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Kappaphycus alvarezii, Sargassum polysystum and *Manihot esculenta* as Photo-Sensitizers in Dye-Sensitized Solar Cells

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A report submitted in fulfillment of the requirements for the degree of Bachelor of Applied Science (Bioindustrial Technology) with Honors

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DECLARATION

I hereby declare that the work embodied in this report is the result of the original research and has not been submitted for a higher degree to any universities or institutions.

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Date: 12/12/2018

I certify that the report of this final year project entitled "*Kappaphycus alvarezii, Sargassum polysystum and Manihot Esculenta* as Photo-Sensitizers in Dye-Sensitized Solar cells" by Ashma Diyanti Binti Affandi, matric number F15A0019 has been examined and all the correction recommended by examiners have been done for the degree Bachelor of Applied Science (Bioindustrial Technology) with Honours, Faculty of Bioengineering and Technology, Universiti Malaysia Kelantan.

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LIST OF ABBREVIATION AND SYMBOLS

K	*Kappaphycus alvarezii* (red algae)
S	*Sargasum polysystum* (brown seaweed)
C	*Manihot esculenta* (cassava leaf)
DSSC	Dye-Sensitized Solar Cell
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
Eg	Bandgap value
UV-vis	Ultraviolet-Visible Spectroscopy
SEM	Scanning electron microscopy
BET	Brunauer-Emmette-Teller
4PP	Four point probe
λ	Absorption edge values in nm
g	gram
cm	Centimeter
EIS	Electrochemical Impedence Spectroscopy
J_{SC}	Short-circuit current
V_{OC}	Open-circuit voltage
FF	Fill factor
PCE	Power conversion efficiency
Chl	Chlorophyll

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Kappaphycus alvarezii, Sargassum polysystum sp. and Manihot esculenta sp. as Photo-Sensitizers in Dye-Sensitized Solar cell

ABSTRACT

The energy crisis is a worldwide serious issue as the increasing demand of non-renewable sources for industrial and urbanization. The use of limited non-renewable sources such oil and fossil fuels undergoes rapid depletion and they cannot survive as primary sources to keep up with energy demand worldwide. Therefore, to overcome the problem on the energy sources depletion, the researchers have discovered the use of renewable sources, such solar energy. The use of extracted natural dyes as photo-sensitizers in dye-sensitized solar cell (DSSC) has been proven and studied by many researchers. The advantages of these natural dyes such as low cost production, abundance, and environmental friendly were considered. Previous study highlighted the presence of chlorophyll in photo-sensitizers of DSSC. The natural dye extract from *Kappaphycus alvarezii sp*. (red algae) (**K**), *Sargasum polysystum sp*. (brown seaweed) (**S**) and *Manihot esculenta sp.* (cassava) leaf (**C**) was successfully prepared and characterized to determine the photo-sensitizer properties. The analysis involved were UV-vis spectroscopy (UV-vis), Scanning electron microscopy (SEM), Brunauer-Emitte-Teller (BET) and four point probe (4pp). It was discovered that from Tauc plot measurement, the band gap value of **C** has the smallest value followed by **S** and **K** with 2.10 eV, 2.41 eV and 2.85 eV respectively. The conductivity shows that **C** has the highest conductivity value followed by **S** and **K** with 2.70 E $^{-4}$ (Scm^{-1}), 2.64 E $^{-4}$ (Scm^{-1}) and 2.34 E $^{-4\ (}$Scm^{-1}) respectively, which has similar trend with the band gap value. The solar cell performance values were determined in which **C** has the highest solar efficiency followed by **S** and **K** with 0.60 %, 0.18 % and 0.06 % respectively. The result from the surface area analysis indicate that with 5.16/m^{2}g^{-1}, **C** has the highest specific surface area followed by **K** and **S** with 2.37/m^{2}g^{-1} and 1.84/m^{2}g^{-1} concluded that the higher specific area could lead to maximize dyes sensitization and thus increase better solar cell performance. Overall, the use of natural dye as photo-sensitizers in DSSC successfully achieved and the study highlighted the importance of specific surface area of dyes for higher solar cell efficiency.

Keywords: photo-sensitizers, natural dye extract, band gap, conductivity.

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Kappaphycus alvarezii, Sargassum polysystum dan *Manihot esculenta* sebagai pemeka cahaya dalam sel solar pewarna sensitif.

ABSTRAK

Krisis tenaga merupakan isu dunia yang serius memandangkan peningkatan permintaan dan penggunaan sumber yang tidak boleh diperbaharui bagi tujuan perindustrian dan pembandaran. Penggunaan sumber tidak boleh diperbaharui yang terhad seperti minyak dan bahan api fosil mengalami pengurangan yang cepat dan mereka tidak dapat bertahan sebagai sumber utama untuk mengikuti permintaan tenaga di seluruh dunia. Oleh itu, untuk mengatasi masalah pengurangan sumber tenaga, para penyelidik telah menemui penggunaan tenaga yang boleh diperbaharui seperti tenaga solar. Penggunaan pewarna semulajadi yang tersari sebagai pemeka cahaya dalam sel suria terpeka pewarna (DSSC) telah terbukti dan dikaji oleh banyak penyelidik. Kelebihan pewarna semulajadi seperti pengeluaran rendah, banyak dan mesra alam telah dipertimbangkan. Kajian terdahulu menunjukkan kehadiran klorofil dalam pewarna semulajadi sebagai pemeka cahaya dalam DSSC. Ekstrak pewarna semula jadi dari *Kappaphycus alvarezii sp*. (alga merah) (**K**), *Sargasum polysystum sp*. (rumpai laut coklat) (**S**) dan *Manihot esculenta sp*. (daun ubi kayu) (**C**) telah berjaya disediakan dan dicirikan untuk menentukan sifat-sifat pemeka cahaya. Analisa yang terlibat adalah spektroskopi UV-vis, mikroskop elektron pengimbasan (SEM), Breneur Emitte Teller (BET) dan prob empat titik (4pp). Hasil pengukuran plot Tauc, nilai sela jalur **C** mempunyai nilai terkecil diikuti oleh **S** dan **K** dengan 2.10 eV, 2.41 eV dan 2.85 eV. Keberaliran menunjukkan bahawa **C** mempunyai nilai keberaliran tertinggi diikuti dengan **S** dan **K** dengan 2.70 E^{-4} (Scm^{-1}), 2.64 E^{-4} (Scm^{-1}) dan 2.34 E^{-4} (Scm^{-1}) yang mempunyai trend yang sama dengan nilai sela jalur. Nilai prestasi sel solar ditentukan di mana **C** mempunyai keberkesanan solar tertinggi diikuti oleh **S** dan **K** dengan 0.60 %, 0.18 % dan 0.06 %. Hasil daripada analisa kawasan permukaan menunjukkan bahawa dengan $5.16/m^2g^{-1}$, C mempunyai kawasan permukaan spesifik tertinggi diikuti oleh K dan S dengan $2.37/m^2g^{-1}$ dan $1.84/m^2g^{-1}$ menunjukkan bahawa kawan spesifik yang luas boleh membawa kepada memaksimumkan pemekaan perwarna dan meningkatkan prestasi sel solar. Keseluruhannya, penggunaan pewarna semula jadi sebagai pemeka cahaya dalam DSSC telah berjaya dicapai dan kajian menekankan kepentingan kawasan permukaan yang spesifik pewarna untuk keberkesanan sel solar yang lebih tinggi.

Kata kunci: pemeka cahaya, ekstrak pewarna semulajadi, sela jalur, keberaliran.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

1.1.1 Energy crisis

The population growth has led to increasing energy demand according to development flow. The rapid depletion of conventional fuel resources and increasing environment awareness has motivated researchers to shift attention towards using renewable energy as alternative energy (Solangi *et al*., 2011). Fossil fuel is a non–renewable energy resource that will eventually replenished in the next thousands or millions of years. As an example coal from fossil fuel and petroleum resulted from the decomposition of died marine animals and organic matter over millions of year (Janaun *et al*., 2013).

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Over-exploitation use of non-renewable energy sources does not only cause environmental damage such as rapid depletion of the resources which caused by oil and gas

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industry (Fadai, 2007). Few types of renewable energy such as wind energy, hydrothermal energy, biomass energy and solar energy. Solar energy offers a limitless supply that is safe, abundance and by getting enormous sunlight exposure during daylight is more enough to meet the world demand (Bagher *et al*., 2015).

1.1.2 Dye – Sensitized solar cells (DSSC$_S$)

Dye-sensitized solar cells (DSSC) is the third generation solar cell which also known as Grätzel, offer a lot of advantages such as, ease of fabrication, adaptability and execution at diffuse light and multicolor choices (Grätzel, 2003). Thus, DSSCs turn out to be increasingly intriguing since a various choices of natural dyes can be utilized as light harvesting components which may act as charge carriers or also called as photo-sensitizers (Hug *et al*., 2014).

Figure 1.1 shows the mechanism of dye-sensitized solar cell which when light sources shines on the glass, the dye molecules get excited from the ground state to higher energy state oxidized and an electron is injected into the conduction band and the electron can move freely. The oxidized dye molecule regenerated by electron donation from iodide ion in the electrolyte which lead to continuous electrical circuit.

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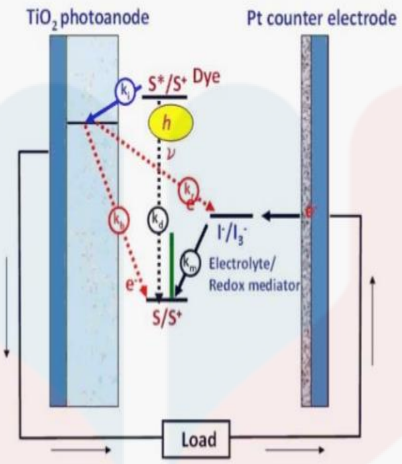

Figure 1.1: The mechanism of Dye-sensitized solar cell (DSSC) (Hug *et al*., 2014)

In this study, the research was focused on the use of *Kappaphycus alvarezii sp*. (red algae), *Sargassum polysystum sp.* (brown seaweed) and *Manihot esculenta* (cassava) leaf, as potential photosensitizers for dye–sensitized solar cell (DSSC). The extracts dyes were further investigated with the application of TiO_2 as photo-anode. To fabricate the full device of DSSC. The conductivity and the solar cell performance of fabricated devices were further evaluated.

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1.1.1 Problem Statement

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The increasing demand for energy sources caused depletion of the sources which will lead to energy crisis. The use of non-renewable sources such fossil fuels and petroleum as a source of energy will be depleted sooner due to rapid industrial activities and urbanization. Besides, it will lead to several environmental issues such air pollution, global warming and water pollution.

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Thus, the use of renewable sources such solar cell is believed could overcome the issue on depletion of energy sources and not contribute to environmental problems.

Fabrication of dye-sensitized solar cell (DSSC) from natural dyes extract become more applicable due to their advantages such low cost, abundance and environmentally friendly (Calogero *et al*., 2014). The potential capabilities of natural dyes in (DSSC) with various natural dyes resulted different solar cell performance. Thus, by using different dyes containing chlorophyll pigment which are *Kappaphycus alvarezii sp.* (red algae), *Sargasum polysystum sp.* (brown seaweed) and *Manihot esculenta sp.* (cassava) leaves to evaluate the potential of these natural dyes in solar cell application.

A series of analysis were also carried out to determine each solar absorption properties and its band gap measurement. The band gap values were compared in forms of conductance trend to study on their ability in solar cells. The effect of surface morphology and specific surface area were also discussed to explain their solar cell performance.

1.3 Objectives

There are few objectives in this study which are:

i. To extract natural dyes from *Kappaphycus alvarezii sp. (*red algae), *Sargasum polysystum sp. (*brown seaweed) and *Manihot Esculent sp. (Cassava)* leaves*,* as potential photo-sensitizers.

ii. To carry out the physical analysis such Ultraviolet –visible spectrophotometer

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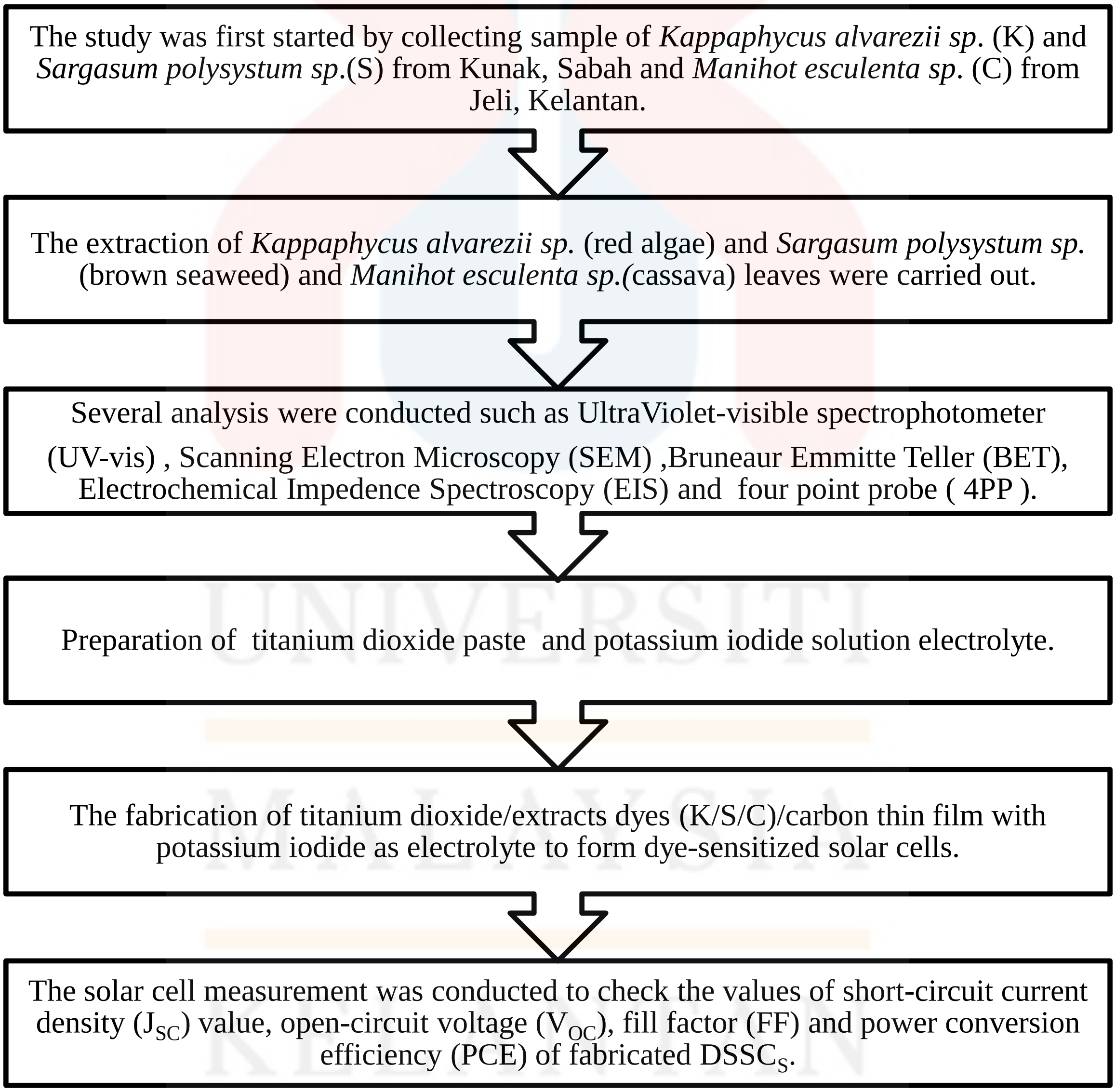
(UV–vis), Scanning Electron microscopy (SEM), Brunauer-Emitte-Teller (BET), Electrochemical Impedence Spectroscopy (EIS) and four point probe (4PP).

iii. To investigate the conductivity and solar cell performance of each extracts dye in solar cell full devices.

1.4 Scope of Study



The study was first started by collecting sample of *Kappaphycus alvarezii sp*. (K) and *Sargasum polysystum sp*.(S) from Kunak, Sabah and *Manihot esculenta sp*. (C) from Jeli, Kelantan.

The extraction of *Kappaphycus alvarezii sp.* (red algae) and *Sargasum polysystum sp.* (brown seaweed) and *Manihot esculenta sp.(*cassava) leaves were carried out.

Several analysis were conducted such as UltraViolet-visible spectrophotometer (UV-vis) , Scanning Electron Microscopy (SEM) ,Bruneaur Emmitte Teller (BET), Electrochemical Impedence Spectroscopy (EIS) and four point probe (4PP).

Preparation of titanium dioxide paste and potassium iodide solution electrolyte.

The fabrication of titanium dioxide/extracts dyes (K/S/C)/carbon thin film with potassium iodide as electrolyte to form dye-sensitized solar cells.

The solar cell measurement was conducted to check the values of short-circuit current density (J_{SC}) value, open-circuit voltage (V_{OC}), fill factor (FF) and power conversion efficiency (PCE) of fabricated $DSSC_S$.

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1.4 Significance of Study

At the end of this study, the extraction of dye from the natural dyes extracted from *Kappaphycus alvarezii sp.* (red algae), *Sargassum polysystum sp.*(brown seaweed) and *Manihot esculenta sp.* (cassava) leaves, were used to evaluate its potential as photo – sensitizers in dye sensitized solar cell DSSC. Besides, the electrical conductivity of K, S and C was tested to figure out their ability to conduct electricity.

The potential of chlorophyll-based dyes photo-sensitizers in DSSC is considered as significant in the development of natural dyes extracts application in DSSC. Further optimization, low-cost, safe and comparable DSSC devices could be proceeded for commercialization.

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CHAPTER 2

LITERATURE REVIEW

2.1 Energy crisis

Throughout the years, the demands for the use of natural sources as energy sources are increasing due to industrial development. Overpopulation and overconsumption are the main reasons that keep natural energy resources depleting. To replenish the natural resources such as coal and fossil fuels, it could take hundreds or thousands of years (Matthew *et al*., 2009). Despite the prediction by the researcher that the depletion of non – renewable natural sources as energy sources, the overexploitation of the resources is still ongoing. The use of renewable energy sources such solar energy, which does not pollute the environment and it can reduce the dependent of the world on the non-renewable resources (Swami *et al*., 2012). Figure 2.1 shows the increasing demand for both energy resources for the next thirty years.

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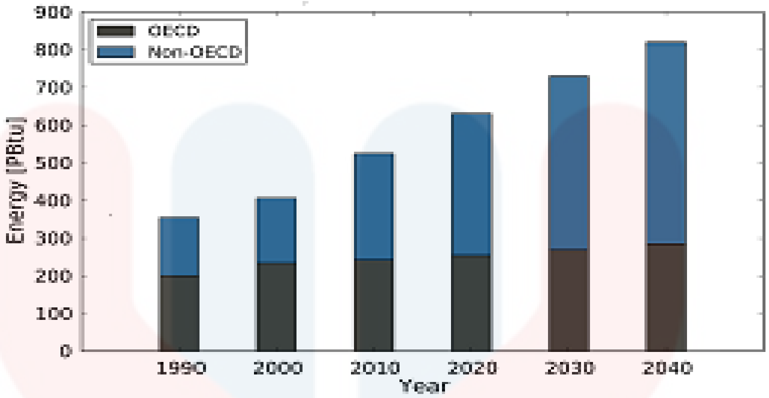

Figure 2.1: Global increasing demand for energy sources up to 2040 (Swami *et al*., 2012).

2.2 Solar Energy

Sunlight-based technology vitality has encountered exceptional development recently with the effort in reducing cost of technology (Timilsina *et al*., 2012). Solar energy is divided into five main generations, classified based on the device configuration and materials. The first generation solar cells were introduced based on silicon-based materials, which yet have the fabrication disadvantages limited source of silicon. Besides, the first generation of solar cell requires expensive technology and high temperature processing (Timilsina *et al*., 2012).

For the second generation solar cells, the devices were based on thin film solar cells, since it has heaps of photon-absorber that assimilate light in wide wavelength region (Sharma *et al*., 2015). The best materials that have been reported for second generation

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solar cell, were micromorphous silicon, cooper indium gallium selenide (GaAs), cadmium telluride (CdTe) and amorphous silicon (Sharma *et al*., 2015).

The third generation solar cells were claimed as the most promising by most researchers such as the materials from nano-crystal based, polymer-based, dye-sensitized and perovskite solar cells (Gong *et al*., 2017). This generation conquers the significant advantages of high solar cell performance with lower assembling cost, compared to previous generation (Gong *et al*., 2017).

2.3 Dye – Sensitized Solar Cell

After discovery of photo-electrochemical (photovoltaic) effect by Alexandre Edmond Becquerel in 1839, the area of solar study has earned attention by the researchers (Jasim, 2007). Dye sensitized solar cells (DSSC) have attracted considerable attention due to the simple preparation procedure, architectural and environmental compatibility and good performance under diffuse light condition. The concept of DSSC was first proposed by Grätzel and his co-workers in the year 1991 where the capabilities of natural dye can be used in solar cell application (O'Regan & Grätzel, 1991). Even though solar performance of DSSC are still lower compared to traditional silicon-based solar based cells, DSSC are considerably much cheaper and ease of fabrication (Jasim, 2007; Prima *et al*., 2017). Moreover, DSSC is the first solar cell that offers both adaptability and straightforward (Wei *et al*., 2010).

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Meanwhile, titanium dioxide (TiO_2) is typical metal oxide that typically used in DSSC, along with other metal oxides such as zinc oxide (ZnO) and stannic oxide (SnO_2). TiO_2 is more preferable than other metal oxides due to its better porous structure, high surface area for dye absorber and better electronic properties for photo-generated electrons collection (Polo *et al*., 2004). The latest research of DSSC focuses on the use of nanostructured-TiO_2 and ZnO anodes, ionic electrolytes, carbon nanotubes, grapheme (Wei *et al*., 2010). Figure 2.2 shows the mechanism of dye-sensitized solar cell (DSSC).

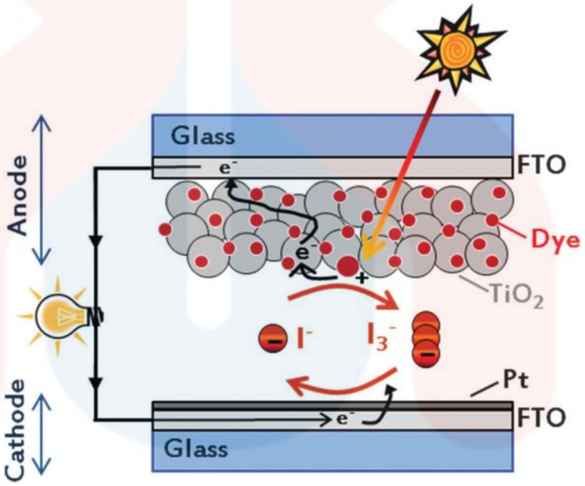

Figure 2.2: Schematic operation of DSSC (Bella, 2015)

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Previously, DSSC that employs ruthenium (II) poly-pyridinic complex as a sensitizer are costly, complicated in sensitizing the complexes and containing heavy metal. Thus, another approach has been introduced by replacing the metal photosensitizers with natural dyes material-based from fruits, plants and leaves. These natural dyes often cost efficiently, non-toxicity and biodegradation (Syafinar *et al*., 2015).

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Based on the DSSC mechanism, the photons strike the dye on the TiO_2 and the energy will be absorbed by the dye and thus will form the excited state of dye (Indriatmoko, 2015). The excited state dye will then inject the electrons directly to the conduction band. The injection of the electrons would be more efficiency if the range between the valence band and conduction band is short (Ekpunobi, 2013).

The valence band is also known as lowest occupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) is referred to conduction band (Ezyanie, 2017). The number of electrons accessible for electrical conduction in a specific material is related to the arrangement of electron states or level with respect to energy and states are occupied by electrons (Sharma *et al*., 2015).

2.4 Natural Dyes

The natural dyes in dye-sensitized solar cell (DSSC) acts as photosensitizer. The metal free natural sensitizers have shown less effectiveness and complicated synthetic route are the basic issues related with these dyes. The natural sensitizer, metal free natural sensitizers and metal complex sensitizers are the three kinds of sensitizers. The metal complex sensitizers are expensive, uncommon and poisonous in nature (Calogero *et al*., 2012). The natural dyes extracted from flowers, fruits, plants, leaves and roots in the form betalains, carotenoids, anthocyanins and chlorophyll pigments (Calogero *et al*., 2012).

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Various natural dyes were studied, for instances, eggplant skin, dark rice, and spinach (Hug *et al*., 2014). It is widely known that natural dyes have common pigments such as anthocyanin and chlorophyll, which the darker pigments of the colors, the higher measure of anthocyanin and chlorophyll the plant has (Calogero *et al*., 2012). Figure 2.3 shows the anthocyanin properties has hydroxyl and carbonyl groups that easier to bind at surface of TiO_2 (Zhang *et al*., 2008).

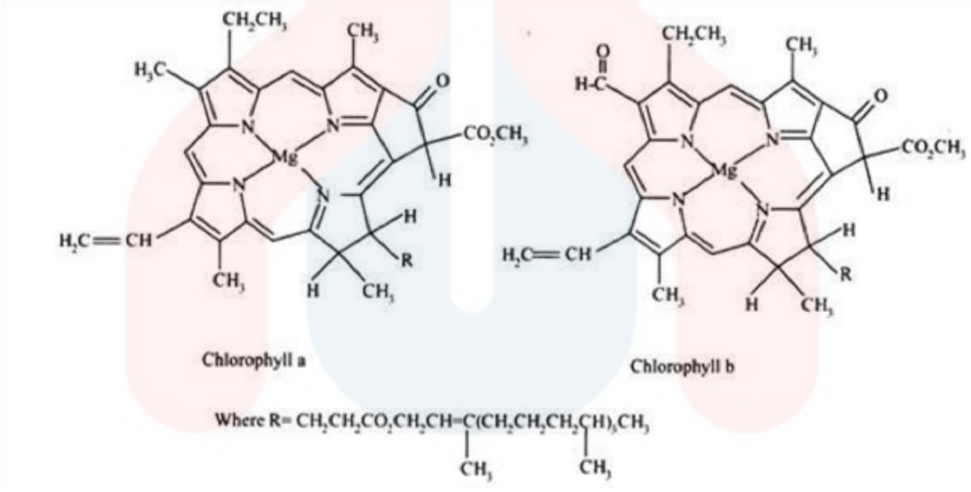

Figure 2.3: The chemical structure of chlorophyll (Zhang *et al*., 2008).

The use of natural dye that has deeper and darker color was reported can increase light absorption in visible spectra (Subodro *et al*., 2017). Past research revealed that the cassava leave dye on TiO_2 layer has a decent visible light reaction with the absorption peaks at wavelength of 410 nm and 665 nm (Nurlela *et al*., 2017). Spectro-electrochemical study indicated that the LUMO energy level (-4.26 eV) of cassava leaf dye slightly above

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the conduction band level of TiO_2 (-4.3 eV), makes it suitable as photo-sensitizer in the DSSC framework (Nurlela *et al*., 2017).

Kappaphycus alvarezii sp. is the elk horn sea moss, is one kind of red algae species. It is one of the most important commercial sources of carrageenana family of gel-forming, polysaccharides. The way that the abundant photosynthetic pigments present in the seaweeds might be utilized as alternative sensitizers has gained attention lead to increasing interest on marine seaweed (Calogero *et al*., 2014). Red seaweed was chosen because of its abundance in nature which acts as a photosensitizers and environmental friendly dye source (Kuo and Sheen, 2011). Red seaweed has chlorophyll a and another accessory pigment called phycoerythrin which can assimilate green region from 695 nm until 750 nm, from 495 nm-570 nm respectively (Pugalendren *et al*., 2012).

Seaweeds can be classified into three groups namely green (Cholorophycea), red (Rhodophyceae) and brown (Phaeophyceae) whilst, *Sargasum polysystum sp.* is categorized under brown seaweed that has chlorophylls, carotenoids and phycobiliproteins (Janaun *et al*., 2013). The natural pigment such chlorophyll, anthocyanin and tannin present in plant parts such leaves, flower and fruits have been discovered can act as organic sensitizer because of their advantages such as low cost, abundance in raw materials and absence of environment risk contrasted with synthetic natural and inorganic dyes (Calogero *et al*., 2014).

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Seaweeds has abundant photosynthetic species containing c-type chlorophylls (Chls), where these c-type Chls, including Chl c1 and Chl c2. The chlorophyll has terminal carboxyl group, which connected to the porphyrin macrocycle through a conjugated double bond which can inject electrons from porphyrin microcycle to TiO_2 (Wang, 2007).

2.5 Band gap and conductivity measurement

The band gap values can be determined based on the absorbance spectra reading from the UV-vis using Tauc model. Band gap energy can be defined as the minimum energy required for electron transfer between conduction band and valance band and it was reported that when the band gap value is smaller, the dyes will have a better solar efficiency (Syafinar *et al*., 2015).

The band gap values are able to determine the optimum energy level between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital for electron injection (Li *et al*., 2017). Therefore, when the band gap is smaller, the conductivity will be higher. As the less energy needed for transition between the HOMO and LUMO, the more current can be produced in the DSSC (Li *et al*., 2017).

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CHAPTER 3

MATERIALS AND METHOD

3.1 Chemicals and Apparatus

The chemicals that were used in the study include titanium dioxide (TiO_2) nanoparticle from (Aldrich), Polyethylene glycol, detergent, acetone, ethanol, silica gel, carbon, potassium iodide crystals and aluminum. The dyes were extracted from *Kappaphycus alvarezii sp.* (red algae), *Sargassum polysystum sp.* (brown seaweed) taken from Kunak, Sabah and *Manihot esculenta sp.* (cassava) leaves from Jeli, Kelantan.

Few apparatus were also used in this study, which are magnetic stirrer, sample bottles, beakers, filter papers, micropipette, mortar and pestle, spatula, adhesive tapes, hair dryer, petri dish, syringe filter, aluminum foil, microscope glass, indium tin oxide (ITO) glass, cuvette, measuring cylinder, knife, clipper, gloves, hotplate, furnace, water bath, centrifugation machine and ultrasonic bath.

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3.2 Equipment

In this study, few equipment were used to analyze the extracts and solar devices include Ultraviolet-visible Spectroscopy (HACH DR6000) (UV-vis), Fourier Transform Infrared Spectroscopy (FTIR) (Thermo Scientific ™ Nicolet iZ10), Scanning Electron Microscopy (SEM) (Jeol JSM-IT100), Four Point Probe (4PP) (Jandel HM21), digital multi-meter (EX540) and Brunauer-Emmet-Teller (BET) (Micromeritics’ ASAP® 2020), Electrochemical Impedence Spectroscopy (EIS) (Methrom Autolabs).

3.3 Methods

3.3.1 Preparation of natural dyes

The extraction of the natural dye was based on references from with some modification (Ghazali, 2017). *Kappaphycus alvarezii sp*. (**K**) and *Sargasum polysystum sp***.** (**S**) were collected from Kunak, Sabah. Firstly, 200 g of samples **K** and **S** were washed with distilled water and dried under sunlight for 16 hours upon drying in the oven for subsequent 12 hours to remove excess water. The dried samples were grinded using blender to make them into powder form and then stored the powder into container without exposure to the light. **K** and **S** powders were dissolved into ethanol solvent and heated in the water bath for three hours before kept the solutions under dark condition at room temperature.

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The solutions were filtered using 0.45 µm Whatman filter paper with the aid of vacuum pump. The extracted dye solutions were stored in dark condition at 16 °C before proceeding to the further steps.

Same goes to the preparation of dye extracted from *Manihot esculenta sp*. (cassava leaves) **(C).** The dried cassava leaves were grinded using blender to get powder form and dissolved into ethanol, heated in the water bath and kept under dark condition. After filtration, the extracts solution was centrifuged to obtain a very homogenous extracts solution.

The extracted dye solution from **K**, **S** and **C** were kept under dark condition at room temperature upon analysis and device fabrication. These solutions were applied as photo-sensitizers in dye- sensitized solar cell (DSSC) application.

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Figure 3.1: Samples and extracts solution of ; (a*) Kappaphycus alvarezii sp.* (Red algae), (b) *Sargasum polysystum sp.* (brown seaweed) and (c*) Manihot esculenta sp.* (cassava) leaves before and after extraction.

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3.3.2 Characterization

The absorption spectra of *Kappaphycus alvarezii sp.* (**K**), *Sargasum polysystum sp.* (**S**) *and Manihot esculenta sp.* (**C**) was determined using HACH DR6000 UV – Visible Spectrophotometer in the wavelength range of 400 nm to 800 nm. From the absorption spectra, the band gap energy of each dye was determined using Tauc plot method. The surface morphology of the **K**, **S** and **C** on TiO_2 was observed using the JEOL JSM IT 100 Scanning Electron Microscope with 1000x magnification. Brunauer–Emmet-Teller (BET) analysis was carried out to determine the surface area and mesoporous volume of **K**, **S** and **C**. Lastly, the digital multi-meter was used to determine the conductivity of the (carbon/aluminium)/photo-sensitizer **(K**,**S**,**C)**/TiO_2/ITO. The photovoltaic parameters such as short circuit current (I_{SC}) value, open-circuit voltage (V_{OC}), fill factor (FF), and power conversion efficiency (PCE) of DSSC devices were collected from IV measurements through potentiostat (Auto-lab PGSTAT30, Eco Chemie B.V., The Netherlands) under light illumination of $100mWcm^{-2}$.

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3.3.3 Preparation of titanium dioxide paste (TiO_2)

The TiO_2 paste was prepared by dissolving 2 g of Titanium dioxide (TiO_2) nano-particles with 5 mL of ethylene glycol and stirred overnight until become homogenous paste.

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3.3.4 Preparation of electrolyte

The electrolyte solution was prepared by mixing 1.08 g potassium iodide powder (KI) with 20 mL acetonitrile, 5 mL ethylene glycol and 0.35 g iodine (I_2) pearl and stirred for about 30 minutes to get homogenous solution. The electrolyte solution was kept under dark condition overnight.

3.3.5 Preparation of Indium tin oxide (ITO) glass

ITO conductive glasses were cut into 2 x 2 cm pieces. The glasses were cleaned in detergent solution by putting them in the ultrasonic bath for five minutes. Then, all glasses were rinsed with water and ethanol followed by sonication for 15 min at 50 ºC before dried using hair dryer.

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3.3.6 Preparation of TiO_2/ITO glass

The paste was deposited on cleaned ITO glass using doctor blade technique, and the coated paste ITO glass was left to dry on hotplate at 70 ºC for 30 minutes, followed with sintering in the furnace at 500 ºC for 30 minutes ramp time.

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3.3.7 Preparation of dyes on TiO_2/ITO glass

The TiO_2 films were then immersed in respective dye extracts solution (**K**, **S** or **C**) for dye sensitization in overnight under dark condition. The resulted ITO/TiO_2/(**K**, **S**, **C**) glass were rinsed with ethanol and dried at 70 ºC for 5 minutes.

3.3.8 Fabrication of Dye-Sensitized Solar Cells

ITO/TiO_2/(**K**, **S**, **C**) and carbon/aluminium electrode on another ITO glass were assembled with the presence of few drops of potassium iodide solution in between the glass. The fabrication of ITO/TiO_2/dyes (**K**,**S**,**C**)/(carbon/aluminium) thin film was completed after both glasses were assembled with the clip hold both glass and ready for solar cell measurement.

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CHAPTER 4

RESULTS AND DISCUSSION

4.1 Physical observation

The color of the dye extracted from three different types of chlorophyll was physically observed. Figure 4.1 shows the image of dye that were extracted from *Kappaphycus alvarezii* (**K**)*, Sargassum polysystum* (**S**) *and Manihot esculenta* (**C**). The sample from **K**, **S** and **C** in powder form and soaked in ethanol solution for 3 hours.

From the observation, it can be seen that the color for each extracted dye differed as (**S**) produced a darker green color when mixed with ethanol as compared with cassava leaves (**C**) solution. Whilst, brown seaweed **(K)** produced light brown color of the extracted dye solution.

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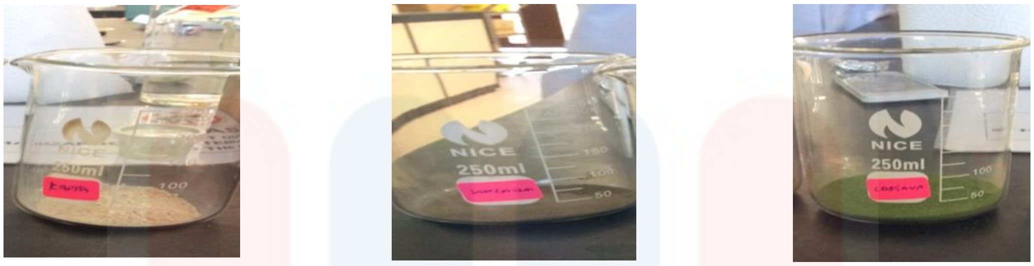

Sargasum polysystum sp. **(S)** *Kappaphcus alvarezii sp*. (**K)** *Manihot esculenta sp*. **(C)**

Figure 4.1: Solutions sample of **K**, **S** and **C**

4.2 UV-vis Absorption Analysis

The UV-vis absorption analysis was conducted to determine the photo-absorption properties of extracted dyes from sample *Kappaphycus alvarezii sp.* (**K**), *Sargasum polysystum* (**S**), and *Manihot esculenta* (**C**) in visible region of wavelength from 400 to 800 nm. Figure 4.2 shows the absorption spectra of the prepared sample. The absorption spectra of all dye extract showed differences in terms of peak locations in the visible region from 400 nm until 800 nm. Two peaks were observed from the spectrum of **K** and **S** at 410 nm and 660 nm, represent the presence of chlorophyll pigment (Porrarud & Pranee, 2010). Past research also revealed that the cassava leave dye on titanium dioxide (TiO_2) layer has a decent visible light reaction with the absorption peaks at wavelength of 410 and 665 nm (Nurlela *et al*., 2017). The chlorophyll pigment is the most common photosynthetic pigment found in all autotrophic plant including seaweed.

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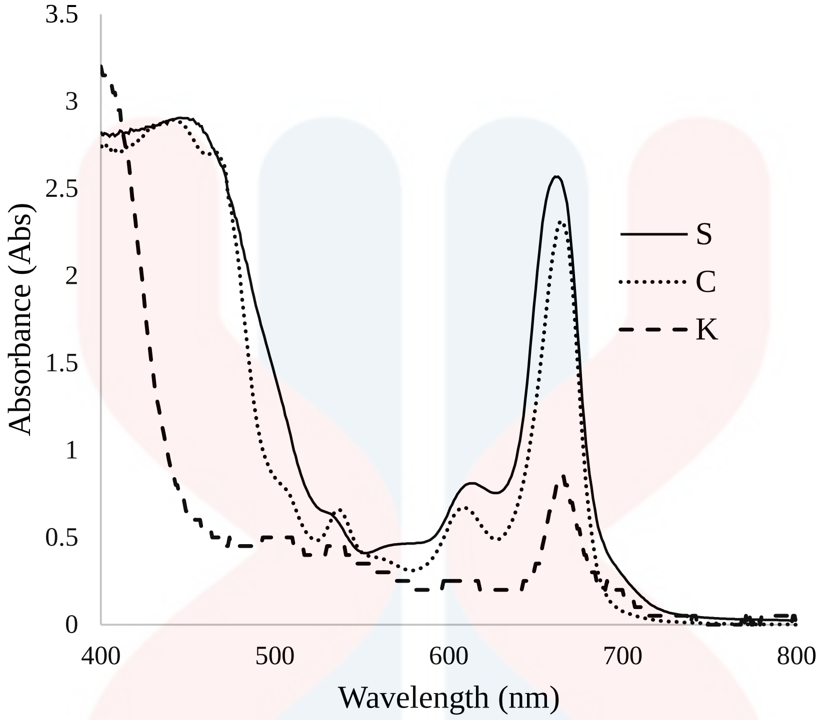

Figure 4.2: The absorption spectra of **K**, **S** and **C**

The peaks from the result obtained, at 410 nm, 440 nm and 675 nm represented the presence of chlorophyll pigment in the dye samples. Cheng in 2017 reported that chlorophyll is an appropriate material as photo-absorber in the visible-light region as chlorophyll displays charge-transfer transition from the highest occupied molecular orbital (HOMO) in ground state to the lowest unoccupied molecular orbital (LUMO) in the excited state.

Since the light capacity and penetration will be affected by seawater, the seaweed are capable of controlling the light capturing ability by the production of different types of photosynthetic pigment (Indriatmoko *et al.*, 2015). From UV-vis analysis, the ability of

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these extracts dyes to absorb photon energy, hv and its potential to be utilized as solar material was determined.

4.3 Band Gap Evaluation

Tauc model is an effective model constitutes and formulate the methodology in calculation of the band gap energy. The optical band gap can be acquired by analyzing the absorption edge and applying the Tauc model where α is the absorption coefficient, h is the Planck's constant, v is frequency of vibration, A is a constant and Eg is the band gap (Bu, 2014). Table 4.1 shows the equation based on Tauc model to calculate the band gap.

Table 4.1: Tauc plot equation (Bu, 2014).

Bandgap Energy (E) = hc/λ				
Planck's constant (h) = 6.63 × 10^{-34} Joules sec				
Speed of light (C) = 3.00 × 10^{8} meter/sec				
Cut - off wavelength (λ) = 420.57 x 10^{-9}				
H	**C**	**Λ**	**E**	**eV**
6.63 E-34	3.00 E+08	From UV-vis spectrum	From calculation	From calculation
Which 1 eV = 1.6 × 10^{-19} Joules (conversion factor)				

Band gap energy is the distance between the valence band electrons and the conduction band (Suib, 2013). According to Suib (2013), the minimum energy that are

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needed to excite an electron up to a state in the conduction band that are represented by the bandgap which will eventually involves in the conduction. Figure 4.3 shows the band gap energy, eV calculated from the Tauc plot graph and derived from UV-vis spectrum. From the analysis, the value of the band gap energy obtained from sample **K**, **S** and **C** are 2.85 eV, 2.41 eV and 2.10 eV respectively, showing that **C** has the lowest band gap energy compared to **K** and **S**.

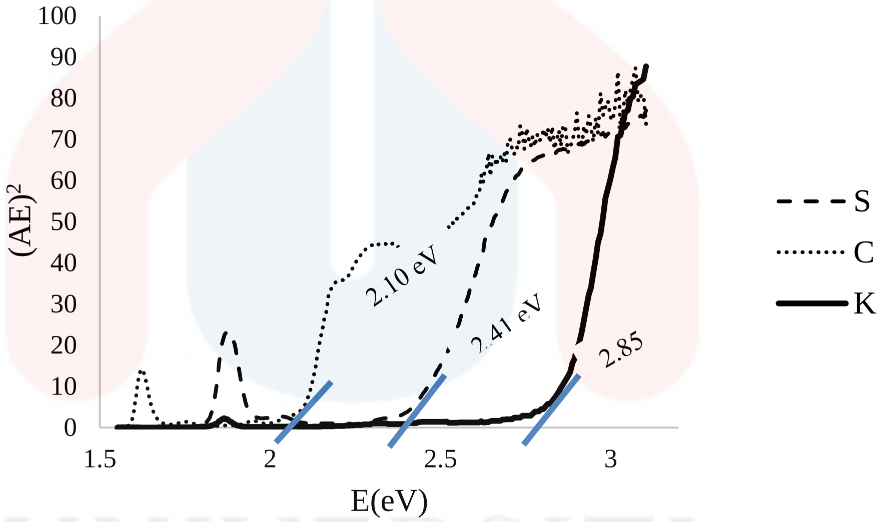

Figure 4.3: Tauc plot of **K**, **S** and **C**.

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From this, it shows that **C** have least amount of energy needed for the transition that which made electrons able to jump from valence band to conduction band followed by **S** and **K** respectively. Band gap energy obtained from the axis of the plotted graph can be used as references to determine the differences in band gap value of each chlorophyll dye samples. The band gap energy and graph analyzed from the UV-Vis spectrophotometry are

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the preliminary steps to further justify the conductivity properties of each dye sample tested. According to Sekar and Gehlot (2010) lower band gap energy value could produce higher conductance properties. Therefore, it shows that **S** and **C** can produced higher conductivity value as it exhibits higher conductance properties due to lower band gap energy based on the band gap value calculated.

4.4 Surface Morphology Analysis

Surface morphology also was scanned using Scanning Electron Microscope (SEM) Jeol JSM-IT100 0.5kV to 30kv with different magnification which is 1000x. The surface morphology of *Kappaphycus alvarezii sp.* (**K**), *Sargasum polysystum sp.* (**S**) *and Manihot esculenta sp*. (**C**) on the TiO_2 layer was observed.

From Figure. 4.4, the morphology of *Kappaphycus alvarezii sp.* (**K**) on TiO_2 layer formed rock - like structure with large surface area by having average size of 10 µm using 1000x magnification. The diameter of the biggest particles formed estimated was about 0.6 cm. The rock like structure is the semi-refined carrageenan extracted from seaweed itself which structures depends on the methods of processing (Dewi *et al*., 2015). Preparation for the plant materials can harm and ultimately change the local structure of the plant cell wall and produced rock-like structure (Costa & Plazanet, 2016).

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Figure 4.4: Surface morphology of *Kappaphycus alvarezii sp*. (**K**)

Meanwhile, surface morphology of *Sargasum polysystum sp.* **(S)** on TiO_2 paste exhibited a porous image. The images were scanned up to 1000 magnification. The black holes in Figure. 4.5 might be related to the pores. From the image scale, the pore diameter size was estimated around 0.3 cm. The image obtained was similar reported previously which the dye on the TiO_2 nanoparticles would produce an irregular porous particle structure look like (Ali *et al*., 2017).

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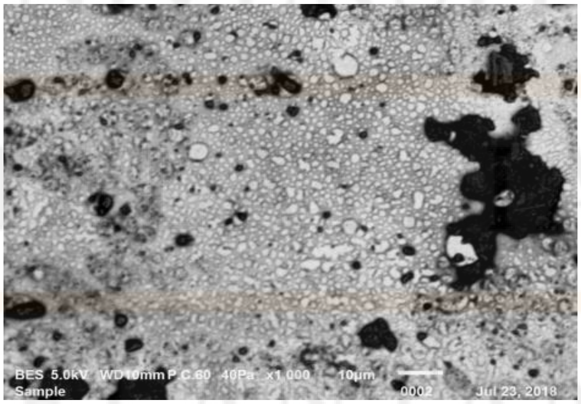

Figure 4.5: Surface morphology of *Sargasum polysystum sp***.** (**S**)

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Figure 4.6 shows the surface morphology images of *Manihot esculenta sp.* with 1000x magnification which exhibited a long-chain of small particles. The dye - coated on TiO_2 produce more compact structure arrangement.

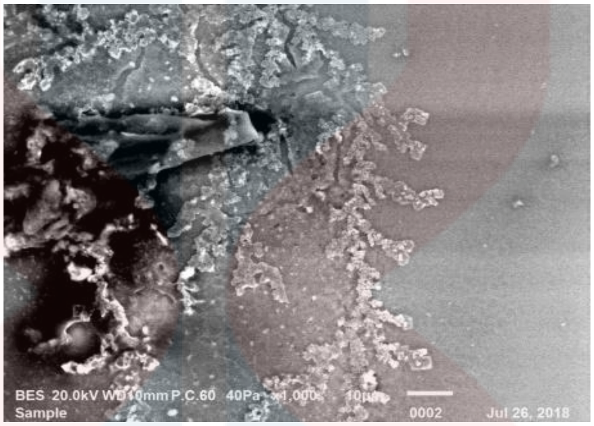

Figure 4.6: Surface morphology of *Manihot esculenta sp*. (**C**)

4.5 Brunauer–Emitte-Teller (BET) analysis

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Brunauer-Emette-Teller surface area analysis provides external area and pore area assessment to determine the total specific surface and to study the impacts of surface porosity and particle size in many applications (Subalakshmi and Senthilselvan, 2018). Table 4.5 shows *Manihot esculenta sp.* (**C**) has the highest specific area and more mesophore volume than *Kappaphysus avarizeii sp.* (**K**) and *Sargasum polysystum sp.* (**S**)**.**

In relation of the surface area analysis with SEM surface morphology, it can be seen that **C** has the long-chain image with small particles, and (**C**) particles might adsorb more on TiO_2 surface. The result from BET supported the theoretical when **C** recorded largest

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surface area that can maximize the dye sensitization. High sensitization will lead to higher light absorption of dye and able to generate more energy in solar cell. The decreasing particle size lead to increasing amount of dye absorbed (Chowdhury and Saha, 2010). For bigger particles, the diffusion limitations are normally occurred and subsequently small amount of molecules can reach the internal surface resulting in low dye uptake capacity (Modesto *et al*., 2010).

Table 4.2 Surface area analysis

SAMPLE	PORE DIAMETER (nm) *BJH METHOD	SPECIFIC SURFACE AREA (S_{BET}) /m^2g^{-1} *BET METHOD	MESOPHORE VOLUME cm^3g^{-1} *T-PLOT METHOD
K	3.99	2.37	0.002
S	9.74	1.84	0.005
C	5.48	5.16	0.007

4.6 Conductivity analysis

The conductivity analysis was conducted to evaluate the efficiency of the photo-absorbers to conduct electricity. According to Ridwan (2018), *Sargasum sp.* (brown algae) dye extracts could perform 1.5 % solar cell efficiency indicated that the dye extract from *Sargasum sp.* (**S**) able to generate electricity. However, there is no previous report of solar cell application from *Kappaphycus alvarezii sp***.** (**K**) and *Manihot esculenta sp.* (**C**)**,** yet it is known that these two dyes extract have chlorophyll pigments which potential can act as photo-sensitizers.

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The band gap energy values and photo-absorption properties from UV-Vis analysis were carried out previously as preliminary steps to justify the conductivity properties of dye extracts. According to Sekar and Gehlot (2012), lower band gap energy value could produce higher conductance properties.

From band gap values, **K** and **C** exhibited band gap value of 2.85 eV and 2.1 eV respectively. As shown in Figure 4.7 the conductivity values of **K**, **S** and **C** shows **C** has the highest conductivity value**.** It was found that the conductivity trend is similar with the band gap value measured. This can be explained due to the ability of electron transport from valence to conduction band in order to conduct electricity.

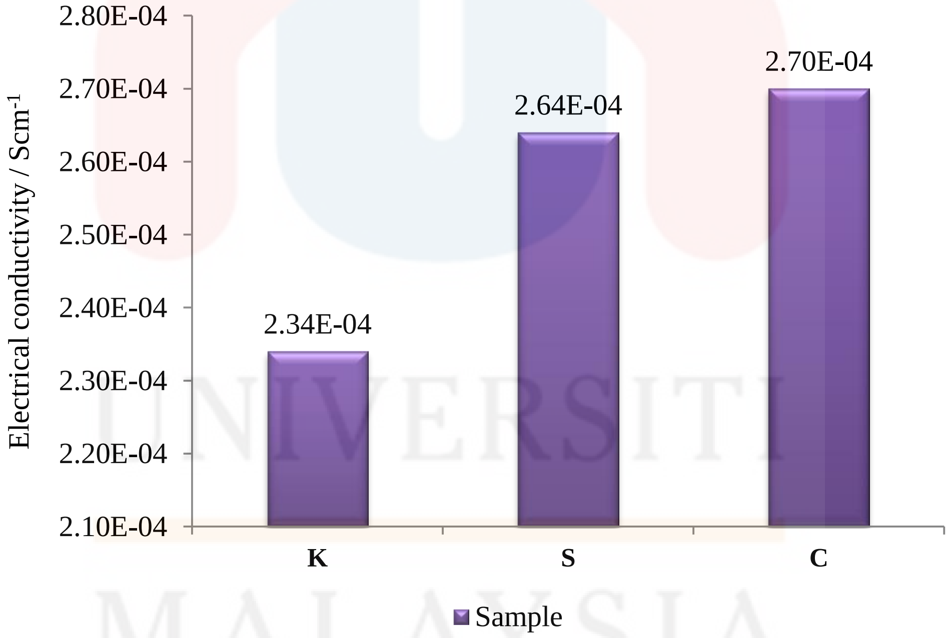

Figure 4.7: The electrical conductivity values of *Kappaphycus alvarezii sp*. (**K**), *Sargasum polysystum sp*. (**S**) and *Manihot esculenta sp*. (**C**)

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4.7 Solar Cell Measurement

The application of **K**, **S** and **C** in solar cell device was evaluated after device fabrication of ITO/TiO_2/dye (**K**, **S** or **C**)**/(**carbon/aluminium). The short-circuit current (I_{SC}) value, open-circuit voltage (V_{OC}), fill factor (ff) and power conversion efficiency (PCE) of DSSC were shown in Table 2.0. Maximum power (Pmax) of DSSC was calculated from the formula: Pmax = (I x V). I is the current value in ampere (A) and V is the voltage in (Mv) while, the FF value was calculated based on the formula FF = (I x V) max /(I_{SC} x V_{OC}) (Ridwan *et al*.,2018).

Overall, the highest solar device was obtained from **C** with 0.60 % efficiency, followed by **S** 0.18 % and **K** 0.06 %.From the observation, the solar devices efficiency obtained was in similar trend with the conductivity value from all three samples with **C** performed highest electrical conductivity followed by **S** and **K** with values of (2.70E-4), (2.64E-4) and (2.34E-4) respectively.

Table 4.3: Photovoltaic parameters of all devices

Sample	Short Circuit Current Density /mA cm^{-2}	Open Circuit Voltage /V	Fill factor	Power Conversion Efficiency /%
K	6.88E-05	0.40	0.04	0.06
S	4.70E-05	0.30	0.25	0.18
C	1.02E-05	0.48	0.24	0.60

The power conversion efficiency (PCE) value of **C** is the highest followed by **S** and **K** which is 0.60 %, 0.18 % and 0.06 % respectively. The TiO_2 is a better material properties when used as an anode material for DSSCs. TiO_2 can be used in DSSC

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application because of its high dye absorption properties which resulted in giving good current density (Thomas *et al*., 2014). PCE value of **K** is the lowest can be supported by which the result in a low and small fill factor, leading to low energy conversion effectiveness (Umang *et al*., 2012). The combination of carbon/aluminium - coated ITO used caused increasing efficiency as counter electrode (CE) due to carbon has properties as an excellent material, like high surface area-to volume ratio, good conductivity and the electro catalytic activity towards the I^- and $/I^{-3}$ redox species (Thomas *et al*, 2014). With only carbon electrode, it was found that the result obtained was very low.

Thus, the analysis was proceeded with the combination of electrodes. Further study should be continued in order to further explain above statement. By improving the CE material, the fill factor (FF) of the cell rises, which is mainly influenced by low series resistance (Rs) of the cell which is related to the slope of the tangent line to the current density (J)–voltage (V) curve at V_{OC} (Thomas *et al*., 2014).

C performed the highest photovoltaic value which is 0.60 % solar cell efficiency might be due to relation of the surface area analysis with SEM surface morphology. It can be seen that **C** has the long-chain image with small particles and (**C**) particles might adsorb more on TiO_2 surface. From the BET analysis, specific surface area of **C** is the highest which is 5.16 m^2g^{-1}, concluded that more dye can be absorbed lead to maximization of dye sensitization. Increasing amount of dye being absorb caused by decreasing particle size (Chowdhury and Saha, 2010).

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CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In this study, the preparation of dye sample from *Kappaphycus alvarezii sp.*, *Sargasum polysystum sp.* and *Manihot esculenta sp.* were successfully extracted and prepared. These dye extracts were characterized using Ultra-Violet spectroscopy (UV-vis), Scanning electron microscopy (SEM) and Breneur Emitte Teller (BET) analysis machine.

These dyes extracts solutions were analyzed using UV-Vis in order to evaluate the solar absorption at the wavelength region from 400 to 800 nm. The results of absorption spectra showed different reading at the visible region and peaks probably due to the differentiation of the photo-absorption properties.

The band gap values were determined from the Tauc plot. From the result, it showed that the sample from *Manihot esculenta sp.* (**C**) had the lowest value of the band gap followed by *Sargasum polysystum sp.* (**S**) and *Kappaphycus alvarezii sp.* (**K**)**,** which is 2.1eV, 2.41eV and 2.85eV respectively. From this, it shows that **C** have least amount of energy needed for the transition that which made electrons able to jump from valence band to conduction band followed by **S** and **K** respectively.

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The surface morphology from sample **K**, **S** and **C** on TiO_2 paste produced a different image. The sample **K** produced a rock-like structure which is the semi-refined carrageenan (SRC) extracted from seaweed itself. The porous structure image of sample **S** produced has the black holes which are associated to the pores formed during the reaction between dyes. The dye-TiO_2 mixed reaction from sample **C** produced an image of veins like structure with branches which caused more compact absorption for the arrangement.

The use of dye extracted from *Kappaphycus alvarezii sp*., *Sargasum polysystum sp*. and *Manihot esculenta sp*. as photo-sensitizers in the application of dye-sensitized solar cell (DSSC) were successfully fabricated. The result from the characterization such UV-vis spectroscopy and the band gap values showed the abilities of the extracted dyes to absorb photon energy, hv and its potential to be utilized as photo-sensitizers.

5.2 Recommendation

The preparation and extraction of the natural dyes must be optimized to produce high yield and quality of the sample which will lead to sample with high conductance properties. The raw materials of the natural dye must be kept in a correct temperature so that the use of fresh raw material for the extraction procedure and characterization will give an accurate reading and good result.

The extracted sample and the fabrication of device must be done properly so that it can prevent any contamination and technical error. During the extraction process, the sample must be kept from non-direct light as the sample is sensitive towards light which

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might alter the composition of the sample. The sample also must be kept in the dark condition to ensure the sample is in good condition.

To ensure accurate and consistent reading for the result, the parameters such temperature, pH and solvent used are important to get an accurate and consistent reading during the measurement or characterization process. The ratio between the sample dye and the solvent must be calculated properly to produce a thicker solution with good composition. Last but not least, the sample must be checked regularly to prevent any residue or contamination before proceeding with further steps.

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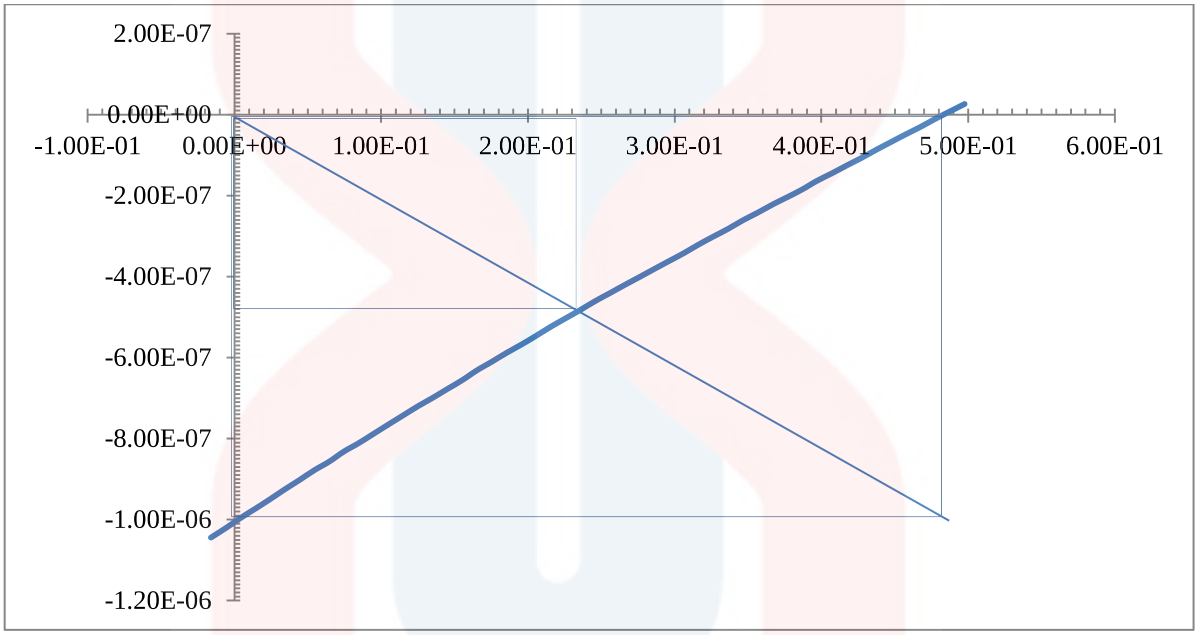
APPENDICES

APPENDIX A: SOLAR CELL EFFICIENCY *Manihot esculenta sp.*



Voc	4.77E-01
Vmax	2.40E-01
Isc	1.02E-06
Imax	4.90E-07
Pin	2.00E-05
Pmax	1.18E-07
FF	2.42E-01
EFF	0.588

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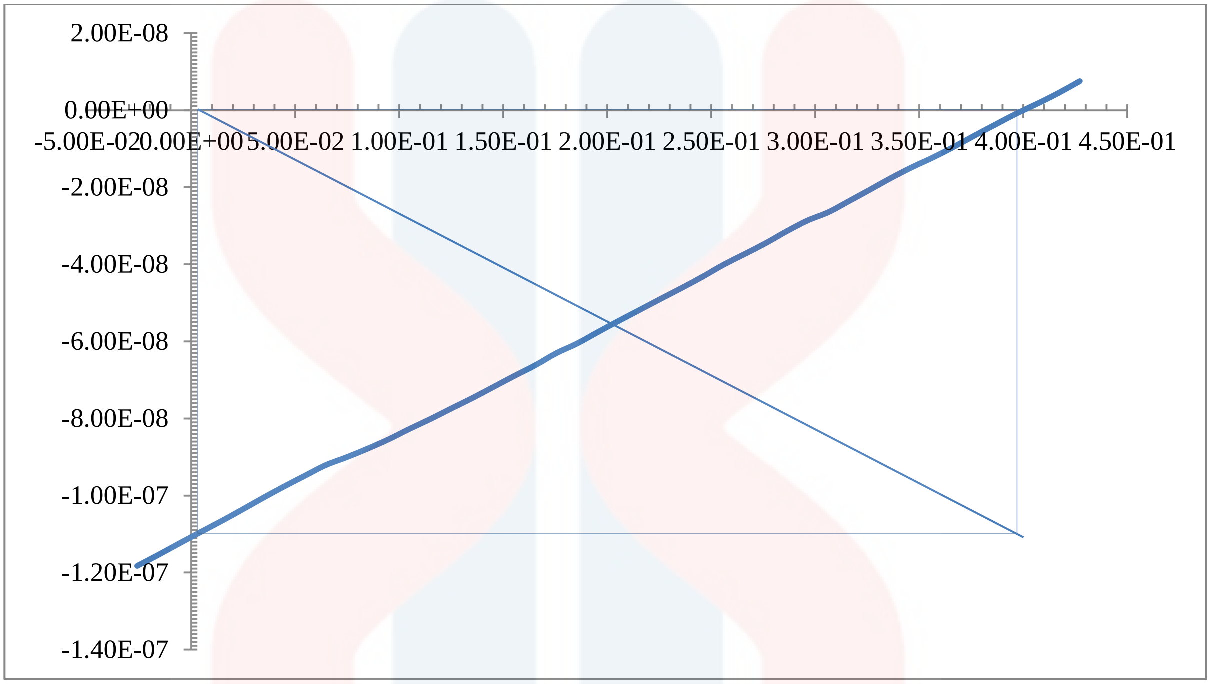
APPENDIX B: SOLAR CELL EFFICIENCY *Kappaphycus alvarezii sp.*



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Vmax	2.06E-01
Isc	1.10E-07
Imax	5.46E-08
Pin	2.00E-05
Pmax	1.12476E-08
FF	4.09E-02
EFF	0.056238

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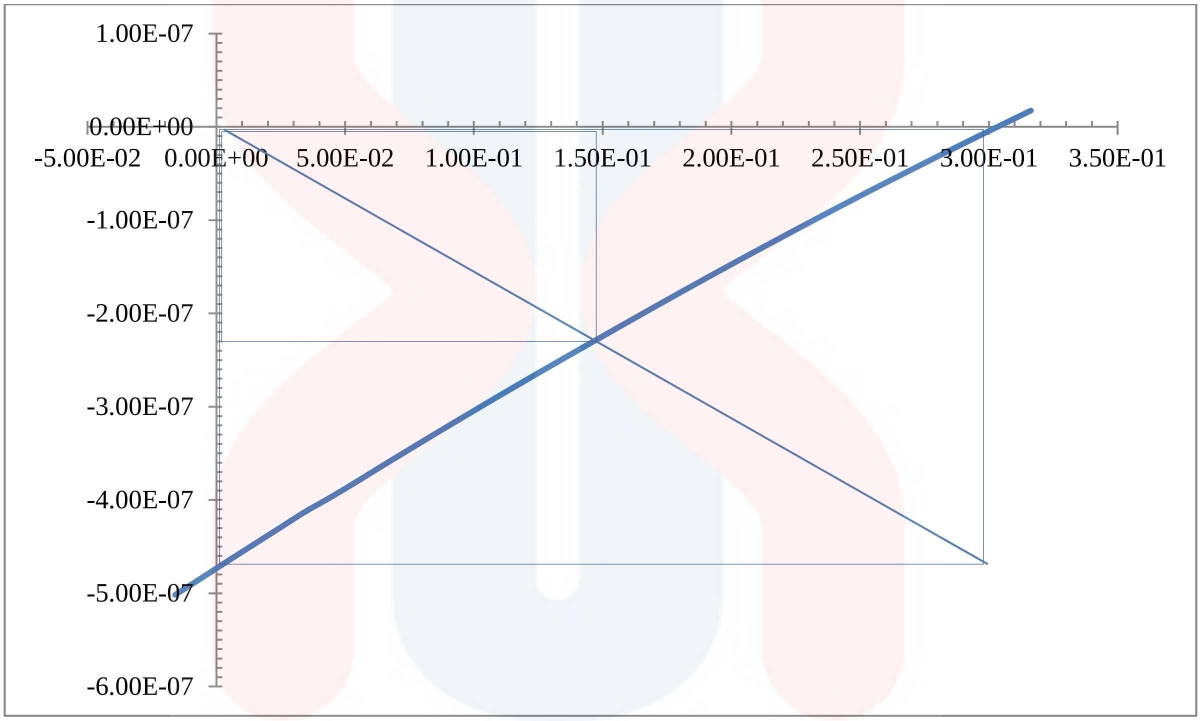
APPENDIX C: SOLAR CELL EFFICIENCY *Sargasum polysystum sp.*



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Vmax	1.50E-01
Isc	4.90E-07
Imax	2.32E-07
Pin	2.00E-05
Pmax	3.48E-08
FF	2.47E-01
EFF	0.174

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