Available online at www.sciencedirect.com
ScienceDirect
Energy Procedia 79 (2015) 896 – 902
Energy Procedia

2015 International Conference on Alternative Energy in Developing Countries and Emerging Economies

Chlorophyll Pigments as Nature Based Dye for Dye-Sensitized Solar Cell (DSSC)

R. Syafinar[a*], N. Gomesh[a], M. Irwanto[a], M. Fareq[a], Y.M. Irwan[a]

[a]*Centre of Excellence for Renewable Energy (CERE), School of Electrical Systems Engineering, Universiti Malaysia Perlis (UniMAP), Malaysia.*

Abstract

Dye-sensitized solar cell (DSSC) was assembled using natural dyes from chlorophyll extracted from spinach as a sensitizer. In this work, the adsorption characteristic has been studied in harvesting sunlight using different solvents. The effect of solvents has been investigated by analyzing the absorption spectrum, bandgap and absorption coefficient of the dyes. From the UV-Vis absorption spectrum, it has been known that chlorophyll extracted with distilled water has the broader region of the visible light spectrum in the range of 400 to 720 nm compared to chlorophyll extracted with ethanol. The lowest bandgap of dye also presented by extracted the chlorophyll with distilled water with 1.83 eV and the absorption coefficient of 1.59 km^{-1}. The photo electrochemical parameter for solar cell by using chlorophyll extracted with DI water solvent showed the open circuit voltage (Voc) of 440 mV, current short circuit (Isc) of 0.35 mA and a fill factor (FF) of 0.49.

Peer-review under responsibility of the Organizing Committee of 2015 AEDCEE

Keywords: Dye sensitized solar cell; chlorophyll; spinach;band gap;absorption coefficient; extracted; spectrum

1. Introduction

Dye is a key role in developing high performance of DSSC. The dye should possess these following requirements such as having a strong absorption in the visible light spectrum, carry a suitable

* Corresponding author. Tel.: +604-9798903; fax: 604-9798903.
E-mail address: syafinar_ramli@yahoo.com

1876-6102
Peer-review under responsibility of the Organizing Committee of 2015 AEDCEE
doi:10.1016/j.egypro.2015.11.584

attachment of the chemical group to be bound with semiconductor and can inject the electrons into a semiconductor surface [1].

Previously, DSSC employs ruthenium (II) polypyridinic complex as a sensitizer of wide-band gap semiconductor but due to costly and complicated in sensitizing the complexes also containing heavy metal and producing environmental polluting, another method is replacing it using natural dyes from fruits, plants and leaves, which offered cost efficiency, non-toxity and complete biodegradation. Natural dyes play a key role in harvesting sunlight and transferring solar energy into electrical energy [2-5].

Some fruits, plants, flowers and leaves displayed various colors and contained several pigments, which can be simply extracted and then used as sensitizer because most of green plants contained a lot of chlorophyll, which help in absorbing photon from sunlight, while anthocyanins, which give color to fruits and plant (red-purple) having light absorbing in the range of 520-550 nm wavelengths [6, 7], tannin and carotene.

Chlorophyll can absorb light from red, blue and violet wavelengths and obtains its color by reflecting the green wavelength. The strong absorption peaks in the visible region located at 420 nm and 660 nm wavelengths that can be used as a natural sensitizer in the visible light range [8]. The photoelectric conversion efficiency (η) based on chlorophyll pigments has been reported before such as spinach is used as a natural based sensitizer and the photolectrical performance showed open circuit voltage (Voc) as much as 550 mV, current short circuit (Isc) is about 0.46 mA and fill factor (FF) was about 51% [9]. Wormwood as a chlorophyll dyes for DSSC resulted open circuit voltage (Voc) as much as 0.585V, current short circuit (Isc) is about 1.96 mA, fill factor (FF) was about 47% and conversion efficiency is 0.538 % [10].

In this work, chlorophyll extracted from spinach was used as a sensitizer in DSSC. The influence of different extracts solvent from ethanol and distilled water to extract the chlorophyll pigments from spinach is shown in Fig. 1 has been investigated from its absorption spectrum, band gap and also absorption coefficient.

Fig. 1. Spinach

2. Materials and methods

2.1 Materials

Materials used are Titanium Dioxide (TiO_2) powder-anatase, Triton X-100, deionized (DI) water, ethanol and Electrolyte.

2.2 Preparation of TiO_2 paste

3.5 g of TiO_2 nano-powder is added in 2 ml of Triton X-100 and 0.5 ml of DI water. Solar bath it uses ultrasonic cleaner for 20 minutes. TiO_2 paste is shown in Fig. 2.

2.3 Extraction methods of extracting the chlorophyll pigment using an ultrasonic cleaner into liquid form.

5g of spinach is crushing using mortar into small size. 10 ml of ethanol is added into the spinach and is placed into the ultrasonic cleaner for 15 minutes with the frequency of 37 Hz using Degas mode for extracting chlorophyll process. After that, enter the solvents into a centrifuge machine for 25 minutes with 2500 rpm. All process has shown in Fig. 2.

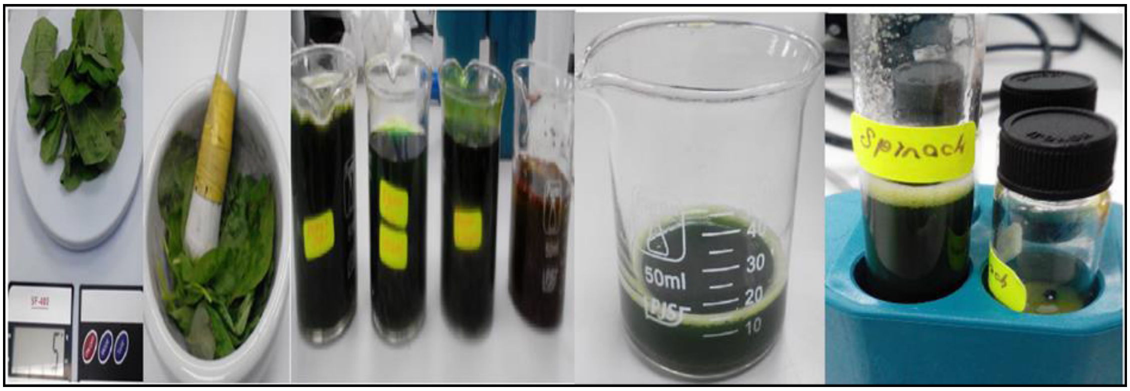

Fig. 2. The process of extracting chlorophyll pigments from spinach

2.4 Preparation of fabricate DSSC using Doctor Blade's method

The scotch tape is applied on four sides of conducting ITO glass to control the thickness of TiO_2 film. The thickness of scotch tape is measured by using digital callipers. The TiO_2 paste is applied to ITO coated glass and flatten it using razor blade until the TiO_2 film become homogenous layer. TiO_2 is annealed using hot plate for 450^{o}C in 30 minutes. After annealing process, the TiO_2 film has cooled for 15 minutes in room temperatures. After cooling process, the TiO_2 is immersed into spinach's dye for 24 hours for "sensitized" process. For counter electrode, graphite from a pencil is used by sketched on the conducting surface of another ITO glass. The TiO_2 film is removed from dye solution and rinsed using ethanol to remove debris. The spacer is placed on ITO glass contained TiO_2 film to mask electric contact strips. Electrolyte solution is dripped into TiO_2 film and both TiO_2 film and counter electrode is combined together using binder clip and measure its electrical performance. The process of fabricate DSSC by using chlorophyll extract has shown in Fig. 3.

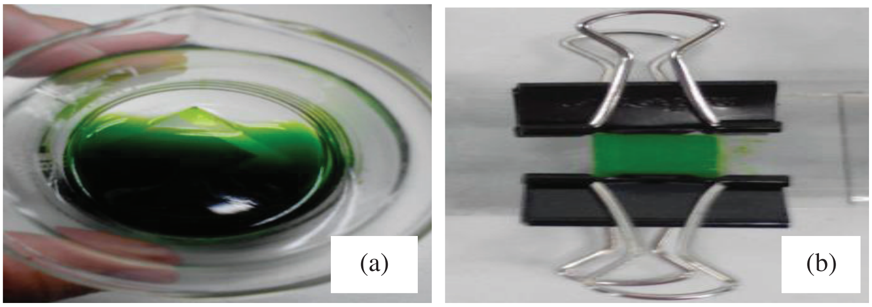

Fig. 3. (a) TiO_2 film is immersed into spinach's dye (b) Solar cell with chlorophyll dye

2.5 Characterization and measurements

The absorption spectra of the dyes were performed using Evolution 201 UV-Vis Spectrophotometer has shown in Fig. 3. UV-Vis spectrophotometer is used to measure the absorbance rate in visible light spectrum. The determination of the band gap of dye absorbed by TiO_2 surface is calculated by using formula in (1). Where h is the Planck's constant, v is the frequency, λ is the wavelength and c is the speed. The numerical values of the symbols are $h = 6.63 \times 10^{-34}$ Js, $c = 3.0 \times 10^{8}$ m/s, $1eV = 1.60 \times 10^{-19}$ J and E stands for photon energy.

$$E = hv \qquad (1)$$

$$= \frac{hc}{\lambda}$$

The absorption coefficient determines how far into a material, light of a particular wavelength can penetrate before it is absorbed. The absorption coefficient of the respective wavelengths is obtained by the division of the absorbance with the wavelength shown in (2) using K Boltzmann constant;

$$absorption\ coefficient = 4\pi k/\lambda \qquad (2)$$

Characterization equipment for measuring the performance of solar cells by using solar simulator 100 mW/m^2 Ketley 2450, SMU unit and Data Logger. The I-V curves were obtained using kick-start software. The short circuit current I_{sc} and the open circuit voltage V_{oc} were determined from the I-V curve. The fill factor FF (3) was calculated using the following relations:

$$FF = \frac{I_{max}V_{max}}{I_{SC}V_{OC}} \qquad (3)$$

3. Result and Discussion

3.1 Absorption spectra

Fig. 4 shows the UV-Vis absorption spectra of spinach extracted with ethanol (S-Etha) and distilled water (S-DI) in the visible light spectrum (400-700 nm) respectively. From Fig. 4, the absorption peak of S-Etha can be seen at a wavelength of 660 nm, and S-DI located at 680 nm. The absorption peak for S-Etha and S-DI attributed to the existing of chlorophyll pigment. Spinach is identified to be rich in chlorophyll because all green plants contained chlorophyll, which capable in photosynthesis process having glucose from simple organic molecules (water and carbon dioxide) under the action of visible light [11]. The high absorption peak when extracted the spinach with ethanol with an absorption range of 600-700 nm and peak absorbance at 610 nm shown in Fig.6 below. The band gap which is the photon energy of TiO_2 is related to the wavelength range absorbed and the band gap decreases with increasing absorption wavelength [12].

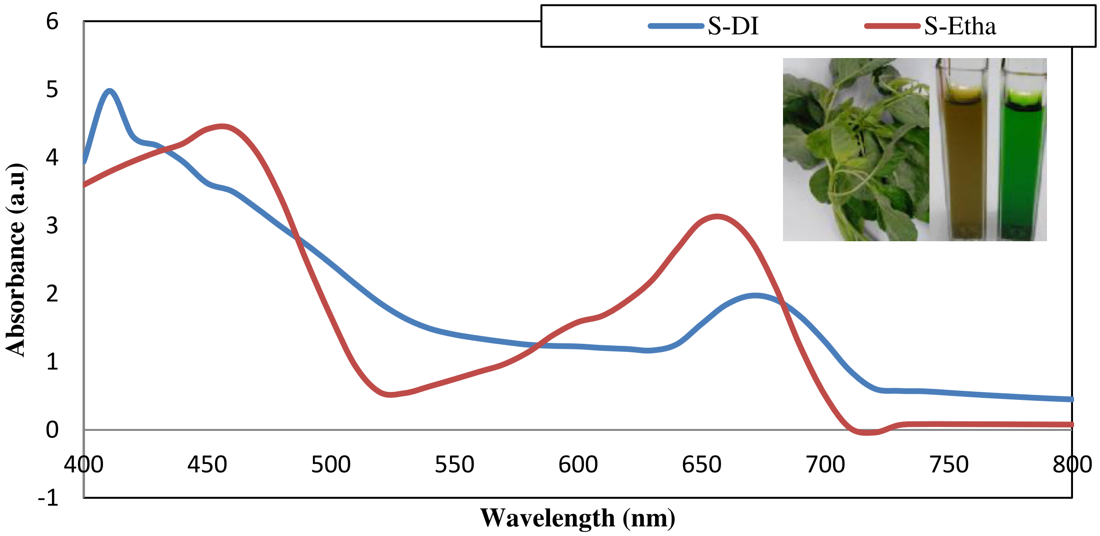

Fig. 4. Absorption spectra of S-Etha and S-DI

3.2 Bandgap estimation and absorption coefficient of the dyes

Between the conduction band and valence band, there is an energy difference which is called as energy band gap and used for analyzing the performance of DSSC which related to solar energy absorbed. Table 1 demonstrates the ethanol and DI water as extract solvents for spinach to extract the chlorophyll pigment. The lowest band gap of the spinach, which extracted with DI water of 1.83 eV compared to spinach with ethanol as high as 1.88 eV. A lowest band gap of dye helps the electron move fast from the valence band to the conduction band and only need less energy to the recombination of electrons and resulted high fill factor.

Table 1. Photon energy and absorption coefficient (α) of the dyes

Dyes	Extract solvent	Peak Absorbance (nm)	Absorption range (nm)	Bandgap (eV)	Absorption coefficient (α) k m^{-1}
Spinach	Ethanol	660	450-700	1.88	1.64
	DI water	680	400-720	1.83	1.59

3.2 Photoelectrical properties of DSCs sensitized with chlorophyll pigment

Photovoltaic tests of DSSC use spinach's dye by using different solvents as sensitizers were performed by measuring the current density-voltage (I-V) current under irradiation with white light (100mW/cm^2). The performance of DSSC is evaluated by the open circuit voltage (V_{oc}), short circuit current (I_{sc}) and fill factor (FF).

As shown in Table 2, the highest fill factor was spinach extracted with DI water of 0.49% compared to spinach extracted with ethanol was only 0.36%. This is due to the absorption intensity which is higher by extracting spinach with DI water and cause broader absorption wavelength. Besides, having higher interaction between the dye and TiO_2 particle will produce good charge-transfer performance and improving the fill factor [8].

Table 2: Photoelectrochemical parameters for DSSC

Dyes	Extract solvent	V_{oc} (mV)	I_{sc} (mA)	Fill Factor, FF (%)
Spinach	Ethanol	384	0.32	0.36
	DI water	440	0.35	0.49

4. Conclusion

Chlorophyll pigments can be used as a dye sensitizer in DSSC because of its ability in absorbing photon from sunlight and having light harvesting invisible light spectrum and it was proven by testing its observed rate using UV-Vis spectrophotometer. However, the efficiency of DSSC in the range of 1-2% lowers than synthetic dyes. But chlorophyll pigment was cheaper, can be disposed easily and easily extracted compared to synthetic dyes. Natural dyes, are having several pigments such as anthocyanin, betalains and chlorophyll have the capability to absorb photon from sunlight and transform it into electrical energy.

Acknowledgement

The authors would like to thank Center of Excellence for Renewable Energy (CERE) and the School of Electrical Systems Engineering, University Malaysia Perlis (UniMAP) for the technical and financial support. This project is funded by FRGS 2011 and RACE 2012 grant scheme.

References

[1] Rosana NTM, JoshuaAmarnath D, Joseph KLV, Anandan S. Mixed Dye from Nerium Oleander and Hibiscus Flowers as a Photosensitizer in Dye Sensitized Solar Cells. *International Journal of ChemTech Research* 2014; Vol. 6, No. 12; 5022-5026.

[2] Polo AS, Iha NYM. Blue sensitizers for solar cells: Natural dyes from Clafate and Jaboticaba. *Solar Energy Materials & Solar Cells* 2006; **90**:1936-1944.

[3] Sinha K, Saha PD, Datta S. Extraction of natural dye from petals of Flame of forest (Butea monosperma) flower: Process optimization using response surface methodology (RSM). *Dyes and Pigments* 2012*;* **94**: 212-216.

[4] Al-Ba'thi SAM, Alaei I, Sopyan I. Natural Photosensitizers for Dye Sensitized Solar Cells. *National Journal of Renewable Energy Research* 2013; Vol. 3, No.1.
[5] Abdel-Latif MS, El-Agez TM, Taya SA, Batniji AY, El-Ghamri HS. Plant Seeds-Based Dye-Sensitized Solar Cells. *Material Sciences and Application* 2013 ;**4**:516-520.
[6] Chang H, Lo YJ. Pomegranate leaves and mulberry fruit as natural sensitizer for dye-sensitized solar cells. *Solar Energy* 2010; **84**:1833-1837.
[7] Kumara NTRN et al. Layered co-sensitization for enhancement of conversion efficiency of natural dye sensitized solar cells. *Journal of Alloys and Compounds* 2013;**581**:186-191.
[8] Al-Alwani MAM, Mohamad AB, Kadhum AAH, Ludin NA. Effect of solvents on the extraction of natural pigments and adsorption onto TiO_2 for dye-sensitized solar cell applications. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 2015;* **138**:130-137.
[9] Chang H, Wu HM, Chen TL, Huang K.D, Jwo CS, Lo YJ. Dye-sensitized solar cell using natural dyes extracted from spinach and ipomea. *Journal of Alloys and Compound.s* 2010;**495**: 606-610.
[10] Chang H, Kao M-J, Chen T-L, Chen C-H, Cho K-C, Lai X-R. Characterization of Natural Dye Extracted from Wormwood and Purple Cabbage for Dye-Sensitization Solar Cells. *International Journal of Photoenergy* 2013; Article ID 159502, 8 pages.
[11] Torchani A, Saadaoui S, Gharbi R, Fathallah M. Sensitized solar cells based on natural dyes. *Current Applied Physics* 2015;**15**: 307-312.
[12] Ananth S, Vivek P, Arumanayagam T, Murugakoothan P. Natural dye extract of Lawsonia inermis seed as photo sensitizer for titanium dioxide based dye sensitized solar cells. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 2014;**128**:420-426.