THE OPTIMIZATION OF TITANIUM DIOXIDE (TiO_2) THICKNESS AND ORGANIC DYE SENSITIZERS TO IMPROVE DYE SENSITIZED SOLAR CELL (DSSC) PERFORMANCE

by

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"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*-

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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

λ	Wavelength
λ_{max}	Maximum Absorbance
η	Efficiency of solar cell
α	Absorption coefficient

KETEBALAN OPTIMUM TITANIUM DIOKSIDA (TiO_2) 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 pencelup semulajadi dan menggunakan dua ketebalan titanium dioksida (TiO_2) iaitu 5 μm dan 10 μm untuk memperbaiki prestasi DSSC. DSSC menggunakan sepuluh jenis pencelup daripada buah beri, buah naga, kubis unggu, bunga raya, bunga kertas, kopi, kunyit, bunga telang dan bunga seri pagi dan lima lagi terdiri daripada hasil gabungan dua pencelup iaitu buah beri dan bunga kertas, kopi dan kunyit, kubis unggu dan buah beri, buah beri dan buah naga dan akhir sekali bunga seri pagi dan kubis unggu. Kesan menggunakan pelarut yang berbeza daripada ethanol dan air suling turut dikaji dan digunakan untuk mengkaji tenaga cahaya dan kebolehan penyerapan pencelup untuk meningkatkan prestasi kecekapan DSSC. Dua ketebalan berbeza untuk TiO_2 elektrod dilakukan di atas permukaan kaca dan dilakukan menggunakan cara "Doctor Blade", dan kemudiannya TiO_2 elektrod akan direndam di dalam pencelup semulajadi untuk process "sensitized". Daripada hasil kajian mendapati, gabungan pencelup 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 pencelup koktel daripada buah beri dan buah naga mewakili kumpulan "carboxyl" dalam pigmen iaitu Betalains, yang membantu untuk bercantum dengan molekul TiO_2 dengan cekap. Bagi koktel pencelup daripada buah beri dan buah naga, elektrod pencelup sensitif dalam etanol pelarut dengan ketebalan optimum filem TiO_2 10 ± 0.01 μm, 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 (η) daripada 1.22% dengan tenaga foton daripada pencelup 2.49 eV dan pekali penyerapan 2.17×10^3 m^{-1} mewakili kecekapan yang tertinggi.

THE OPTIMIZATION OF TITANIUM DIOXIDE (TiO_2) 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 μm and 10 μm of titanium dioxide (TiO_2) 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 TiO_2 films with two different thicknesses (5 and 10 μm) 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 (COOH) in dye cocktails from blueberry and dragon fruit represented in Betalains pigment helps to anchor with 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 TiO_2 film of 10 $\pm$0.01 μm yields a short circuit current (I_{SC}) of 3 mA , an open circuit voltage (V_{OC}) of 0.8 V, and a fill factor of 0.51, corresponding to the highest energy conversion efficiency (η) of 1.22%.

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 19th 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 (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 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 TiO_2 towards electrical characterization of DSSC. Scan Electron Microscopy (SEM) of TiO_2 surface also has been investigated to observe the structure and morphology of TiO_2 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_2 thickness also investigates towards overall DSSC electric performance. The optimum thickness of TiO_2 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_2 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; η, UV-V_{is} absorbance spectra (nm), absorption coefficient (σ), 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_2 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_2 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.