FABRICATION AND CHARACTERIZATION OF DYE SENSITIZED SOLAR CELLS USING NATURAL DYES

BY

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A thesis submitted in fulfilment of the requirement for the degree of Master of Science (Materials Engineering)

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ABSTRACT

This work concerns the fabrication and characterization of DSSCs for photovoltaic applications. The main objectives of this research are fabricate TiO_2 photo anode with three different thicknesses (4.54µm, 7.12µm and 12.3µm), to extract three different organic dyes from natural sensitizers (sumac, humic acid and red onion), to fabricate CNT counter electrode and to assemble solar cells with three different configurations (ITO/TiO_2-Sumac/CNT/ITO, ITO/TiO_2-Humic Acid/CNT/ITO and ITO/TiO_2-Red Onion/CNT/ITO) and to determine the cells photovoltaic properties. The photo anode was prepared from TiO_2 paste and deposited on the ITO conductive glass by doctor blade method with different thicknesses. The energy gap of the TiO_2 photo anode was determined by UV-VIS spectroscopy. SEM images of the TiO_2 photo anode suggested that the optimum thickness of TiO_2 photo anode was 7.12µm. The pH scale of the three different dyes were optimized by the light absorption spectra from UV-VIS spectroscopy. The optimized pH of sumac, humic acid and red onion were 2.5, 2.5 and 2 respectively. The TiO_2 photo anodes were soaked overnight in the dye solutions for sensitization. The absorbtion spectra of the TiO_2 photo anode were increased by 8.79%, 8.68% and 12.68% for sumac, humic acid and red onion dye solution after soaking in the dyes. The counter electrode was fabricated with carbon nanotube in powder form and deposited on ITO glass by doctor blade method. The SEM images of carbon nanotube counter electrode suggested that the average diameter of the CNT was between 13.20-18.22μm. Three types of cell with ITO/TiO_2-Sumac/CNT/ITO, ITO/TiO_2-Humic Acid/CNT/ITO and ITO/TiO_2-Red Onion/CNT/ITO configurations were assembled by mounting the photo anode on the counter electrode and by injecting 2-3 drops of liquid lithium iodide electrolyte into the cell. The photovoltaic properties of the cells were determined by I-V characteristic curve. The best photovoltaic performance was determined by ITO/TiO_2-Sumac/CNT/ITO cell with 0.663V open circuit voltage (Voc), 4.64mAcm-^{2} short circuit current density, 0.637 fill factor and 1.96% efficiency. ITO/TiO_2-Humic Acid/CNT/ITO cell provided 0.568V open circuit voltage (Voc), 5.86mAcm^{-2} short circuit current density, 0.563 fill factor and 1.87% efficiency. ITO/TiO_2-Red Onion/CNT/ITO cell provided 0.445V open circuit voltage (Voc), 5.3mAcm^{-2} short circuit current density, 0.67 fill factor and 1.58% efficiency.

خلاصة البحث

يهدف هذا العمل الى تصنيع وتوصيف التطبيقات الضوئية DSSCs. وتتمثل الأهداف الرئيسية لهذا البحث في تصنيع وتوصيف القطب الأنود ثنائي أكسيد التيتانيوم وثلاثة انواع مختلفة من السُمُوكٌ (4.54µm، 7.12µm ، 12.3µm)، لاستخراج ثلاثة أصباغ عضوية مختلفة من محسسات طبيعية (سوماك sumac، حمض الهيوميك humic acid وبصل أحمر red onion)لتصنيع وتوصيف عداد القطب الكهربائ CNT ولتجميع ثلاثة تشكيلات مختلفة من الخلايا الشمسية (ITO/TiO_2-Sumac/CNT/ITO, ITO/TiO_2-Humic Acid/CNT/ITO and ITO/TiO_2-Red Onion/CNT/ITO) ، بالاضافة الى تحديد خصائص الخلايا الضوئية. تم إعداد صورة القطب الأنود من معجون TiO_2 وأودعت على موصل الزجاج ITO بواسطة طريقة شفرة الطبيب مع سُمُوكٌ مختلفة.وقد تم تحديد فجوة الطاقة لصورة القطب الأنود TiO_2 بواسطة التحليل الطيفي UV-VIS. صور SEM لصورة القطب الأنود TiO2 تشير الى أن السمك الأمثل للقطب الأنود TiO2 هو µm7.12. تم تحسين مقياس درجة الحموضة للأصباغ الثلاثة المختلفة من خلال أطياف امتصاص الضوء من الأشعة فوق البنفسجية التحليل الطيفي UV-VIS . وكان الرقم الهيدروجيني الأمثل من السوماك، حامض الهوميك والبصل الأحمر 2.5 و 2.5 و 2 على التوالي. صورة أقطاب الأنود TiO_2 بين عشية وضحاها غرقة في محلول صبغ التوعية. تم زيادة أطياف الامتصاص من صورة أقطاب الأنود TiO_2 بنسبة 8.79٪، 8.68٪ و 12.68٪ ل سوماك، حامض الحمض والبصل الأحمر محلول صبغ بعد نقعه في الأصباغ. كان عداد القطب الكهربائي مع أنابيب الكربون في شكل مسحوق وترسب على الزجاج ITO باستخدام طريقة شفرة الطبيب. صور أنابيب الكربون للعداد القطبي تقترح أن متوسط قطر CNT كان بين 13.20 -18.22 µm. تم تجميع ثلاثة أنواع من الخلايا بالتشكيلات (ITO/TiO_2-Sumac/CNT/ITO, ITO/TiO_2-Humic Acid/CNT/ITO and ITO/TiO_2-Red Onion/CNT/ITO)عن طريق تركيب صورة القطب الأنود على القطب العداد و عن طريق حقن 2-3 قطرات من السائل ليثيوم يوديد المنحل بالكهرباء في الخلية. تم تحديد الخصائص الكهروضوئية للخلايا بواسطة منحنى السمه I-V.و تم تحديد أفضل أداء ضوئي بواسطة الخلية (ITO / CNT / Sumac-TiO_2 / ITO) عند الدائرة الفولطية المفتوحة (Voc) 0.663 فولط ، كثافة تياردائرة كهربائية قصيرة 4.64 $mAcm^{-2}$ ، وعامل التعبئة 0.637 و كفاءة 1.96٪. خلية (ITO/TiO_2-Humic Acid/CNT/IT) تشكل دائرة فولطية مفتوحة (Voc) V0.568 ، كثافة تيار 5.86 $mAcm^{-2}$ للدائرة الكهربائية القصيرة ، عامل تعبئة 0.563 و كفاءة 1.87٪. خلية (ITO/TiO_2-Red Onion/CNT/ITO) تشكل دائرة مفتوحة بفولطية (Voc) V0.445 ، كثافة تيار 5.3 $mAcm^{-2}$ للدائرة الكهربائية القصيرة ، عامل تعبئة 0.67 وكفاءة 1.58٪.

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APPROVAL PAGE

I certify that I have supervised and read this study and that in my opinion, it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a thesis for the degree of Master of Science (Materials Engineering).

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DECLARATION

I hereby declare that this thesis is the result of my own investigations, except where otherwise stated. I also declare that it has not been previously or concurrently Submit ted as a whole for any other degrees at IIUM or other institutions.

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LIST OF SYMBOLS

Al	Aluminium
Ag	Silver
CO_2	Carbon di oxide
CH_4	Methane
EtOH	Ethyl alcohol
HCl	Hydrochloric acid
HNO_3	Nitric acid
J_{sc}	Short circuit current
KI	Potassium Iodide
Mo	Molybdenum
MnO_2	Manganese dioxide
NaOH	Sodium hydroxide
PVB	Polyvinyl butyral
Pt	Platinum
Ru	Ruthenium
SnO_2	Tin Oxide
SDS	Sodium dodecyl sulfate
SDBS	Sodium dodecyl benzene sulfonate
S	Sensitizer
S^*	Excited state of the sensitizer
S^+	Oxidized state of thhe sensitizer
S^0	Ground state of the sensitizer

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TTIP	Titanium tetraisopropoxide
TiO_2	Titanium oxide
V_{oc}	Open circuit voltage
ZnO	Zinc oxide
η	Efficiency

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LIST OF ABBREVIATIONS

AFM	Atomic force micoscopy
A.D	After decade
AM	Atomic mass
a-Si	Amorphous silicon
CIGS	Copper Indium Gallium Diselenide
CVD	Chemical Vapor Decomposition
CNT	Carbon nano tube
CdTe	Cadmium Telluride
CdS	Cadmium sulfide
DSSCs	Dye sensitized solar cells
et al	(et alia):and others
FF	Fill factor
FESEM	Field Emission Scanning Electron Microscope
FTO	Fluorine doped tin oxide
HA	Humic acid
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
ITO	Indium tin oxide
IPCC	Intergovernmental Panel on Climate Change
i.e	(id est) that is
MWCNT	Multi walled carbon nano tube
MPP	Maximum power point

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PV	Photovoltaic
PLD	Pulse laser deposition
PVA	Poly vinyl acetate
SEI	Secondary electron image
SEM	Scanning electron microscope.
TCO	Transparent conductive oxide
WFT	Wet film thickness
MEMS	Micro electro mechanical system
MWCNTs	Multi wall carbon nano tubes

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CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

Dye Sensitized Solar Cells (DSSCs) belongs to thin film technology discovered by Graetzel and O'Regan in 1991 (Graetzel & O'Regan, 1991). This type of cells are based on photosynthesis principle. DSSCs consist of photo anode having TiO_2 porous layer covered by dye sensitizer molecule that absorbs photons from the sunlight just like chlorophyll in the green leaves. The counter electrode is generally the platinum or carbon nanotube that closes the external circuit of the cell. The fabrication process of dye sensitized is very economical and the basic design is very simple that can be used for large scale production. Pin-Ning Wang, T.-H. H., Chin-Lung Chiang, and Ming-Yuan Shen. Has reported that the involvement of latest technology to fabricate this solar cell has already provided 11% efficiency with chemical sensitizers (Wang et al., 2015). Currently silicon solar cell technology is dictating the photovoltaic market and this trend will last for next 8-10 years. According to the article by M. Oftadeh, A. Aghtar, & M. N. Mir, in the year of 2010, 87% of global PV sales were comprised from crystalline silicon photovoltaic cells (Oftadeh et al., 2012). Since silicon cells are well established, fabrication cost reduction is expected to be achieved to make the PV cell affordable for indoor or outdoor applications. Regarding the cost effectiveness, DSSC is getting emerging popularities for its inexpensive and basic design. Dye sensitized solar cell can become strong competitor of silicon solar cells since it provides cost effectiveness as well as physical flexibility with easy fabrication process. Today, non-silicon PV market is rapidly growing and the non-silicon PV market has captured 20% of the global sell of solar cells (Archer & Hill, 2015).

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The concept of using the photosynthesis to convert the suns power into electricity was presented by Melvin Calvin in 1974 (Calvin, 1974). In the study, he proposed a synthetic membrane cell where the absorption of light was carried out by the sensitizer and an electron was transferred to the carotenoid. Later the electron was diffused through the membrane where it was collected by the electron acceptor. This theoretical model was first taken into account to convert the sunlight into electricity by using natural membranes and pigments.

In 1991, Micheal Graetzel assembled the first DSSCs where sunlight was used to excite the electrons of pigments which was mainly metal complex ruthenium (Graetzel & Brian, 1991). The excited electrons captured higher energy to jump towards the conduction band of TiO_2 wide band gap semiconductor. This phenomenon causes the charge separation in DSSC. This process is very similar to photosynthesis, since the dye sensitizer plays the role of chlorophyll and the counter electrode completes the charge transportation circuit. The performance of DSSCs, highly depends on the dye sensitizer which can be determined with the dye absorption spectrum. M.K. Nazeeruddin , Zakeeruddin SM, Humphry-Baker R, Jirousek M, Liska P, Vlachopoulos N. has reported the highest efficiency 12% recorded with Ru metal complex sensitizer (Nazeeruddin et al., 1999). But metal complexes are expensive, toxic and degrades in water. Using natural dye sensitizers are economic and environment friendly as they are easily accessible to extract from natural plants, leaves, roots, fruits or flowers and completely harm free. Due to the cost effectiveness, non-toxicity, abundance in the nature and natural complete biodegradation process has made natural sensitizer a promising replacement of chemical or metal complex dyes.

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1.2 PRINCIPLE OF DSSCS

Like other solar cells, DSSCs converts the solar energy directly into direct electric current. Figure 1.1 shows basic mechanism of DSSCs.

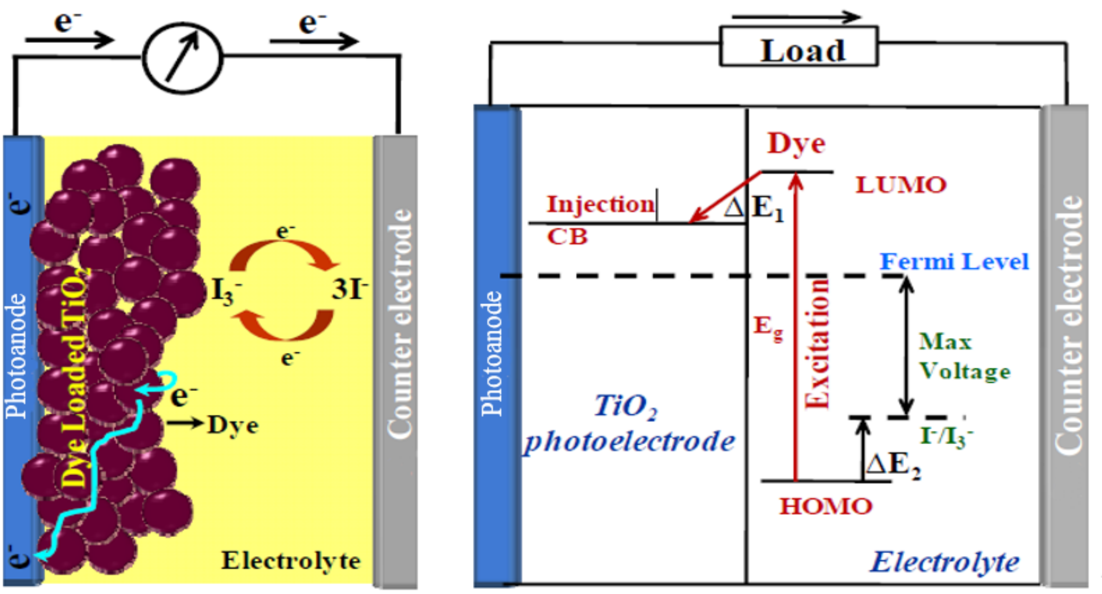

Figure 1.1 Schematic Diagram and Working Mechanism of DSSC.

The basic mechanism of DSSC includes:

1. A transparent conductive anode made from glass sheet treated with oxide layer of indium doped tin oxide (ITO), fluorine doped tin oxide (FTO) and aluminium doped zinc oxide (AZO).

2. A mesoporous semiconductor layer (TiO_2 or ZnO) deposited on the transparent conductive glass to stimulate electron conduction.

3. Dye sensitizer for pigment absorbtion of the photo anode to improve the light absorbtion.

4. Electrolyte solution comprising redox mediator to transport the electronscarried from the counter electrode to dye solution.

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5. A cathode or counter electrode made from carbon nanotube or platinum to facilitate the electron collection from the external circuit.

The following steps are attained throughout the whole process

TiO_2| S + hν → TiO_2|S* Excitation of dye molecule upon light irradiation (1.1)

TiO_2| S* → TiO_2|S+ + e^- Oxidation of dye for injecting of electrons into TiO_2 (1.2)

TiO_2| S^+ + e^- → TiO_2|S Dye recovering the initial state (1.3)

TiO_2| S^+ + 3/2I^- → TiO_2|S + 1/2I_3^- Oxidization of electrolyte molecule (1.4)

1/2I_3^- + e- → 3/2I^- Imposition of electrolyte at counter electrode (1.5)

When sunlight hits the solar cell, dye sensitizer excites and allocate electron from the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) state and the electrons jump to conduction band of semiconductor oxide (TiO_2 or ZnO). The electrons then used by the outer circuit and collected by counter electrode (CNT or Pt). The electrons then collected by the electrolyte and transports to the dye sensitizer. This way the electron cycle completes and current is supplied to the load. The overall performance of the solar cell can be estimated with respect to cell efficiency (η) and fill factor (FF) expressed as

$$\eta = \frac{P_m}{P_{in}} = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \quad (1.6)$$

$$FF = \frac{J_m \times V_m}{J_{sc} \times V_{oc}} \quad (1.7)$$

Where Jsc refers to short-circuit current density (mA/cm^2), Voc stands for open-circuit voltage (V) and Pin for incident light power. Jm and Vm stands for maximum current and maximum voltage, respectively.

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1.2.1 Short Circuit Current Density (Jsc)

Short circuit current is achieved when solar cell has zero resistance as load. The amount of current depends on electrons and the charge separation of electron and holes. In case of solar cell, it is measured as short circuit current density Jsc=Isc/A (mA/cm^2), where A refers to effective area.

1.2.2 Open-Circuit Voltage (Voc)

Open circuit voltage is defined as the maximum voltage obtained from solar cell by keeping the load with infinite resistance. It is the obtained by the potential difference between the Fermi level of electrons from the semiconductor conduction band and the redox potential of electrolyte.

1.2.3 Fill Factor (FF)

Fill factor is defined as the maximum power output from the solar cell. It is obtained by the I-V characteristic curve. It is measured by multiplying the maximum current (Jm) to the product of maximum voltage (Vm) divided by open circuit voltage (Voc) and short circuit current density (Jsc)

$$FF = \frac{J_m \times V_m}{J_{sc} \times V_{oc}} \qquad (1.8)$$

1.2.4 Efficiency of Cell (η)

Efficiency of solar cell is determined by the ratio of maximum electrical energy output to the energy input. The mathematical expression is as follows

$$\eta = \frac{Voc \times Jsc \times FF}{Pin} \times 100 \qquad (1.9)$$

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Pin refers to power input from the light source. The efficiency depends on the cells performance as well as on the incident light.

1.3 PROBLEM STATEMENT

Today, power production with zero environmental effect is one of the major concerns both economically and environmentally. Therefore, renewable energy has enlighten the doorways for achieving electricity replacing the use of fossil fuels, coal energy and nuclear energy without any environmental hazard. Developing inexpensive and efficient alternative renewable energy sources has become a challenge globally to meet the energy crisis in recent future. Among all the renewable energies, solar cell is considered as the most viable system to meet the future energy crisis. Wide range of solar cells are currently being investigated throughout the world to utilize sun's power to convert it into electricity. Silicon solar cells were developed in the first generation for electricity conversion from sunlight. However, silicon cells are brittle, bulky and not economical. As a result, the investigation for replacing silicon based solar cell led to second generation solar cells and third generation solar cells. Second generation solar cells are depended on the thin epitaxial deposits of semiconductor materials. Whereas, third generation solar cells are different in nature and not depended on the typical p-n junction photo generation technique. The new types of solar cells include dye-sensitized solar cells and organic and hybrid solar cells. In dye sensitized solar cells the dyes mostly used are chemical which makes the cell expensive and also harmful for nature. Researchers are investigating to divert the dye from inorganic to organic to reduce the fabrication cost and also to discover eco-friendly solar cell. In this research three different types of DSSCs will be assembled and characterized based on three different organic dyes.

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1.4 OBJECTIVES OF THE RESEARCH

- To fabricate TiO_2 photoanode on Indium tin oxide conducting subtrate by "Doctor Blade" method.

- To extract 3 different dyes (sumac, humic acid and red onion) from natural sources for soaking up the TiO_2 photoanode.

- To fabricate carbon nanotube (CNT) counter electrode on ITO conducting substrate by "Doctor Blade" method.
- To measure the cell's photovoltaic properties such as open circuit voltage V_{oc}, short circuit current I_{sc}, fill factor FF and efficiency η with ITO/TiO_2+Sumac/CNT/ITO, ITO/TiO_2+Humic Acid/CNT/ITO and ITO/TiO_2+Red Onion/CNT/ITO configurations.

1.5 SCOPE OF THE RESEARCH

The main purpose of this research work is to propose three working solar cell based on TiO_2 photo anode, three different natural dyes and carbon nanotube working electrode to determine their eligibility to be used as dyes in organic solar cells. The paste of the TiO_2 was optimized by varying the deposition thickness and also by balancing the usage of acetic acid and detergent solution. However, the goal was to achieve the best dye solution with the minimum usage of chemicals and treatment. The scope of the research can be outlined as the follows.

a) Optimization of the TiO_2 photo anode by varying the thickness of the TiO_2 paste,
b) Optimization of dye preparation by varying the pH scale.
c) Fabrication of carbon nanotube counter electrode on ITO conducting glass.