

# Fabrication of dye-sensitized solar cell using chlorophylls pigment from sargassum

M A Ridwan<sup>\*1</sup>, E Noor<sup>2</sup>, M S Rusli<sup>2</sup>, Akhiruddin<sup>2</sup>

<sup>1</sup> Departement of Agroindustrial Technology, Pangkep State Polytechnic of Agriculture Kabupaten Pangkep 90761 South Sulawesi, Indonesia

<sup>2</sup> Departement of Agroindustrial Technology, Faculty of Agricultural Technology, Bogor Agriculture University, Bogor 16680 West Java, Indonesia

\*Corresponding Author: [erlizanoor@yahoo.com](mailto:erlizanoor@yahoo.com)

**Abstract** Dye-sensitized solar cell (DSSC) is a new generation of the solar cell. Its development in the dye-sensitized system is varied. Natural dyes have been the choice in developing DSSC. This study used a dye-sensitized chlorophyll pigment from Sargassum sp. as a dye-sensitized solar cell. This study aims to obtain chlorophyll pigment extract to be used as a dye in DSSC and to obtain the best energy conversion efficiency from DSSC. The chlorophyll pigments were extracted using APHA method (2012), and the TiO<sub>2</sub> coating method used was doctor blade method. The two fabricated cells have an area of 1 cm<sup>2</sup> immersed with chlorophyll dye for 30 hours. Then these cells were tested using direct sun radiation. The concentration value of chlorophyll in acetone solution was 61.176 mg/L. The efficiency value obtained was 1.50% with VOC of 241 mV, ISC 2.9 x 10<sup>-4</sup> mA and fill factor 0.432.

## 1. Introduction

The organic solar cell is an alternative device to convert solar energy into environment-friendly electric energy. Commercial solar cells are generally made of inorganic materials such as silicon (Si) and germanium (Ge). Types of silicone-based and germanium-based solar cells have an energy efficiency of about 14%-17% with cell working time of 25 years, but the high cost of raw materials and expensive production cost make the selling prices of solar cells in the market are relatively high [1].

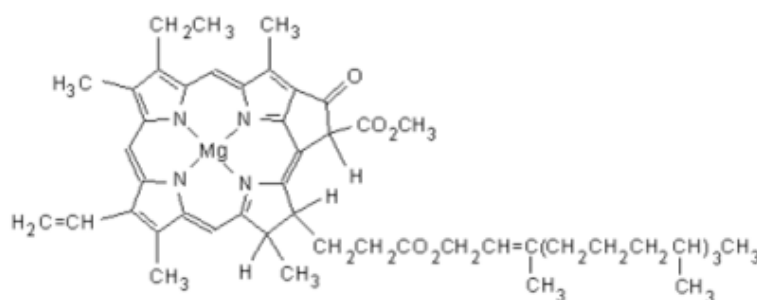
Therefore, researchers start to make a new breakthrough by using organic materials. The use of raw materials and easy developing technique are believed to result in the inexpensive solar panel. DSSC is a dye-sensitized solar cell developed as an alternative concept to the conventional solar cell. Dye-sensitized solar cell (DSSC) is a photoelectrochemical solar cell primarily consisting of photoelectrode, electrolyte, and opposite electrode. Titanium dioxide (TiO<sub>2</sub>) has been a favorite semiconductor in various studies. Unfortunately, due to great band gap (3 to 3.2 eV), TiO<sub>2</sub> absorb only the ultraviolet part of sunlight making it having slow conversion efficiency [17]. Many studies were conducted to study the potential of DSSC as solar cell recently [2]. Dye extract or pigment of plants used as photosynthesizer include the chlorophyll extract [2] or anthocyanin [3].

Chlorophyll is the main pigment effective as photosynthesizer in photosynthesis process of plants, with maximum absorption at 670 nm, so that chlorophyll is an interesting component as the



visible part of photosynthesis [2]. There are some types of chlorophyll found as photosynthesis product, but the commonly found types in higher plants are chlorophyll a and b [4].

Chlorophyll has chemical formula as shown in Figure 1. Both types of the chlorophyll, chlorophyll a and b, have light absorption at two different wavelengths, namely at 400 nm-490 nm and 620 nm-680 nm.



**Figure 1.** Molecular formula of chlorophylls [5]

This paper discusses the relationship between chlorophyll pigment extract content and absorption spectrum and sensitizer properties for DSSC dye.

## 2. Method

### 2.1 Chlorophyll Pigment Extract from Sargassum

Pigment extraction referred to APHA method [10]. One hundred grams of Sargassum powder with a size of 20 mesh was extracted using maceration method in technical acetone solution: distilled water (9:1)(v/v) for 24 hours. The ratio of alga and acetone solvent required in the extraction was 1:4 (b/v). Pigment-acetone solution was filtered, and the pigment filtrate was concentrated with rotary vacuum evaporator (Yamato) at a temperature of  $\pm 50^{\circ}\text{C}$  until free of solvent.

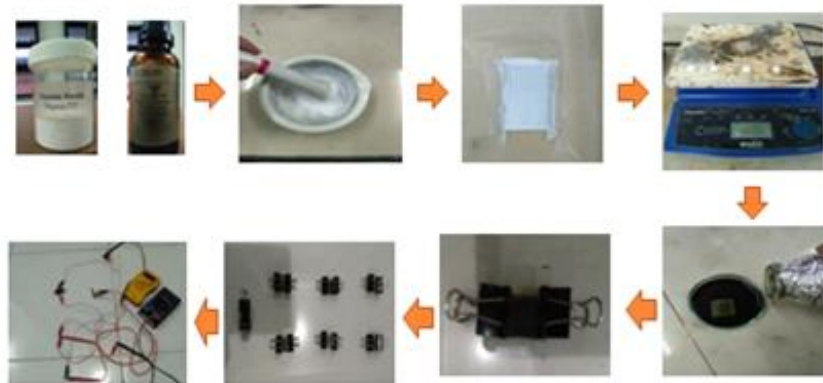
Absorption wavelengths were characterized by using UV-Vis Hewlett Packard spectrophotometer (200-800 nm). 3 mL of each chlorophyll solution was used to analyze the color absorption wavelength with a spectrophotometer. The extracted pigment concentration was calculated by measuring the extract absorbance at a specific wavelength. The following is the formula to calculate chlorophyll concentration according to Wintermans and De Mots[6].

### 2.2 Dye-Sensitized Solar Cell Prototype and $\text{TiO}_2$ Plate Voltage Current Value

Photoexcitation in the dye-sensitized solar cell does not occur in semiconductor electrode but occurs at light-absorbing dye or on the interface between dye-sensitized semiconductor and electrolyte. Injection of electrons from dye to  $\text{TiO}_2$  requires more reductive dye excitation than the conduction band of  $\text{TiO}_2$ . Electrons in the conduction band of semiconductor were collected in counter electrode and flow through the external circuit. Electrons then flow through the electrode to opposite electrode. The oxidized dye will require electron transfer from the electrolyte to bring it back to ground state. Redox reaction in the electrolyte was triggered by the presence of electrons coming into the electrolyte solution. Therefore, this cell is also called photoelectrochemical cell [7].

The thin layer was developed according to modified ICE method [16], with colloid development and coating on TCO. The colloid was developed by mixing 0.5 g and 1 mL of acetic acid with pH 3-4 and Triton X-100. The mixture was then scraped slowly until the colloid was formed. Triton X-100 functions as a surfactant to improve the adhesion in the substrate. Next, colloid was coated onto TCO which had been pre-washed with soap and immersed in ethanol. This was achieved by covering the

TCO sides with scotch tape leaving a blank cross-section (1x1 cm<sup>2</sup>). After that, colloid was applied and distributed evenly on TCO glass with the glass bar. Then, the layer in TCO was air-dried for 2 minutes and scotch tape was removed gently. Layer on TCO was heated with hotplate until the layer adhered perfectly and then put into a container prefilled with silica gel.



**Figure 2.** Prototype DSS Solar Cell in Chlorophyll Pigment

Figure 2 shows the solar cell that has been immersed in chlorophyll pigment solution. The light brown cross-section measuring 1x1 cm<sup>2</sup> is the thin layer of TiO<sub>2</sub> that have absorbed chlorophyll pigment. The left and right side of the solar cell are clipped with Binder Clips No. 107 to avoid the movement of the glass. The solar cell was then tested for current and voltage. Characterization of current and voltage was conducted by testing the output current and voltage from the sample by utilizing the sunlight energy at intensity of 0.085 mW/cm<sup>2</sup>. The curve obtained from the measurement results indicated a slope. This was in accordance with a study by Chou et al [9].

### 2.3 Experimental Setup

**2.3.1 Immersion of TiO<sub>2</sub> layer in dye-sensitizer Solutions.** Immersion of TiO<sub>2</sub> layer was achieved by varying the time: 5 hours, 15 hours, 30 hours, and 45 hours. TiO<sub>2</sub> layer on TCO glass was immersed in chlorophyll nano pigment solution in dark room for the pigment solution to completely absorbed. After immersion, the layered conductive glass was dripped and drained, and then the current and voltage of the solar cell kit were characterized.

**2.3.2 Characterization of current-voltage.** The light source used in this study was sunlight at 12.00-13.00 p.m. The current and voltage were measured using voltmeter and amperemeter which were combined parallel. The potentiometer was used as a dummy load to determine the current value variatively. The measurement was performed by rotating the potentiometer so that the resistance value changed. This resistance value change will be readable in voltmeter and amperemeter. The values were documented when a value change occurred on amperemeter. The values were then plotted in the graphic form. The observed parameters included open circuit voltage (Voc), namely the voltage when the applied external load is high. Voc was obtained when there is a value change in resistance by a potentiometer, the readable current was zero. Whereas, short circuit current (Isc) was obtained when the readable voltage value was zero. Maximum voltage value (Vmax) and maximum current (Imax) were obtained by observing the highest values from multiplication between voltage and current of each data [9].

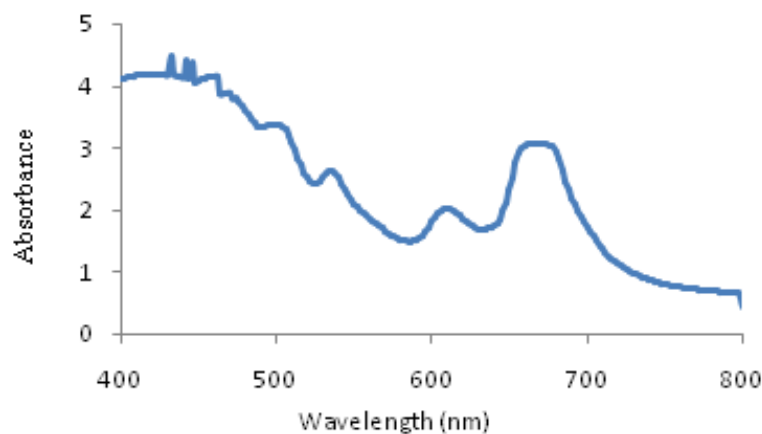
### 3. Result and discussion

#### 3.1 UV-Vis absorption spectra

Absorption is a quantity that expresses the ability of a material to absorb light. Organic compounds are able to absorb light due to their valence electrons that can be excited to higher energy level. One of the organic compounds is chlorophyll from *Sargassum Sp*.

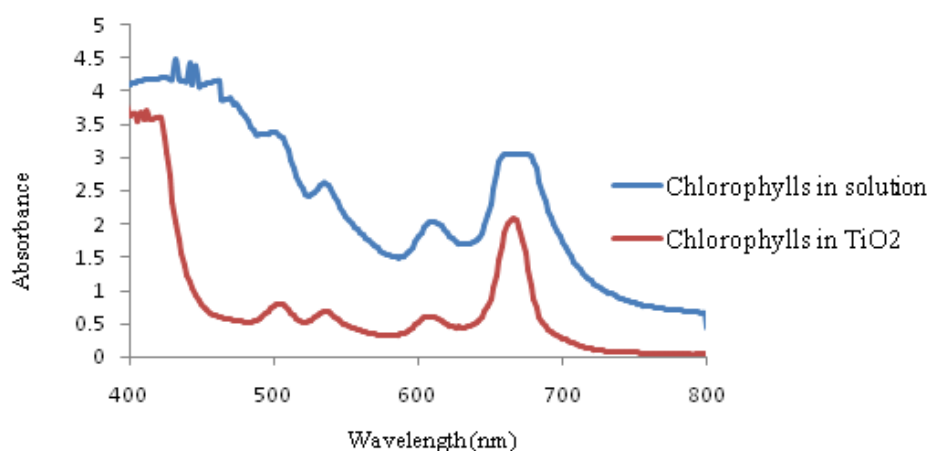
The important role in the dye-sensitized solar cell is the ability of the dye to absorb sunlight and convert it to electric energy. Generally, the dye used is ruthenium complex. But in its development, organic dye begins to be developed because it is cheaper than ruthenium complex, having high absorption coefficient due to  $\delta - \delta$  intramolecular transition, and no worry about the limited resources, because it doesn't contain noble metal like ruthenium [15].

Test against chlorophyll extract dye using UV-Vis spectrophotometer to determine the absorbance of chlorophyll pigment. The principle of spectrophotometry is the light absorption by molecules. Molecules can absorb radiation from UV-Vis region because it contains electron [14]. The results of UV-Vis absorption of *Sargassum Sp* chlorophyll are shown in Figure 3.



**Figure 3.** Absorption spectra of chlorophylls in solution

According to Figure 3, chlorophyll concentration in the sample in acetone solution is 61.176 mg/L, as calculated by the formula of Wintermans and de Mots [8].

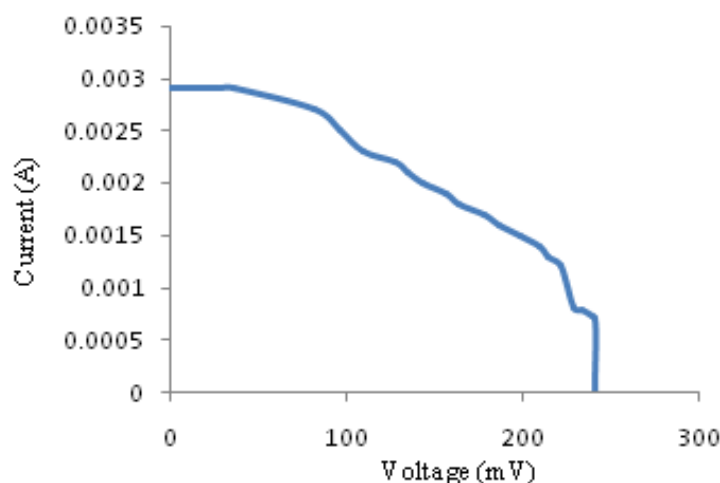


**Figure 4.** Absorption spectra of chlorophylls in solution and TiO<sub>2</sub>

From figure 4 we can see the absorbance value in chlorophyll that had been applied in  $\text{TiO}_2$  decreases. This is due to not all chlorophyll in chlorophyll pigment extract solution adhere to  $\text{TiO}_2$ . In the application of solar cell, this DSSC uses  $\text{TiO}_2$  with nanometer size.  $\text{TiO}_2$  in nanometer size has an advantage namely can hold more dye because there are many cavities its layers. Bigger sizes have only a few cavities so they can hold only few dye and the efficiency is smaller because produce few electron-hole pair. DSSC performance depends more on dye sensitizer. Dye absorption spectrum and adherence to semiconductor  $\text{TiO}_2$  surface is an important factor in determining the efficiency of DSSC [11].

### 3.2 Photovoltaic performance of DSSC

Photovoltaic test for DSSC using chlorophyll pigment extract as sensitizer was performed by measuring the characteristic I-V curves under radiation with sunlight at 1.00 – 12.00. For example, characteristic I-V curves of DSC sensitized with black rice extract is shown in Figure 5. According to figure 5, the short-circuit current ( $I_{SC}$ ) value, open-circuit voltage ( $V_{OC}$ ) of DSSC can be obtained directly as shown in Table 1, respectively. Maximum power ( $P_{max}$ ) of DSSC was confirmed based on the formula:  $P_{max} = (I \times V)$ . The FF value (fill factor) was calculated based on the formula  $FF = (I \times V)_{max} / (I_{SC} \times V_{OC})$ . Photoelectric parameters of DSSC sensitized with chlorophyll pigment extract from seaweed of sargassum type was measured and calculated, the results are shown in Table 1.



**Figure 5.** I-V characteristics of DSCs sensitized

From the characteristic I-V curves in Figure 5, we can calculate several parameter values in solar cell including the open voltage ( $V_{oc}$ ), short-current density, maximum voltage ( $V_{max}$ ), maximum current density ( $I_{max}$ ), maximum power ( $P_{max}$ ), fill factor (FF) and efficiency ( $\eta$ ) that can be seen from Table 1.

**Table 1.** Photoelectrochemical parameters of DSCs sensitized with chlorophylls at the working area of  $1.0 \text{ cm}^2$

Dye	Parameter						
	Voc (mV)	Isc (mA)	Vmax (mV)	Imax (mA)	P max (mW)	FF	$\eta$ (%)
Chlorophylls	241	0.0029	178	0.0017	0.3003	0.432	1.50

Table 1 shows that fill factor produced is 0.43 with the efficiency of 1.5%. The obtained results were higher compared to previous studies (0.4%) with a fill factor of 0.336). It is worth to mention that this value was higher than those reported by Wang et. Al.[12].

Experimental data obtained with photoelectrochemical studies were reported in Figure 7, where shown the I-V curves marked with the following parameters:  $V_{oc}$  0,36,  $J_{sc}$  0,8 mA/cm<sup>2</sup> and efficiency of 0.178%. The more important point for sargassum-based DSSC is the very good efficiency (1.50%). It is worth to mention that this value was higher than reported by Wang et. al. [13], obtained by using pure sargassum as dye sensitizer. Moreover, by considering the increased photoelectrochemical obtained by these researchers with the increased dye concentration [13], the increased performance (according to current efficiency) was also expected for DSSC which was based on higher dye content of sargassum. Finally, the comparison of the obtained results with the results in the literature showed that for green alga [13]

#### 4. Conclusions

This study was conducted to extract chlorophyll pigment from sargassum, by using simple purification method that can avoid complex procedures used by Wang et. Al. However, the use of chlorophyll pigment as a dye for DSSC cells can be an interesting alternative solution for cheap cell production. In addition, the use of chlorophyll extracted from these species will have an advantage in ecological sustainability.

The results of chlorophyll extract de in acetone solution by using UV-Vis spectrophotometer at a wavelength of 200 to 668 nm and obtained chlorophyll concentration of 61.176 mg/L. Whereas the measurement of chlorophyll absorbance in TiO<sub>2</sub> plat indicated smaller absorption properties compared to absorption properties in chlorophyll extract solution. This was due to the fact that not all chlorophyll in dye solution adheres to TiO<sub>2</sub> plate.

Chlorophyll extract obtained from *Sargassum sp* was used as a sensitizer in DSSC and produced higher fill factor and better current density when compared to data available in the literature. The DSSC made with sargassum sp extract indicates the efficiency of about 1.5%, respectively for  $J_{sc}$ ,  $V_{oc}$ , fill factor. Increased cell efficiency based on sargassum extract was caused by the optimum procedure used for DSSC assembly ad better sensitization properties from chlorophyll compared to other chlorophyll types.

#### Acknowledgments

The authors would like to express gratitude to the Ministry of Research, Technology and Higher Education of the Republic of Indonesia for the financial support of this work under the research grant National Strategic Research (STRANAS) for the academic year 2015-2016.

#### References

- [1] M. Fahlman, W.R. Salaneck, Surface, and interfaces in polymer-based electronic, surface science, 500 (2002), 904-922
- [2] Y. Amao, Y.Yamada, K. Aoki, Journal of Photochemistry and Photobiology A: Chemistry 164(2004), 47-51.
- [3] K. Wongcharee, V Meeyoo, S Chavadej, Solar Energy Materials and Solar Cells 91 (2007), 566-571
- [4] R. Sastrawan, Photovoltaic Modules of Dye Solar Cells, Dissertation University of Freiburg (2006).
- [5] Nurhayati dan Veinardi S. 2011. Isolation of chlorophyll a from spinach leaves and modification center ion with a Zn<sup>2+</sup> study on its optical stability. *Journal of Mathematics and Science*, 16(2): 65-31.



- [6] Wintermans JFGM, De Mots A. (1965). Spectrophotometric Characteristics of Chlorophylls A and B and Their Phenophytins in Ethanol. *Biochimica et Biophysica Acta (BBA) Biophysics including Photosynthesis*, 109(2), 448-453.
- [7] Wei D, Amaratunga G. 2007. Photoelectrochemical cell and its application in optoelectronics. *International Journals of Electrochemical Science* 2: 897-912.
- [8] Wintermans JFGM, De Mots A. (1965). Spectrophotometric Characteristics of Chlorophylls A and B and Their Phenophytins in Ethanol. *Biochimica et Biophysica Acta (BBA)-Biophysics including Photosynthesis*, 109(2), 448-453.
- [9] Chou TP, Zhang Q, Cao G. 2007. Effects of dye loading conditions on the energy conversion efficiency of ZnO and TiO<sub>2</sub> dye-sensitized solar cells. *The Journal of Physical Chemistry C* 111.50: 18804-18811.
- [10] [APHA] American Public Health Association. 2012. *Standard Methods for the Examiner of Water and Wastewater 22<sup>nd</sup> Edition*. Washington DC: APHA Publisher.
- [11] Khwanchit W, Meeyoo V, Chavadej S. 2006. Dye-sensitized solar cell using natural dyes extracted from Rosella and blue pea flowers. *Sol Energy Mater Sol Cell*. 91: 566 –571.
- [12] Wang XF, Kitao O, Hosono E, Zhou H, Sasaki SI, Tamiaki H. 2010. TiO<sub>2</sub>-and ZnO-Based Solar Cells Using A Chlorophyll A Derivative Sensitizer for Light-Harvesting and Energy Conversion. *Journal of Photochemistry and Photobiology A: Chemistry*, 210(2), 145-152.
- [13] Desai U.V, Xu Chengkun, Wu Jiamin, dan Gao Di, 2012, Solid-state-Dye Sensitized Solar Cell Based on Ordered ZnO nanowire arrays, *Nanotechnology*, (23).205-401
- [14] Hardjono S. 1991. Spektroskopi, Yogyakarta: Liberty.
- [15] Kathiravan A, Chandramohan M, Renganathan R, Sekar S. 2009. Photoinduced Electron Transfer from Phycoerythrin to Colloidal Metal Semiconductor Nanoparticles. *Spectrochimica Acta Part A: Molecular and biomolecular spectroscopy*, 72(3), 496-501.
- [16] ICE (Institute for Chemical Education). 2008. Nanocrystalline solar cell kit recreating photosynthesis. Madison : University of Wisconsin-Madison.
- [17] Gratzel M. 2005. Solar energy conversion by dye-sensitized photovoltaic cells. *Inorganic Chemistry* 2005;4. 4;6 841 – 51.