates. The complete cell is shown in Figure 1. Subsequently, the two binder clips were alternately opened and closed to promote the uniform dispersion of the iodide/iodine electrolyte between the slides. Then, the alligator clips that were attached to the edges were connected to the multimeter. The negative and positive terminals were attached to the stained titanium dioxide (electrode) and graphite stained (counter electrode) slides, respectively and then the sample was exposed to sunlight.

4.5 Result of fabricated dye sensitized solar cell

Table shows JV Result and Discussion:

Natural dye	Voc (V)	Jsc (mA/cm ²)	FF (%)	Efficiency (%)	Reference
Clitoria Ternetia(blue coloured dye)	0.621	2.910	64.21	1.9	This paper
Hibiscus(red coloured dye)	0.390	0.890	50.34	0.18	This paper
Mixed	0.690	1.990	71.06	0.8	This paper
Lemon leafs	0.225	0.017	54.1	0.040	[70]
Lyceum	0.580	0.420	42	0.100	[71]
Olive grain	0.5500	0.580	38	0.120	[72]
Iycium shawii	0.62	1.20	43	0.32	[72]
Zizyphus leaves	0.68	1.50	40	0.40	[72]
Yellow rose	0.609	0.74	57.1	0.26	[73]
Flowery knotweed	0.554	0.60	62.7	0.21	[73]
Chinese rose	0.483	0.90	61.9	0.27	[73]
Marigold	0.542	0.51	83.1	0.23	[74]

Table 5 - Parameter comparison table of three DSSc fabricated in this paper with other

DSSc fabricated using different dye sensitizer containing anthocyanin and chlorophyll. Table 5.1 shows all the interesting parameters like Short circuit current density (Jsc), open circuit voltage (Voc), fill factor (FF), efficiency (η), and from the table we can observe the highest open circuit voltage is obtained from blue dye (Clitoria ternatea) i.e. 0.72V and lowest from red dye (hibiscus) i.e. 0.47V, whereas current varied from 5.5 mA/cm² to 1.79 mA/cm². Mixed dye showed average performance Voc of 0.68V and Jsc of 2.89 mA/cm². DSSCs fabricated from various dye sensitizers. It can also be observed from the table that efficiencies obtained in this experiment are considerably higher than the other DSSc. This is due to good charge transfer between the dye and TiO₂. Power conversion efficiency of DSSc depends on

light absorption capacity of dye, the structure of dye. The dye with more functional group availability of functional group (it act as syringe to insert electron in conduction band of TiO_2) could generate more J_{sc} , and the dye whose distance between anchoring H to LUMO is small, that dye shows more J_{sc} (shorter the distance between the excited state electron density, the more efficient electron could be injected into TiO_2). TiO_2 is a wide band gap semiconductor that only absorbs UV light and reflects all visible light, its function is to provide a lower energy level than LUMO of the dye such that the electron from LUMO of dye could be injected to the conduction band of TiO_2 . In this study the TiO_2 layer is made mesoporous and surface structure is patterned like surface of rose petal, this helped in increasing surface area of TiO_2 , consequently number of dye adsorbed to the surface of TiO_2 (Still increased number of dye molecule can be adsorbed on surface of TiO_2 if the surface of TiO_2 is made hollow nanowire). Beside absorption capacity and structure of dye, Trap state is another factor that affects the Power conversion efficiency of DSSC. Trap state is nearest energy level to LUMO, it is unavoidable inorganic materials so one needs to know how many trap states are there.

$$\text{CBTiO}_2 < \text{E}_{\text{trap state}} < \text{LUMOdye}$$

It may occur due to the structural defect of dye, chemical impurities that alter dye's electronic properties or adsorbed water in dye. This trap state is undesirable as an electron that is supposed to be injected from LUMO of dye to the conduction band of TiO_2 gets trapped in this state, consequently J_{sc} decreases. Figure 2 shows the working principle of DSSC with trap states. Fig3, 4, 5 shows the open circuit voltage to short-circuit current density of three different dye i.e. Blue, mixed and red dye.

The efficiency and Fill Factor is given by:

$$\eta = \frac{V_{oc} * I_{sc}}{E * A_c} * FF * 100\%$$

P_{max} = Maximun power output, E = Incident radiation flux, A = Area of collector

$$FF = \frac{P_{max}}{I_{sc} * V_{oc}}$$

Short circuit current and open circuit voltage measurement are done under arc lamp using illumination of 1 Sun.

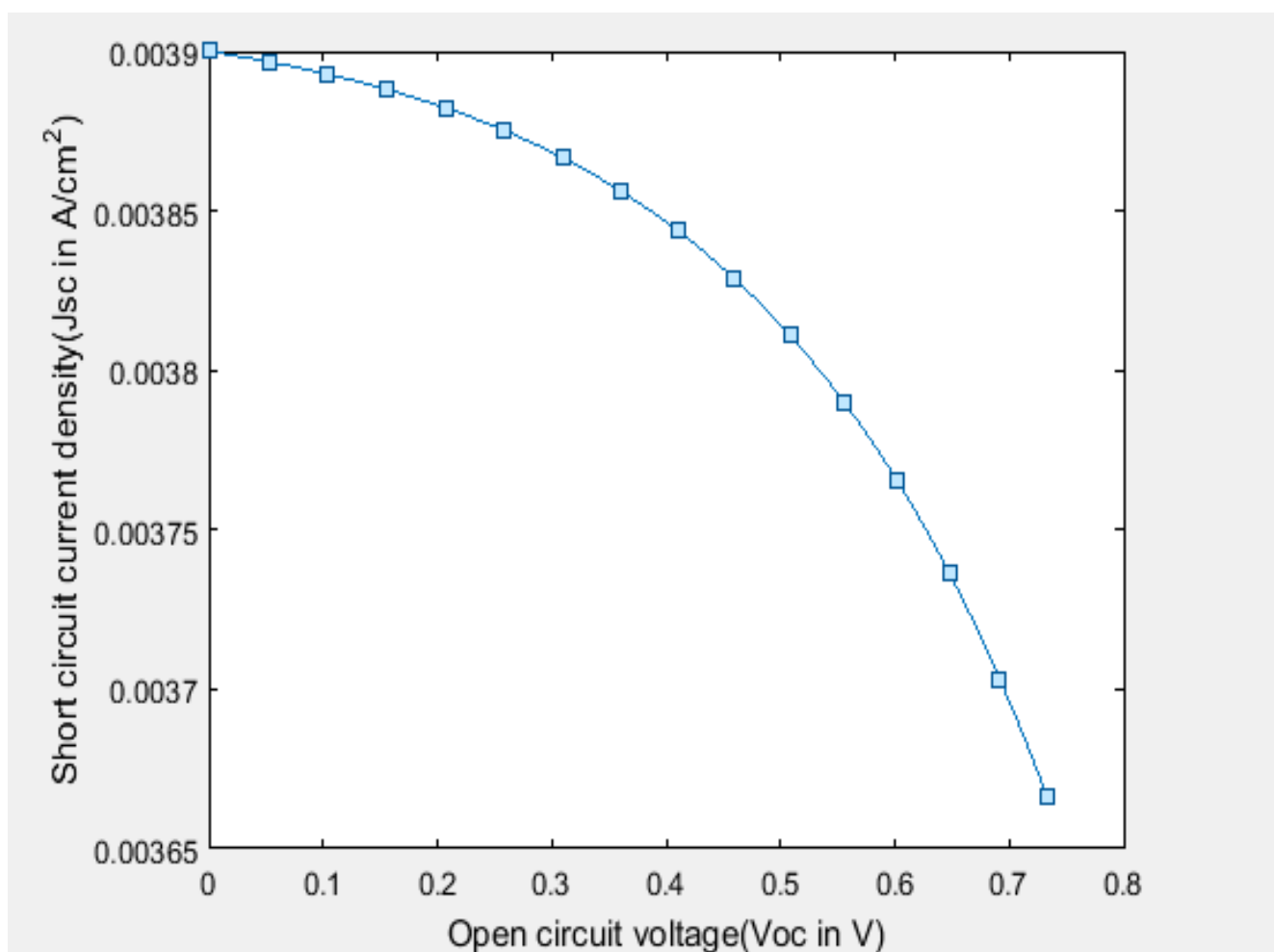


Fig. 5.2 (a) JV characteristics of dye extracted from *Clitoria ternatea* (blue dye)

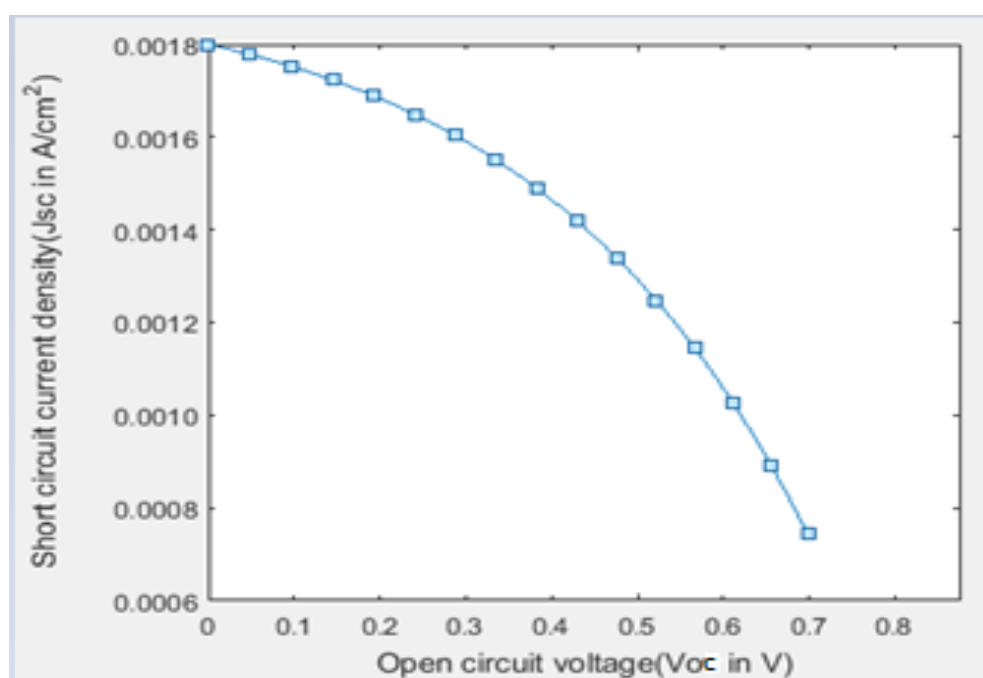


Fig. 5.2 (b) JV characteristics of dye extracted from mixed dye

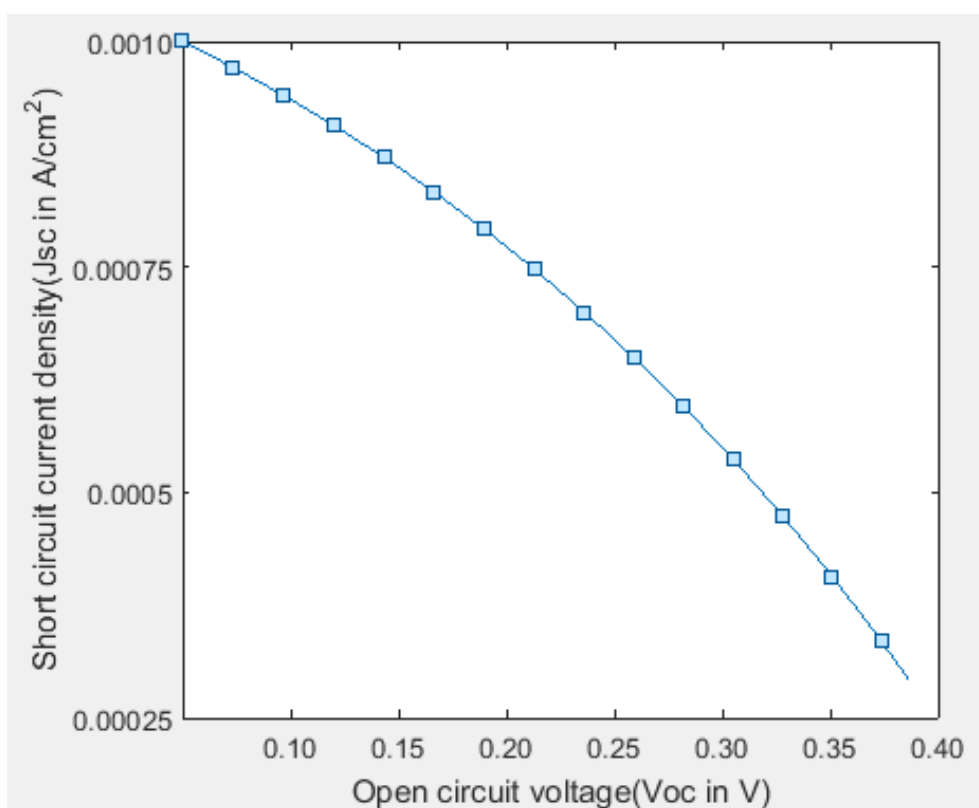


Fig. 5.2 (c) JV characteristics of dye extracted from hibiscus (red dye)

Highest fill factor and Efficiency is recorded for blue (*Clitoria ternatea*) dye. This is the comparatively high-efficiency record till date for blue dye.

CHAPTER 5

Conclusion

This thesis has contributed its work in dye sensitized solar cell. Three different natural dye sensitized solar cells were fabricated; first sample of dye was extracted using extracted from Clitoria (blue), second from Hibiscus and the third from a combination of these two different dyes. The maximum efficiency was obtained for the first sample (1.922%), followed by the third sample (0.18%) and finally the second sample (0.8%), respectively. In the DSSC all the available wavelengths of colours apart from the dye colour are absorbed. This is the reason why the third sample (Mixed) yields lower efficiency than the first sample (blue dye). With regards to our observations, the most suitable dye to achieve good efficiency is from Clitoria ternatea (blue dye). As the global trend is shifting towards tapping unconventional energy sources and eco-friendly materials, dye-sensitized solar cells are attracting the interest of researchers and industries alike. Commercialization of the DSSC can result in low-cost, easily-to-fabricate, environment-friendly alternatives to existing solar cell technology.

Future scope

Dye sensitized solar cell is one of the potential replacement in the field of solar technology as it is cost effective and efficient, but very less has been done in this field. As it is discussed that TiO_2 is main semiconductor material in dye sensitized solar cell. In future we can do research in finding alternative semiconductor material with conductivity and better stability. One of the such material is SnO_2 that has been emerged with appreciable performance apart from TiO_2 .

REFERENCE

- [1] R. A. Messenger and J. Ventre, Photovoltaic systems engineering: CRC, 2003.
- [2] (2012). How much carbon dioxide is produced by burning gasoline and diesel fuel? Available: <http://www.eia.gov/tools/faqs/faq.cfm?id=307&t=11>
- [3] R. Gross, M. Leach, and A. Bauen, "Progress in renewable energy," Environment International, vol. 29, pp. 105-122, 2003. 87
- [4] N. Gupta, G. Alapatt, R. Podila, R. Singh, and K. Poole, "Prospects of nanostructure-based solar cells for manufacturing future generations of photovoltaic modules," International Journal of Photoenergy, vol. 2009, 2009.
- [5] M. A. Green, K. Emery, Y. Hishikawa, W. Warta, and E. D. Dunlop, "Solar cell efficiency tables (version 39)," Progress in Photovoltaics: Research and Applications, vol. 20, pp. 12-20, 2012.
- [6] J. Zhao, A. Wang, M. A. Green, and F. Ferrazza, "19.8% efficient “honeycomb” textured multicrystalline and 24.4% monocrystalline silicon solar cells," Applied Physics Letters, vol. 73, pp. 1991-1993, 1998.
- [7] M. A. Green, K. Emery, Y. Hishikawa, and W. Warta, "Solar cell efficiency tables (version 36)," Progress in Photovoltaics: Research and Applications, vol. 18, pp. 346-352, 2010
- [8] S. Razza, S. Castro-Hermosa, A. D. Carlo, and T. M. Brown, “Research update: Large-area deposition, coating, printing, and processing techniques for the upscaling of perovskite solar cell technology,” APL Mater., vol. 4, no. 9, pp. 91508–91515, Sep. 2016, doi: 10.1063/1.4962478
- [9]. Xiao Wu, Dan Xie, Yu Chen, Tingting Feng, He Tian, TianlingRen Comparison of Photovoltaic Performance Enhancement in BiFeO₃ by Using Graphene and Carbon Nanotubes as Transparent Electrode

- [10] A. Dubey, N. Adhikari, S. Venkatesan, S. Gu, D. Khatiwada, Q. Wang, et al., "Solution processed pristine PDPP3T polymer as hole transport layer for efficient perovskite solar cells with slower degradation," *Solar Energy Materials and Solar Cells*, vol. 145, pp. 193-199, 2016
- [11] A. Dubey, N. Adhikari, S. Venkatesan, S. Gu, D. Khatiwada, Q. Wang, et al., "Shelf life stability comparison in air for solution processed pristine PDPP3T polymer and doped spiro-OMeTAD as hole transport layer for perovskite solar cell," *Data in Brief*, vol. 7, pp. 139-142, 2016.
- [12] A. Kojima, K. Teshima, Y. Shirai, and T. Miyasaka, "Organometal halide perovskites as visible-light sensitizers for photovoltaic cells," *Journal of the American Chemical Society*, vol. 131, pp. 6050-6051, 2009.
- [13] G. E. Eperon, V. M. Burlakov, P. Docampo, A. Goriely, and H. J. Snaith, "Morphological Control for High Performance, Solution-Processed Planar Heterojunction Perovskite Solar Cells," *Advanced Functional Materials*, vol. 24, pp. 151-157, 2014.
- [14] V. T. Breslin and S. A. Sañudo-Wilhelmy, "The lead project. An environmental instrumental analysis case study," *J. Chem. Educ*, vol. 78, p. 1647, 2001.
- [15] B. P. Lanphear, T. D. Matte, J. Rogers, R. P. Clickner, B. Dietz, R. L. Bornschein, et al., "The contribution of lead-contaminated house dust and residential soil to children's blood lead levels: a pooled analysis of 12 epidemiologic studies," *Environmental research*, vol. 79, pp. 51-68, 1998.
- [16] P. Gao, M. Grätzel, and M. K. Nazeeruddin, "Organohalide lead perovskites for photovoltaic applications," *Energy & Environmental Science*, vol. 7, pp. 2448- 2463, 2014.
- [17] F. Hao, C. C. Stoumpos, D. H. Cao, R. P. Chang, and M. G. Kanatzidis, "Leadfree solid-state organic-inorganic halide perovskite solar cells," *Nature Photonics*, vol. 8, pp. 489-494, 2014. 92

- [18] D. B. Mitzi, C. Feild, Z. Schlesinger, and R. Laibowitz, "Transport, optical, and magnetic properties of the conducting halide perovskite $\text{CH}_3\text{NH}_3\text{SnI}_3$," *Journal of Solid State Chemistry*, vol. 114, pp. 159-163, 1995.
- [19] Y. Takahashi, R. Obara, Z.-Z. Lin, Y. Takahashi, T. Naito, T. Inabe, et al., "Charge-transport in tin-iodide perovskite $\text{CH}_3\text{NH}_3\text{SnI}_3$: origin of high conductivity," *Dalton Transactions*, vol. 40, pp. 5563-5568, 2011.
- [20] S.Y. Yang, L.W. Martin, S.J. Byrnes, T.E. Conry, S.R. Basu, D. Paran, et al, Photovoltaic effects in BiFeO_3 , *Appl. Phys. Lett.* 95 (2009) 062909.
- [21] B. Yu, M. Li, Z. Hu, L. Pei, D. Guo, X. Zhao, S. Dong, Enhanced multiferroic properties of the high-valence Pr doped BiFeO_3 thin film, *Appl. Phys. Lett.* 93 (2008) 182909-182911.
- [22] R.K. Katiyar, P. Misra, F. Mendoza, G. Morell, R.S. Katina, Switchable photovoltaic effect in bilayer graphene/ BiFeO_3 /Pt heterostructures, *Appl. Phys. Lett.* 105 (2014) 142902-142911.
- [23] J. He, R. Guo, L. Fang, W. Dong, F. Zheng, M. Shen, Characterization and visible light photocatalytic mechanism of size-controlled BiFeO_3 nanoparticles, *Mat. Res. Bull.* 48 (2013) 3017–3024.
- [24] Y. Sharma, P. Misra, R.K. Katiyar, R.S. Katina, Photovoltaic effect and enhanced magnetization in $0.9(\text{BiFeO}_3)\text{--}0.1(\text{YCrO}_3)$ composite thin film fabricated using sequential pulsed laser deposition, *J. Phys. D: Appl. Phys.* 47 (2014) 435303.
- [25] Rachel Fran Mansa,* Gobinat Govindasamy, Yan Yan Farm, Hafeza Abu Bakar, Jedol Dayou and Coswald Stephen Sipaut Hibiscus Flower Extract as a Natural Dye Sensitiser for a Dye-sensitised Solar Cell.
- [26] I. C. Maurya, Neetu, A. K. Gupta, P. Srivastava, and L. Bahadur, —Natural Dye Extracted From *Saraca asoca* Flowers as Sensitizer for TiO_2 -Based Dye-Sensitized Solar Cell, *J. Sol. Energy Eng.*, vol.138, no. 5, p. 51006, Jul. 2016.

- [27] G. Richhariya, A. Kumar, P. Tekasakul, and B. Gupta, —Natural dyes for dye sensitized solar cell: A review, *Renew. Sustain. Energy Rev.*, vol. 69, no. April 2015, pp. 705–718, Mar. 2017
- [28] A. Kojima, K. Teshima, Y. Shirai, and T. Miyasaka, "Organometal halide perovskites as visible-light sensitizers for photovoltaic cells," *Journal of the American Chemical Society*, vol. 131, pp. 6050-6051, 2009.
- [29] H.-S. Kim, C.-R. Lee, J.-H. Im, K.-B. Lee, T. Moehl, A. Marchioro, et al., "Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%," *Scientific reports*, vol. 2, 2012
- [30] D. F. Marrón, A. Meeder, S. Sadewasser, R. Würz, C. Kaufmann, T. Glatzel, et al., "Lift-off process and rear-side characterization of CuGaSe₂ chalcopyrite thin films and solar cells," *Journal of applied physics*, vol. 97, p. 094915, 2005
- [31] J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin, et al., "Sequential deposition as a route to high-performance perovskite-sensitized solar cells," *Nature*, vol. 499, pp. 316-319, 2013.
- [32] M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, and H. J. Snaith, "Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites," *Science*, vol. 338, pp. 643-647, 2012.
- [33] G. E. Eperon, V. M. Burlakov, P. Docampo, A. Goriely, and H. J. Snaith, "Morphological Control for High Performance, Solution-Processed Planar Heterojunction Perovskite Solar Cells," *Advanced Functional Materials*, vol. 24, pp. 151-157, 2014.
- [34] M. A. Green, "Corrigendum to 'Solar cell efficiency tables (version 46)'[Prog. Photovolt: Res. Appl. 2015; 23: 805–812]," *Progress in Photovoltaics: Research and Applications*, vol. 23, pp. 1202-1202, 2015. 94
- [35] A. Kojima, K. Teshima, Y. Shirai, and T. Miyasaka, "Organometal halide perovskites as visible-light sensitizers for photovoltaic cells," *Journal of the American Chemical Society*, vol. 131, pp. 6050-6051, 2009.

[36] C. C. Stoumpos, C. D. Malliakas, and M. G. Kanatzidis, "Semiconducting tin and lead iodide perovskites with organic cations: phase transitions, high mobilities, and near-infrared photoluminescent properties," *Inorganic chemistry*, vol. 52, pp. 9019-9038, 2013.

[37] 3 Yi-Ting Peng, Shan-Haw Chiou, Ching-Hung Hsiao, Chuenhou (Hao) Ouyang & Chi-Shun TRemarkably enhanced photovoltaic effects and first-principles calculations in neodymium doped BiFeO₃. *Scientific Reports* **volume7**, Article number: 45164 (2017)

[38] Enhanced performance with bismuth ferrite perovskite in ZnO nanorod solid state solar cells Leonard Loh,^{ab} Joe Briscoe^{*a} and Steve Dunn^a

[39]Characterization and Photovoltaic Properties of BiFeO₃ Thin Films.

Yasuhiro Shirahata and Takeo Oku * Department of Materials Science, The University of Shiga Prefecture, 2500 Hassaka, Hikone, Shiga 522-8533, Japan.

[40] S.Y. Yang, J. Seidel, S.J. Byrnes, P. Shafer, C.H. Yang, M.D. Rossell, et al, Above-bandgap voltages from ferroelectric photovoltaic devices, *Nature Nanotech.* 5 (2010) 143-147.