



**THE OPTIMIZATION OF TITANIUM DIOXIDE  
(TiO<sub>2</sub>) THICKNESS AND ORGANIC DYE  
SENSITIZERS TO IMPROVE DYE SENSITIZED  
SOLAR CELL (DSSC) PERFORMANCE**

by

**SYAFINAR BINTI RAMLI  
(1430911276)**

A thesis submitted  
In fulfillment of the requirements for the degree of  
Master of Science in Electrical Sytem Engineering

**SCHOOL OF ELECTRICAL SYSTEM ENGINEERING  
UNIVERSITI MALAYSIA PERLIS**

**2015**

# UNIVERSITI MALAYSIA PERLIS

## DECLARATION OF THESIS

Author's full name : SYAFINAR BINTI RAMLI  
Date of birth : 30 SEPTEMBER 1989  
Title : THE OPTIMIZATION OF TITANIUM DIOXIDE (TiO<sub>2</sub>) THICKNESS  
AND ORGANIC DYE SENSITIZERS TO IMPROVE DYE SENSITIZED  
SOLAR CELL (DSSC) PERFORMANCE  
Academic Session : 2014/2015

I hereby declare that the thesis becomes the property of Universiti Malaysia Perlis (UniMAP) and to be placed at the library of UniMAP. This thesis is classified as :

- CONFIDENTIAL** (Contains confidential information under the Official Secret Act 1972)\*
- RESTRICTED** (Contains restricted information as specified by the organization where research was done)\*
- OPEN ACCESS** I agree that my thesis is to be made immediately available as hard copy or on-line open access (full text)

I, the author, give permission to the UniMAP to reproduce this thesis in whole or in part for the purpose of research or academic exchange only (except during a period of \_\_\_\_\_ years, if so requested above).

Certified by:

\_\_\_\_\_  
**SIGNATURE**

890930-02-5894

\_\_\_\_\_  
**(NEW IC NO. / PASSPORT NO.)**

Date : \_\_\_\_\_

\_\_\_\_\_  
**SIGNATURE OF SUPERVISOR**

DR. MUHAMMAD IRWANTO BIN MISRUN

\_\_\_\_\_  
**NAME OF SUPERVISOR**

Date : \_\_\_\_\_

**NOTES :** \* If the thesis is CONFIDENTIAL or RESTRICTED, please attach with the letter from the organization with period and reasons for confidentiality or restriction.

## ACKNOWLEDGEMENT

“You simply will not be the same person two months from now after consciously giving thanks each day for the abundance that exists in your life. And you will have set in motion an ancient spiritual law: the more you have and are grateful for, the more will be given you.” -*Sarah Ban Breathnach*-

Alhamdulillah, thanks to Allah SWT

There are many individuals whom I would like to thank for their support and guidance that made it possible for me to successfully complete this Master of Science research work. First of all, my sincere gratitude goes to my beloved family, to my beloved husband for giving me life in the first place and for unconditional support and encouragement to pursue and to finish my studies in master by research.

The special thank goes to my helpful supervisors, Dr. Gomesh Nair a/l Shasidharan and Dr. Muhammad Irwanto. The supervision and support that they gave truly help the progression and smoothness of my research work. The co-operation is much indeed appreciated, and I am so honored to have both of you as my supervisors.

Lastly, I would like to express my gratitude to all my colleagues, especially Nur Zhafarina, Amelia, Leow Wai Zhe and those who work together to complete the final research work.

## TABLE OF CONTENTS

	<b>PAGE</b>
<b>THESIS DECLARATION</b>	i
<b>ACKNOWLEDGEMENT</b>	ii
<b>TABLE OF CONTENT</b>	iii
<b>LIST OF TABLE</b>	vi
<b>LIST OF FIGURES</b>	vii
<b>LIST OF ABBREVIATIONS</b>	xii
<b>LIST OF SYMBOLS</b>	xiv
<b>ABSTRAK</b>	xv
<b>ABSTRACT</b>	xvi
<b>CHAPTER 1 INTRODUCTION</b>	
1.1 Introduction	1
1.2 Research Problem Statement	3
1.3 Research Objectives	3
1.4 Thesis Organization	4
<b>CHAPTER 2 LITERATURE REVIEW</b>	
2.1 Review on Solar Cell Generation	6
2.2 Dye Sensitized Solar Cell (DSSC)	8
2.3 Origin Of DSSC	8
2.4 Materials in DSSC	9
2.5 Operating Principle	12
2.6 Optical Characterization of Dye	14
2.6.1 Energy of the Photon (eV)	15
2.6.2 Absorption Coefficient	15
2.6.3 Fourier Transform Spectroscopy (FTIR)	16
2.7 Solar Cell Importance Parameter	16
2.8 Natural Dye Sensitizer in DSSC	19
2.9 Review on Organic Dyes	24

2.10	Review on Dye Cocktails	28
2.11	Review on Effect of Solvent in Extracting Pigments From Plants	30
2.12	Review on the thickness of Titanium Dioxide (TiO <sub>2</sub> ) film	31
<b>CHAPTER 3</b>	<b>METHODOLOGY</b>	
3.1	Introduction	34
3.2	Experimental Setup	36
3.2.1	Equipment	36
3.2.2	Chemical Solutions	38
3.3	Extraction Process of Nature Based Dye	40
3.3.1	Extracting Anthocyanin and Betalain Pigments From Fruit and Flowers	41
3.3.2	Extraction Chlorophyll Pigments From Spinach Leaves	43
3.3.3	Preparation of Dyes Cocktails	45
3.4	Fabrication of Dye Sensitized Solar Cells by Using “Doctor Blade” Methods	48
3.4.1	Preparation of Conductive Glass, Indium Tin Oxide (ITO) for Dye Sensitized	49
3.4.2	Preparation of Semiconductor for DSSC Titanium Dioxide (TiO <sub>2</sub> ) Paste	50
3.4.3	Procedure of Fabrication of Dye Sensitized Solar Cell by Using “Doctor Blade” Method	51
3.5	Optical Characterization	56
3.5.1	UV-Vis Characterization of Natural Based Dye	56
3.5.2	Procedure Taken to Measure the Absorbance Spectrum Using UV-Vis Spectrophotometer	58
3.6	FTIR Spectroscopy	64
3.7	Photoelectrical Characterization of DSSC Sample	66
3.8	Measure the Thickness of Titanium Dioxide Layer	72
3.9	Morphological and Microstructure Characterization	74

<b>CHAPTER 4</b>	<b>RESULT AND DISCUSSION</b>	
4.1	Introduction	78
4.2	Optical Characteristics of Nature based Dyes	79
4.2.1	UV-Vis Absorption Spectra for Single Dye and Effects of Solvents in Extracting Pigments Towards Photon Energy and Absorption Coefficient of the Single Dyes	79
4.2.2	UV-Vis Absorption Spectra for Dye Cocktails and Effects of Solvents in Extracting Pigments Towards Photon Energy and Absorption Coefficient of the Dye Cocktails	96
4.3	FTIR Spectra	106
4.4	TiO <sub>2</sub> Film Thickness Measurement Result	115
4.4.1	TiO <sub>2</sub> Film Thickness Measurement by Using Thickness Profiler	115
4.4.2	Effect of TiO <sub>2</sub> Thickness on Solar cell Efficiency	116
4.5	Electrical Characteristic of Nature Based Dye	118
4.5.1	Electrical Characteristic of Nature Based Dye Absorbed to $\pm 10$ $\mu\text{m}$ TiO <sub>2</sub> Film	118
4.5.2	Overall Photovoltaic Parameter of Fabricated DSSC	128
4.6	Scan Electron Microscopy (SEM) of TiO <sub>2</sub> Film	131
<b>CHAPTER 5</b>	<b>CONCLUSION AND RECOMMEDATION</b>	
5.1	Introduction	135
5.2	Conclusion	136
5.3	Recommendation of Future Advancement	137
<b>REFERENCES</b>		138
<b>APPENDIX A</b>	Publications	146
<b>APPENDIX B</b>	Exhibitions	148
<b>APPENDIX C</b>	Technical Specification of Equipment used	151
<b>APPENDIX D</b>	Table of FTIR	158

©This item is protected by original copyright

## LIST OF TABLES

NO.		PAGE.
2.1	Photoelectrochemical properties of solar cells with natural dyes	26
2.2	Photoelectrochemical properties of solar cells with dye cocktails	30
2.3	Previous studies on the thickness of TiO <sub>2</sub> film to generate high performance of DSSC	33
3.1	List of solution with their functions	39
3.2	List of fruits and flowers used in the extraction method for natural dye sample	45
4.1	Photon energy and absorption coefficient of the single dyes	94
4.2	Photon energy and absorption coefficient of the dye cocktails	103
4.3	FTIR spectra peak values and functional group obtained from fruits and flowers with different extract solvents	113
4.4	TiO <sub>2</sub> electrode thickness based on Dr. Blade Method	115
4.5	Overall performance of TiO <sub>2</sub> with different thickness	117
4.6	Photoelectrical parameters of the DSSC fabricated with blueberry (B) and reference sample of dragon fruit (D) extracts	119
4.7	Photoelectrical parameters of the DSSC fabricated with dragon fruit (D) extracts	121
4.8	Photoelectrical parameters of the DSSC fabricated with dye cocktail from blueberry and dragon fruit (M) and reference sample of dragon fruit (D) extracts	123
4.9	Photoelectrical parameters of the DSSC fabricated with hibiscus (H) and reference sample of dragon fruit (D) extracts	125
4.10	Photoelectrical parameters of the DSSC fabricated with bougainvillea (BOU) and reference sample of dragon fruit (D) extracts	127
4.10	Photoelectrical parameters of fabricated DSSC	131



## LIST OF FIGURES

NO.		PAGE
2.1.	Chart of photovoltaic cell developments from 1975 to 2010	7
2.2.	Dye Sensitized Solar Cell cross section	9
2.3.	Schematic structure of DSSC	14
2.4.	I-V Curve of solar cell	18
2.5.	Absorption spectra of freshly isolated Chlorophyll-a and Chlorophyll-b in diethyl ether (pure solvent)	21
2.6.	Structure of natural chlorophyll derivatives: chlorophyll	22
2.7.	(a) Basic chemical structures of the most abundant anthocyanidins (b) Chemical structures of anthocyanidins in acidic and basic media (c) Chelation mechanism of anthocyanidins with TiO <sub>2</sub>	23
2.8.	General structures of the main betalain a) betaxanthin (R <sub>1</sub> = H and R <sub>2</sub> = amine or amino acid group b) betacyanin (R = b-D-glucose)	24
3.1	Process flow of the project	35
3.2	Research equipments; (a) UV-Vis Spectroscopy (b) Ultrasonic Bath (c) Hot plate (d) Solar Simulator (e) Thickness Profiler (f) Centrifuge Machine (g) Perkin Elmer Spectrum 65 FTIR	37
3.3	Equipment and materials	40
3.4	(a) bougainvillea's flower (b) dried plants were crushed (c) dried plants was placed with two different solvents (d) the samples is placed into ultrasonic cleaner (e) the setting of ultrasonic cleaner (f) the sample is placed into centrifuge machine	42
3.5	(a) bougainvillea extracted with ethanol, (b) bougainvillea extracted with di-water	43
3.6	(a) spinach (b) dried spinach is crushed (c) dried plant is placed into two different solvents (d) the samples is ready to be placed in centrifuge machine (e) ready sample	44
3.7	ITO Glass	49

3.8	Resistivity reading of ITO Glass	49
3.9	Process of making TiO <sub>2</sub> paste	50
3.10	Ultrasonic cleaner reading	51
3.11	(a) ITO coated glass (b) apply scotch tape (c) TiO <sub>2</sub> paste on ITO coated glass (d) flatter TiO <sub>2</sub> paste (e) TiO <sub>2</sub> film	52
3.12	Sintered TiO <sub>2</sub> film with hot plate	53
3.13	(a) chlorophyll's dye (b) immerse TiO <sub>2</sub> film into chlorophyll's dye	54
3.14	TiO <sub>2</sub> film after "sensitized" process	54
3.15	Graphite pencil into ITO Glass	55
3.16	Solar cell with chlorophyll dye	56
3.17	Evolution 201 UV-Vis Spectrophotometer	57
3.18	a) reference sample: di-water or ethanol, b) test sample	57
3.19	Refill the cuvette	58
3.20	Dye in cuvette	58
3.21	a) bougainvillea with ethanol b) bougainvillea with di-water c) hibiscus with ethanol d) hibiscus with di-water	59
3.22	Setting the input data of UV-Vis Spectroscopy	60
3.23	Measuring the reference solution	61
3.24	Loading guide screen	62
3.25	Loading guide screen	63
3.26	UV-Vis absorbance for dye sample	63
3.27	FTIR spectroscopy	64
3.28	a) inside of FTIR spectroscopy, (b) ATR holder	65
3.29	Result of FTIR	66
3.30	Solar light 1 sun simulator	67

3.31	(a) pyranometer under a collimating lens (b) pyranometer is connected to radiometer (c) reading of solar irradiance $W/m^2$ (d) DSSC sample is placed under a collimating lens (e) solar cell is connected with probe (f) complete set up of solar simulator	68
3.32	Light source from halogen lamp in dark room and the cell configuration	69
3.33	SMU unit is connected to PC interface	70
3.34	Parameter setup for current and voltage potential	71
3.35	I-V curve has been simulated	72
3.36	Process of measuring the thickness of $TiO_2$ film	73
3.37	$TiO_2$ thickness measurement data	74
3.38	SEM tools	75
3.39	$TiO_2$ paste on sample tray of SEM	76
3.40	Tower is touch down on the surface of $TiO_2$ inside vacuum compartment	76
3.41	SEM images for $TiO_2$ surface	77
4.1	Absorption spectra of blueberry extracted by using di-water (BB-DI) and ethanol (BB-Etha)	80
4.2	Absorption spectra of Bougainvillea extracted by using ethanol (BOU-Etha)	81
4.3	Absorption spectra of bougainvillea extracted by using di-water (B-DI)	82
4.4	Absorption spectra of dragon fruit extracted by using di-water (D-DI) and ethanol (D-Etha)	83
4.5	Absorption spectra of hibiscus extracted by using di-water (H-DI) and ethanol (H-Etha)	84
4.6	Absorption spectra of purple cabbage extracted by using di-water (P-DI) and ethanol (P-Etha)	85
4.7	Absorption spectra of turmeric extracted by using di-water (T-DI) and ethanol (T-Etha)	86
4.8	Absorption spectra of coffee extracted by using ethanol (C-Etha) and di-water (C-DI)	87

4.9	Absorption spectra of blue pea's flower extracted by using ethanol (BP-Etha) and di water (BP-DI)	88
4.10	Absorption spectra of morning glory's flower extracted by using ethanol (MG-Etha) and di-water (MG-DI)	89
4.11	Absorption spectra of spinach extracted by using ethanol (S-Etha) and di- water (S-DI)	90
4.12	Photon energy of nature dyes with ethanol and di-water as extract solvents for single dyes	95
4.13	Absorption coefficient of nature syes with ethanol and di-water as extract solvents	95
4.14	Absorption spectra of dye cocktail from blueberry and dragon fruit extracted by using ethanol (BB+DF-Etha) and di-water (BB+DF-DI)	97
4.15	Absorption spectra of dye cocktail from blueberry and purple cabbage extracted by using ethanol (P+B-Etha) and di-water (P+B-DI)	98
4.16	Absorption spectra of dye cocktail from coffee and turmeric extracted by using ethanol (C+T-Etha) and di-water (C+T-DI)	99
4.17	Absorption spectra of dye cocktail from blueberry and bougainvillea extracted by using ethanol (BB+B-Etha) and di-water (BB+B-DI)	100
4.18	Absorption spectra of dye cocktail from morning glory's flower and purple cabbage extracted by using ethanol (P+MG-Etha) and di-water (P+MG-DI)	101
4.19	Photon energy of nature dyes with ethanol and di-water as extract solvents	103
4.20	Absorption coefficient of nature dyes with ethanol and di-water as extract solvents	104
4.21	Absorption spectra of five nature based dyes extract by ethanol (Etha) and di-water (DI)	105
4.22	FTIR spectrum of dye cocktail of blueberry and dragon fruit extracted by di-water (B+DF-DI) and ethanol (B+DF-Etha)	107
4.23	FTIR spectrum of dragon fruit extracted by di-water (D-DI) and ethanol (D-Etha)	108

4.24	FTIR spectrum of hibiscus extracted by di-water (H-DI) and ethanol (H-Etha)	109
4.25	FTIR spectrum of bougainvillea natural dye extracted by di-water (B-DI) and ethanol (B-Etha)	111
4.26	FTIR spectra of blueberry natural dye extracted by di-water (BB-DI) and ethanol (BB-Etha)	112
4.27	Photovoltaic measurement of TiO <sub>2</sub> film substrate with thickness of 5±0.01 μm and 10±0.01 μm	117
4.28	Current voltage characteristic curve of blueberry dye coated of TiO <sub>2</sub> with 10 ±0.01 μm film thickness	119
4.29	Power – voltage characteristic of the DSSC sensitized by blueberry dye	120
4.30	Current voltage characteristic curve of dragon fruit dye coated with TiO <sub>2</sub> with 10 ±0.01 μm film thickness	121
4.31	Power – voltage characteristic of the DSSC sensitized by dragon fruit dye	122
4.32	Current voltage characteristic curve of dye cocktail from blueberry and dragon fruit coated with TiO <sub>2</sub> with 10 ±0.01 μm film thickness	123
4.33	Power – voltage characteristic of the DSSC sensitized by dye cocktail from blueberry and dragon fruit	124
4.34	Current voltage characteristic curve of hibiscus dye coated with TiO <sub>2</sub> with 10 ±0.01 μm film thickness	125
4.35	Power – voltage characteristic of the DSSC sensitized by hibiscus dye	126
4.36	Current voltage characteristic curve of bougainvillea coated of TiO <sub>2</sub> with 10 ±0.01 μm film thickness	127
4.37	Power – voltage characteristic of the DSSC sensitized by bougainvillea dye	128
4.38	Particle size of TiO <sub>2</sub> (a) 5±0.01μm (b) 10±0.01 μm	133
4.39	TiO <sub>2</sub> rough surface at (a) x10,000, (b) x 20,000, (c) x 40,000, (d) 60,000 respectively	133

## LIST OF ABBREVIATIONS

AM	Air Mass
Bn	Betanin
Bx	Betaxanthins
CdTe	Cadmium Telluride
CE	Counter Electrode
CIGS	Copper Indium Gallium Selenite
Etha	Ethanol
DI-water	Deionized water
COOH	Carboxyl Group
C=O	Carbonyl Group
O-H	Hydroxyl Group
DSSC	Dye Sensitized Solar Cell
E	Energy
eV	Electron Volt
FF	Fill Factor
FTIR	Fourier Transform Infrared Spectra
HUMO	Highest Occupied Molecular Orbital

LUMO	Lowest Unoccupied Molecular Orbital
$I_3^-$	Triiodide ions
$I_{\max}$	Maximum Current
IR	Infrared
$I_{SC}$	Short Circuit Current
ITO	Indium Tin Oxide
I-V	Current-voltage
$P_{in}$	Incident Power
PV	Photovoltaic
$S^*$	Excited Electrons
SEM	Scan Electron Microscopy
$TiO_2$	Titanium Dioxide
UV	Ultraviolet
UV-Vis	Ultraviolet Visible Spectral Region
$V_{\max}$	Maximum Voltage
$I_{\max}$	Maximum Current
$V_{OC}$	Open Circuit Voltage

## LIST OF SYMBOLS

$\lambda$	Wavelength
$\lambda_{\max}$	Maximum Absorbance
$\eta$	Efficiency of solar cell
$\alpha$	Absorption coefficient

©This item is protected by original copyright



# KETEBALAN OPTIMUM TITANIUM DIOKSIDA (TiO<sub>2</sub>) DAN PENCELUP SEMULAJADI BAGI MENINGKATKAN PRESTASI PENCELUP PEMEKA SEL SURIA (DSSC)

## ABSTRAK

Tenaga boleh diperbaharui terutamanya tenaga suria telah menarik banyak perhatian disebabkan oleh ciri-cirinya yang memberikan tenaga tanpa had untuk menukarkan cahaya matahari kepada tenaga elektrik tanpa membahayakan alam sekitar. Sel solar berasaskan silikon telah memonopoli pasaran sel solar disebabkan oleh kecekapan yang tinggi dalam menghasilkan tenaga elektrik daripada cahaya matahari. Namun demikian, sel solar daripada silikon dijual dengan harga yang tinggi di dalam pasaran kerana penghasilannya yang rumit dan ini membawa kepada penghasilan Pecelup Pemeka Sel Suria (DSSC) pada tahun 1991 oleh Micheal Gratzel dan Brian O'Regan. DSSC menjanjikan kos yang murah dan proses pembuatannya yang mudah, malah boleh beroperasi dalam keadaan keamatan cahaya yang rendah. DSSC menggunakan pecelup daripada ruthenium (Ru) yang menghasilkan kecekapan yang tinggi sebanyak 11.1 %, akan tetapi penghasilannya menggunakan kos yang tinggi dan juga langkah pembuatan yang rumit. Untuk mengatasi masalah ini, pecelup semulajadi digunakan untuk menggantikan pecelup daripada Ru (II). Projek ini memperkenalkan penggunaan 15 jenis pecelup semulajadi dan menggunakan dua ketebalan titanium dioksida (TiO<sub>2</sub>) iaitu 5  $\mu\text{m}$  dan 10  $\mu\text{m}$  untuk memperbaiki prestasi DSSC. DSSC menggunakan sepuluh jenis pecelup daripada buah beri, buah naga, kubis ungu, bunga raya, bunga kertas, kopi, kunyit, bunga telang dan bunga seri pagi dan lima lagi terdiri daripada hasil gabungan dua pecelup iaitu buah beri dan bunga kertas, kopi dan kunyit, kubis ungu dan buah beri, buah beri dan buah naga dan akhir sekali bunga seri pagi dan kubis ungu. Kesan menggunakan pelarut yang berbeza daripada ethanol dan air suling turut dikaji dan digunakan untuk mengkaji tenaga cahaya dan kebolehan penyerapan pecelup untuk meningkatkan prestasi kecekapan DSSC. Dua ketebalan berbeza untuk TiO<sub>2</sub> elektrod dilakukan di atas permukaan kaca dan dilakukan menggunakan cara "Doctor Blade", dan kemudiannya TiO<sub>2</sub> elektrod akan direndam di dalam pecelup semulajadi untuk proses "sensitized". Daripada hasil kajian mendapati, gabungan pecelup daripada buah beri dan buah naga menghasilkan penyerapan cahaya matahari maksima dalam lingkungan 450 nm ke 650 nm dan memudahkan DSSC untuk menyerap keseluruhan spektrum cahaya dengan berkesan pada tenaga sinaran suria yang rendah dan meningkatkan prestasi keseluruhan sel solar. Dari spektrum FTIR, kehadiran C=O yang terdiri dari kumpulan "carbonyl" dan OH yang terdiri daripada kumpulan "hydroxyl" dalam pecelup koktel daripada buah beri dan buah naga mewakili kumpulan "carboxyl" dalam pigmen iaitu Betalains, yang membantu untuk bercantum dengan molekul TiO<sub>2</sub> dengan cekap. Bagi koktel pecelup daripada buah beri dan buah naga, elektrod pecelup sensitif dalam etanol pelarut dengan ketebalan optimum filem TiO<sub>2</sub>  $10 \pm 0.01 \mu\text{m}$ , menghasilkan arus litar pintas ( $I_{sc}$ ) 3 mA, voltan ( $V_{oc}$ ) 0.8 V, dan "fill factor" sebanyak 0.51, bersamaan dengan kecekapan penukaran tenaga ( $\eta$ ) daripada 1.22% dengan tenaga foton daripada pecelup 2.49 eV dan pekali penyerapan  $2.17 \times 10^3 \text{ m}^{-1}$  mewakili kecekapan yang tertinggi.

# THE OPTIMIZATION OF TITANIUM DIOXIDE (TiO<sub>2</sub>) THICKNESS AND ORGANIC DYE SENSITIZERS TO IMPROVE DYE SENSITIZED SOLAR CELL (DSSC) PERFORMANCE

## ABSTRACT

Renewable energy especially solar energy has attracted much attention due to its features which provides free energy by converting sunlight into electrical energy without harming the environment. Silicon based solar cell has pioneered the photovoltaic market due to its potential in converting more radiance of the sun into electrical energy thus having high conversion efficiency and by far, is a reliable mechanism in light harvesting. Despite having all odds in its favor, a typical silicon based photovoltaic is produced and sold at high cost due to its tedious production step and this is when dye sensitized solar cell (DSSC) has been introduced in 1991 by Micheal Gratzel and Brian O'Regan. DSSC promises an easy and low cost of manufacturing process at which can also operate in low light condition. DSSC uses ruthenium (Ru) based dyes compound which provides relatively high efficiency of 11.1%, yet, there are several drawbacks on the use of Ru complexes such as limited amount of noble metals, high cost and sophisticated synthesis steps. To address this issue, metal-free organic dyes have been prepared and applied in DSSC to replace Ru (II) based dyes. This thesis introduces the uses of 15 types of nature based dyes and different thickness of 5  $\mu\text{m}$  and 10  $\mu\text{m}$  of titanium dioxide (TiO<sub>2</sub>) film to improve the performance of DSSC. DSSC were assembled using ten types of single dyes extracted from blueberry, dragon fruit, purple cabbage, hibiscus, bougainvillea, coffee, turmeric, blue pea's flower and morning glory's flower as well as five types of cocktail dye from the combination of two natural dyes consist of blueberry and bougainvillea, coffee and turmeric, purple cabbage and blueberry, blueberry and dragon fruit and finally morning glory's flower and purple cabbage. The effect of extracting solvents from ethanol and deionized water (di-water) were investigated and used in sensitization process to calculate the photon energy

and absorption coefficient of the dye for better improvement in DSSC's conversion efficiency. The nanocrystalline anatase of  $\text{TiO}_2$  films with two different thicknesses (5 and 10  $\mu\text{m}$ ) have been fabricated on ITO coated glass substrates by a Doctor Blade method and then was immersed into nature based dye sensitizer for "sensitized" process. From the overall experiment result, dye cocktail which consist of blueberry and dragon fruit exhibits broad bands absorption in the range of 450 to 650 nm facilitate DSSC to absorb entire visible light spectrum effectively at low energy solar radiation and improved overall photovoltaic performance. From FTIR spectra, the presence of carboxyl group ( $\text{COOH}$ ) in dye cocktails from blueberry and dragon fruit represented in Betalains pigment helps to anchor with  $\text{TiO}_2$  surface efficiently. As for the dye cocktails from blueberry and dragon fruit, dye-sensitized electrode in ethanol solvent with the optimum thickness of  $\text{TiO}_2$  film of  $10 \pm 0.01 \mu\text{m}$  yields a short circuit current ( $I_{\text{SC}}$ ) of 3 mA, an open circuit voltage ( $V_{\text{OC}}$ ) of 0.8 V, and a fill factor of 0.51, corresponding to the highest energy conversion efficiency ( $\eta$ ) of 1.22%.

©This item is protected by original copyright

# CHAPTER 1

## INTRODUCTION

### 1.1 Introduction

Nowadays, researchers are seeking an alternative to replace the fossil fuel such as coal and natural gas with renewable energy technologies, which provided low cost solution and abundance in resources. Photovoltaic (PV) has been introduced as preferred renewable energy instead of other renewable energy such as hydro power and biomass energy because PV use solar energy sources which obvious source of clean and cheap energy to develop electrical energy. PV is a device which converts sunlight into electrical energy and makes it long-lasting and dependable. The concept of PV are divided into two conditions as the charge generation at the semiconductor-dye interface and charge transport is done by the semiconductor and electrolyte (Grätzel, 2003; Nazeeruddin et al., 2011).

The history of PV started in the 19<sup>th</sup> century by Charles Fritts which introduced primitive photovoltaic cell composed of selenium and a thin layer of gold. Herman Wilhelm Vogel found a method to produce black-and-white photographic films with the increase the photographic emulsion sensitivity and associated with silver halide emulsion with dye that are having band gaps oat 2.7-3.2 eV. This finding is the first significant study on the dye sensitization of semiconductors (Ludin et al., 2014). So far, silicon-based solar cell currently dominate the commercial PV market which usually

made from mono and poly-crystalline silicon doped. Up to now, the highest efficiency of mono crystalline silicon is achieved up to 21 % but due to long fabrication process, thin film technologies have been introduced. Thin film photovoltaic cell's materials such as copper indium gallium selenite (CIGS) and cadmium telluride (CdTe) require high cost, contained toxic chemical and have low natural abundance (Nazeeruddin et al., 2011). Organic photovoltaic is proposed to overcome these problems and tend to introduce the third generation of solar cell.

Dye sensitized solar cell (DSSC) was invented by Micheal Gratzel in 1991 (O'Regan & Gratzel, 1991) as an alternative in solar cell development because of its speciality on simple procedure of fabrication, low production cost and use safer material in fabrication (Gong et al., 2012). DSSC is introduced because DSSC can be fabricated at low cost to harvest green energy from sunlight instead of using silicon-based solar cell. DSSC has the potential in developing for solar panel productions in the future with a new method of fabricate the DSSC. The performance and efficiency of DSSC are dependent on the counter electrode, the structure and morphology of the titanium dioxide ( $\text{TiO}_2$ ) of the photo electrode, dye molecules and also electrolyte.

Based on the statement above, this work is investigated on the dye molecules from nature-based dyes and the thickness of  $\text{TiO}_2$  film. This thesis is divided into two major researchs on DSSC which consist of optical characterization of nature-based dyes from fruits, plants and flowers from its ability to absorb the photon from sunlight in the visible-light spectrum from the UV- $V_{is}$  absorbance spectra results, the active compound of natural based dye by using FTIR analysis, the photon of energy of the dyes and absorption coefficient of the dyes. The second major research is the effect of thickness of nanocrystalline  $\text{TiO}_2$  towards electrical characterization of DSSC. Scan Electron Microscopy (SEM) of  $\text{TiO}_2$  surface also has been investigated to observe the structure

and morphology of TiO<sub>2</sub> surface. Overall investigations are characterized based on optimum thickness with optimum dye sensitizer to develop high conversion efficiency of DSSC.

## **1.2 Research Problem Statement**

The problem statements are as follows:

Ruthenium polypyridyl complexes are considered as the effective sensitizer because of their intense charge transfer absorption in the visible range of the solar spectrum but these sensitizers contain heavy metal, which is expensive, rare and has the toxic effect. Natural dye is then proposed as an alternative sensitizer because of biodegradable, environmental friendly and also has the low production cost (Al-Ghamdi et al., 2014). The second problem is the effect of TiO<sub>2</sub> thickness also investigates towards overall DSSC electric performance. The optimum thickness of TiO<sub>2</sub> film will have available surface area for dye chemisorption which can provide essential absorption for all incident light (Narayan, 2011).

## **1.3 Research Objectives**

The objectives of this research are:

1. To fabricate the dye sensitized solar cell (DSSC) with anatase nanocrystalline TiO<sub>2</sub> film at 5 and 10 μm and sensitized with nature based dyes.

2. To characterized DSSC based on open circuit voltage;  $V_{OC}$ , short circuit current;  $I_{SC}$ , fill factor; FF, solar cell efficiency;  $\eta$ , UV- $V_{is}$  absorbance spectra (nm), absorption coefficient ( $\sigma$ ), photon energy (eV) and Fourier Transform Infrared Spectra (FTIR) of the dye and microstructure of  $TiO_2$  by Scan Electron Microscopy (SEM).
3. To propose an ideal nature based dye sensitized solar cell (DSSC) based on optimum thickness and potential based dye sensitizer towards optimum photoelectrical performance.

#### **1.4 Thesis Organization**

The thesis is covered into five main sections, which involve of introduction, literature review, research methodology, result and discussion and lastly with the conclusion.

Chapter 1 introduces the background of the current energy predicament on electricity generation and then followed by problem statements, project objectives and finally the organization of this thesis.

Chapter 2 recovers the reviews in dye sensitized solar cell in terms of nature-based dyes and the effect of solvent in extracting the pigments from fruits and flowers from previous researchers. This chapter presents the overall types of solar cells, cross section of DSSC, the operation principles of DSSC and important parameters for DSSC. Plant pigmentation such as chlorophyll, anthocyanin and betalains pigments also has been explained in this chapter.

Chapter 3 displays the research methodology in fabricating DSSC by using Dr. Blade method to vary the TiO<sub>2</sub> film thickness. This chapter also demonstrates methods in extracting pigments from fruits and flowers, and cocktail dyes are introduced in this chapter. The procedure on measuring UV-Vis absorbance of the extracted nature-based dyes and preparation of the counter electrodes (CE) by using carbon from pencil has been explained in this chapter.

Chapter 4 shows the overall experimental results and discussion on the electrical characteristics of nature-based dye sensitizers for DSSC. This chapter is divided into four major parts consists of the effect of extract solvent in extracting pigments from natural based dye from UV-Vis absorbance, active compound in nature-based dyes, photon energy (eV) and absorption coefficient of nature-based dye. This chapter also includes the effect on the thickness of TiO<sub>2</sub> film towards DSSC electrical characterization.

Chapter 5 concludes the overall project and findings according to experimental work and proposes an optimum nature-based solar cell, relating to projecting objectives and gives a recommendation for future work.