Natural Dyes from Roselle Flower as a Sensitizer in Dye-Sensitized Solar Cell (DSSC)

S. Dayang[1]*, M. Irwanto[2], N. Gomesh[3], B. Ismail[4]
[1,2,4]Centre of Excellence for Renewable Energy, School of Electrical System Engineering, Universiti Malaysia Perlis (UniMAP), Pauh 02600 Perlis, Malaysia
[2]Department of Electrical Engineering, Institut Teknologi Medan (ITM) Medan, 20217 North Sumatera, Indonesia
[3]Engineering Department, School of Engineering Computing & Built Environment, KDU Penang University College, Pulau Pinang, Malaysia

Article Info

Article history:

Received Aug 29, 2017
Revised Nov 18, 2017
Accepted Dec 4, 2017

Keywords:

Anthocyanin
Dye-sensitized solar cell
Roselle
Solvents
Spectrum

ABSTRACT

Hibiscus Sabdariffa L. well known as Roselle flower was used as sensitizers for Dye-Sensitized Solar Cell (DSSC). The dyes were extracted using distilled water (DI) and ethanol (E) extract solvent in an ultrasonic cleaner for 30 minutes with a frequency of 37 Hz by using 'degas' mode at the temperature of 30°. Doctor blade method was applied in the fabrication of titanium dioxide (TiO_2) on ITO glass. Absorption spectra of Roselle dye with different extract solvent were tested using Evolution 201 UV-Vis Spectrophotometer. Fourier-Transform Infrared (FTIR) was used to identify the functional active group in extract dye. Based on FTIR result, the broad absorption at peak 2889 cm-^{1}, 2976 cm-^{1}, and 3366 cm-^{1} attributed to the O-H stretching which is the presence of hydroxyl group. The use Field Emission Scanning Electron Microscopy (FESEM) and Energy-Dispersive Spectroscopy (EDS) analysis are to characterize the surface morphology and element in the TiO_2 thin film.

Corresponding Author:

S. Dayang,
Centre of Excellence for Renewable Energy,
School of Electrical System Engineering,
Universiti Malaysia Perlis (UniMAP),
Pauh 02600 Perlis, Malaysia.
Email: dayangsurianini@gmail.com

1. INTRODUCTION

With the increase of the human population nowadays, much more electricity is needed in the next 30 years. The challenges that we have to face are the increase in power consumption. The rapidly increasing of fossil fuel consumption and excessive greenhouse gas emission has affected the environmental surrounding [1-3]. Thus, the development of renewable energies becomes a focus as an alternative to deplete the use of fossil fuels. The most abundant and remarkable energy source is the photovoltaic or solar energy which converts solar energy directly into electrical energy through solar cells [4].

The new innovative method Dye-Sensitized Solar Cell (DSSC) has caught recent attention due to their low cost, ease of fabrication and environmentally friendly sources of technology [5]. The DSSC was first introduced in 1991 by O'Regan and Gratzel [6]. The highest efficiency between 10-12% has been recorded by using metal Ruthenium (Ru) which is considered the best dyes for DSSC. However, the disadvantage of using Ru is a difficult purification, high cost and causing the environmental impact [7]. Thus, the natural dyes were become a proposed solution to replace the Ru which is a low-cost and environmental friendly dye sensitizer.

The DSSC composed of a dye, photoelectrode, electrolyte, counter electrodes, and substrates glass. Several researchers were focused to investigate the factors affecting the performance of dye-sensitized solar cell. Comparison extracting solvent from de-ionized water and ethanol was investigated by LK Singh et al [8] which have conversion efficiency of 1.37% and 0.72% respectively. The cell fabricated using dye extract in ethanol degrades faster than the cell fabricated in de-ionized water. This underlying reason is that the dye is not properly soluble in ethanol and functional groups are not properly attached to the TiO_2 surface. M Murugiah et al [9] constructed an experiment at different temperature of 250°C and 500°C. The result shows that the higher temperature annealing condition gave significant outcome in producing higher grade of ZnO with reduced impurity and increased absorption intensity. AKM Muaz et al [10] reported that at a higher annealing temperatures, the band gap between the valence band and conduction bands became smaller and consequently, smaller energy was used for electrons to be excited from the valence band to the conduction band.

Huizhi Zhou et al [11] had proposed twenty natural dyes extracted from natural dyes in surrounding. Mangosteen pericarp extract has achieved the highest conversion efficiency 1.17% and anthocyanin contain in this extract are the factors effected of the high efficiency. V Shanmugam et al [12] developed the performance of DSSC using natural dyes extracts from fruits of ivy gourd and red frangipani flowers. The presence of anthocyanin in alcoholic group demonstrated the improved efficiency in red frangipani flowers with 0.30% conversion efficiency. Carbonyl and hydroxyl groups present in the anthocyanin molecules can be bonded to the surface of a porous TiO_2 film. This makes electron transfer from the anthocyanin molecule to the conduction band of TiO_2 feasible [13].

Roselle also known as Hibiscus Sabdariffa is a tropical wild plant belonging to Malvaceae family [14]. Roselle is chosen as a potential candidate for dye-sensitized solar cell since it is rich in anthocyanins, and could be used as a good source for producing a brilliant red colorant for many foods. It was reported that anthocyanin obtained from Rosella are delphinidin and cyanidin complexes (Figure 1) [15].

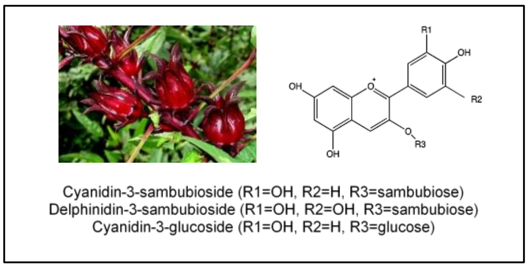


Figure 1. Structure of the delphinidin and cyanidin

1.1. Working Principles of DSSC

The process flow and cross section of DSSC are shown in Figure 2.

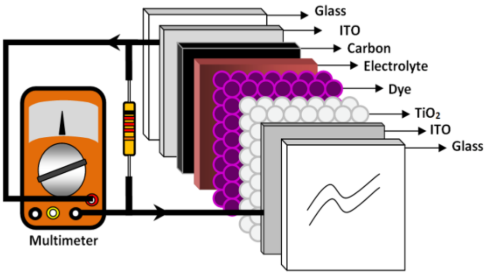


Figure 2. Cross section of DSSC

As the sunlight strikes on the surface of DSSC, the dye molecules collect photons and produce the excited electrons. Light passes through the transparent anode and excites the dye molecules. The excited dye molecules inject electrons into the conduction band of the TiO_2 layer which acts as a semiconductor. The dye molecules that lost electrons are then oxidized. The injected electrons travel through the nano-porous TiO_2 thin film toward the transparent conductive electrode (working electrode) and reach to a load where work is performed and delivered in the form of electrical energy. The electrons now travel back through an external load and reach the counter electrode and thus complete the whole circuit [16].

2. RESEARCH METHOD

2.1. Materials

The materials used are Titanium Dioxide (TiO_2) paste, Triton X-100, distilled water (DI), ethanol, Indium tin oxide (ITO) coated glass slide. The method of fabrication and extraction also can be referred at [17-18].

2.2. Preparation of Natural Dye Sensitizer Extracts

For roselle dye of weight 10 g were cut into small pieces and crushed using a mortar until a liquefied paste was formed as shown in Figure 3. The roselle dye then immersed in the solvent which consists of distilled water (DI) and ethanol (E) at room temperature and then placed into the ultrasonic cleaner as shown in Figure 4. The ultrasonic is used to further extract colored dye pigment for 30 minutes with a frequency of 37 Hz by using 'degas' mode at the temperature of 30°C.

Figure 3. Preparation of roselle dye sensitizer extract

Figure 4. Extracting colored dye using ultrasonic cleaner

2.3. Preparation of ITO glass

Figure 5 show, the ITO glass was cleaned and rinsed using ethanol. To prepare a TiO_2 paste, 5 g of TiO_2 powder and 3 drops of Triton X-100 was mixed. This mixture was stirred well until evenly distributed and turns into a homogeneous solution using a glass rod or a spatula. The scotch tape was pasted on the conductive side of ITO glass to fix the active area as 2 cm^2 (1cm x 1cm). Then, apply the TiO_2 paste and the suspension was spread uniformly by using glass stirring rod on ITO glass. This method is well known as doctor blade method. Two coated glass then was placed on the hot plate at a temperature of 450°C for 30 minutes and was kept cool for 15 minutes at room temperature. One ITO glass titania was dip into the roselle dye extract solution for a day. Meanwhile, another ITO glass was left with its original pure TiO_2.

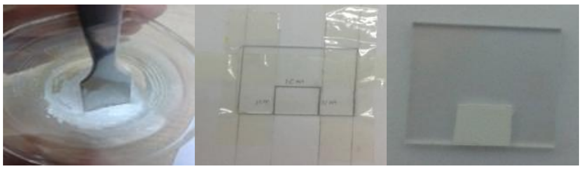


Figure 5. Preparation of TiO_2 paste on the ITO glass

2.4. Characterization and Measurement

The wavelength of light absorbed was tested using Evolution 201 UV-Vis Spectrophotometer as shown in Figure 6 which used to determine the absorbance rate in the visible light spectrum and the intensity compositions of dye color. The band gap of dye absorbed by TiO_2 surface determines by using the formula in Equation (1). Where h is the Planck's constant, c is the speed, λ is the wavelength and E stand for photon energy [14]. The numerical value of the symbols are: h=6.63 x 10^{-34} Js, c=3.0 x 10^{8} m/s, 1eV = 1.60 x 10^{-19} J.

$$E = \frac{hc}{\lambda} \quad (1)$$

The absorption coefficient determines how far into a material; a 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 Equation (2).

$$\text{Absorption coefficient, } \alpha = \frac{4\pi k}{\lambda} \quad (2)$$

Where λ (nm) is taken from the cutoff wavelength of the dyes and K is the Boltzman constant with value of 8.617 x 10^{-5} eV/K.

Figure 6. UV-Vis Spectrophotometer

3. RESULTS AND ANALYSIS

3.1. UV-Vis Absorption Spectra Analysis

The absorption spectra of the Roselle dye samples which were diluted in distilled water (R-DI) and ethanol (R-E) were measured using UV-Vis Spectrophotometer as shown in Figure 7. A light red colored solution of roselle dye was observed extracted by using distilled water compared to roselle extracted with ethanol which shows the deep red colored solution. From Figure 7, the maximum peak of R-DI is 490 nm which absorb the wavelength from 400 nm to 600 nm. The peak of an absorption spectrum of R-E is 540 nm in the range of 480 nm to 620 nm. This absorption range of 400 nm to 600 nm proved the presence of anthocyanin pigment of roselle. Roselle is potentially a good source and good colorant since it contains high anthocyanin.

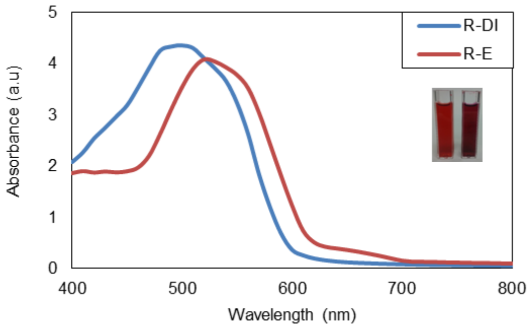


Figure 7. Absorption spectra of Roselle extracted using Distilled Water (R-DI) and Ethanol (R-E)

Table 1. Photon energy and absorption coefficient of natural dyes

Dyes	Extract Solvent	Peak absorbance (nm)	Photon energy (eV)	Absorption coefficient (α) km^{-1}
Roselle	Distilled water	490	2.54	2.21
	Ethanol	540	2.30	2.01

The photon energy and absorption coefficient (α) of the roselle dyes with different extract solvent from distilled water and ethanol is shown in Table 1. From Table 1, the lowest photon energy (eV) and absorption coefficient (α) is R-E with 2.30 eV and 2.01 km^{-1}. Meanwhile, the highest photon energy (eV) and absorption coefficient (α) is extracted dye using distilled water (R-DI), which is about 2.54 eV and 2.01 km^{-1}.

3.2. Fourier-Transform Infrared (FTIR) Analysis

Figure 8 show, the functional group of roselle dye is confirmed by its FTIR spectra using solvent from distilled water (R-DI) and ethanol (R-E). For R-DI, the sharp peak at 1639 cm^{-1} corresponds to the C=O stretching which represented the carbonyl group for ketone structure. The peak at 2141 cm^{-1} corresponds to the C≡C stretch. The broad absorption at peak 3366 cm^{-1} attributed to the O-H stretching which is the hydroxyl group in roselle dye

FTIR spectra of R-E shows the peak at 879 cm^{-1} arises due to the aromatics group with C-H stretching vibration. The two sharp peak located at 1046 cm^{-1} and 1087 cm^{-1} are attributed to esters group which having C-O stretching vibrations. A band at 1382 cm^{-1} is assigned as N=O bend. The C=O stretching vibration confirms the presence of ketones functional group at 1646 cm^{-1}. The absorption at peak 2889 cm^{-1}, 2976 cm^{-1}, and 3366 cm^{-1} are attributed to the O-H stretching which is the presence of hydrogen bonding in roselle diluted with ethanol solvent.

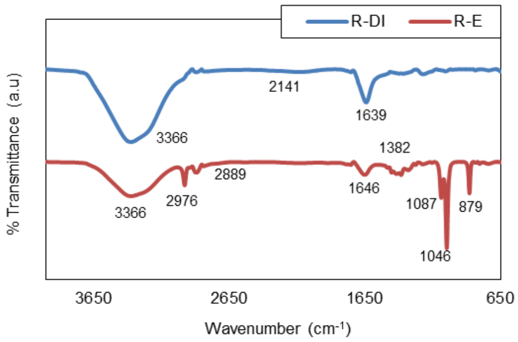
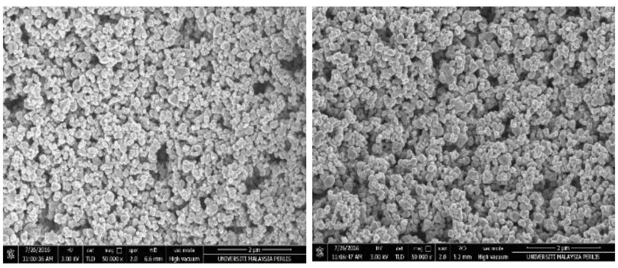


Figure 8. FTIR spectrum of Roselle extracted using Distilled Water (R-DI) and Ethanol (R-E)

3.3. Field Emission Scanning Electron Microscopy (FESEM) Analysis

The morphology and the structure of the pure TiO_2 and roselle dyed TiO_2 using extract solvent from distilled water annealed at 450°C were investigated using Field Emission Scanning Electron Microscopy (FESEM) at a magnification X50000 as shown in Figure 9 (a) and Figure 9(b). It can be obviously seen from the microstructure of roselle dyed TiO_2, that more porosity appears than pure TiO_2. Nanoclusters were formed when the TiO_2 nanoparticles have aggregated together. These kinds of nanoclusters will influence the catalytic behavior of TiO_2 as a working electrode component in the dye-sensitized solar cell. To minimize this aggregation, therefore capping agent is required to prevents the formation of nanoclusters. The morphology of TiO_2 has slightly improved as nearly spherical shape and uniform size adsorption of dye on TiO_2 was produced due to the dye rich in anthocyanin. Hence, the anthocyanin act as a capping agent takes an additional role in a DSSC.

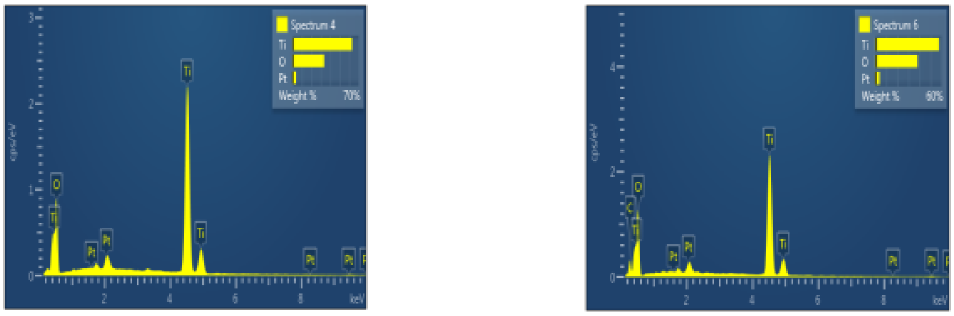


(a) (b)

Figure 9. FESEM surface morphology at mag. X50000 (a) Pure TiO_2 (b) Roselle dyed TiO_2

3.4. Energy-Dispersive Spectroscopy (EDS) Analysis

The EDS analysis was used to identify the elements or materials contained in the thin films. As can be seen in Figure 10 (a) and Figure 10 (b), the presence of Titanium (Ti) and Oxide (O) was detected in the spectra. The presence of Platinum (Pt) is due to the used of a spin coater for precise and uniform deposition of thin films. Figure 10 (a) shows the weight contributions for of Ti and O are 62.94% and 33.4% respectively, which confirms the high purity of pure TiO_2 particles that will be used as photo materials with the natural dyes. The additional element of Carbon (C) in Figure 10 (b) is due to the presence of roselle dye extract contain in the TiO_2 thin film. The weight contributions for of Ti, O, and Pt are 57.72%, 38.41% and 3.87% respectively and they contribute 100% of the total weight.



(a) (b)

Figure 10. EDS spectra of (a) Pure TiO_2 (b) Roselle dyed TiO_2

4. CONCLUSION

The implementation using Roselle dyes shows the potential of nature-based dyes being applied in DSSC. The absorption spectrum using UV-Vis Spectrophotometer shows the maximum peak at 490 nm for distilled water extract solvent (R-DI) and at 540 nm for ethanol extract solvent (R-E). The FTIR analysis was carried out to identify the functional active group in Roselle extract. The presence of carbonyl (C=O) and hydroxyl group (OH) in roselle dye contained the anthocyanin pigment will improve the electron transfer and enhance the efficiency of DSSC. The surface morphology using FESEM and EDS revealed the presence element of Titanium (Ti), Oxide (O) and Carbon (C) of roselle dye extract contain in TiO_2 thin film. With continuous advanced studies and research, the natural dye sensitizer still can be a future new technology in solar cell application.

REFERENCES

[1] Karl MK. Design, Synthesis and Properties of Organic Sensitizers for Dye-Sensitized Solar Cells. Doctoral Thesis. Sweden; Royal Institute of Technology Stockholm; 2011.

[2] Renuga Verayiah, Anusiya Iyadurai. A Comparison Study on Types of PV for Grid Connected Photovoltaic Power. *Indonesian Journal of Electrical Engineering and Computer Science (IJEECS).* 2017; 6(2): 349-356.

[3] M Tripathy, PK Sadhu. Building Integrated Photovoltaic is a Cost Effective and Environmental Friendly Solution. *TELKOMNIKA Indonesian Journal of Electrical Engineering*. 2015; 14(1): 49-54.

[4] WZ Leow, YM Irwan, M Asri, M Irwanto, AR Amelia, Z Syafiqah, I Safwati. Investigation of Solar Panel Performance Based on Different Wind Velocity Using ANSYS. *Indonesian Journal of Electrical Engineering and Computer Science (IJEECS).* 2016; 1(3): 456-463.

[5] NA Ludin, AM Al-Alwani Mahmoud, AB Mohamad, ABH Kadhum, K Sopian, NSA Karim. Review on the Development of Natural Dye Photosensitizer for Dye-Sensitized Solar Cell. *Renewable and Sustainable Energy Reviews*. 2014; 31: 386-396.

[6] BO Regan, M Gratzel. A Low-Cost, High-Efficiency Solar Cell Based on Dye-Sensitized Colloidal TiO_2 Films. Institute of Physical Chemistry Swiss Federal Institute of Technology, Switzerland. 1991; 353: 737-740.

[7] Ishwar CM, Pankaj S, Lal B. Dye-Sensitized Solar Cell using Extract from Petals of Male Flowers Luffa Cylindrica L. as a Natural Sensitizer. *Optical Materials*. 2016; 52: 150-156.

[8] LK Singh, T Karlo, A Pandey. Performance of Fruit Extract of Melastoma malabathricum L. as sensitizer in DSSCs. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 2014; 118: 938-943.

[9] M Murugiah, J Hashim, U Nirmal, MY Yuhazri. Synthesis and Fabrication of An Effectual Dye Sensitized Solar Cell. *Global Engineers & Technologists Review*. 2012; 2(3): 9-15.

[10] AKM Muaz, U Hashim, F Ibrahim, KL Thong, MS Mokhtar, WW Liu. Effect of annealing temperatures on the morphology, optical and electrical properties of TiO_2 thin films synthesized by the sol-gel method and deposited on $Al/TiO_2/SiO_2/p$-Si. *Microsyst Technology*. 2015.
[11] H Zhou, L Wu, Y Gao, T Ma. Dye-Sensitized Solar Cells Using 20 Natural Dyes as Sensitizers. *Journal of Photochemistry and Photobiology A: Chemistry*. 2011; 219: 188-194.
[12] V Shanmugam, S Manoharan, S Anandan, R Murugan. Performance of dye-sensitized solar cells fabricated with extracts from fruits of ivy gourd and flowers of red frangipani as sensitizers. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 2013; 104: 35-40.
[13] Sönmezoğlu S, Akyürek C, Akin S. High-efficiency Dye-Sensitized Solar Cells Using Ferrocene-based Electrolytes and Natural Photosensitizers. Journal of Physics D: Applied Physics. 2012; 45, 425101
[14] Patel S. Hibiscus sabdariffa : An Ideal yet Under-exploited Candidate for Nutraceutical Applications. *Biomedicine & Preventive Nutrition*. 2014; 4(1): 23-27.
[15] Wongcharee K, Meeyoo V, Chavadej S. Dye-sensitized Solar Cell Using Natural Dyes Extracted from Rosella and Blue Pea Flowers. *Solar Energy Materials and Solar Cel*ls. 2007; 91: 566–571.
[16] Geetam R, Anil K, Perapong T, Bhupendra G. Natural Dyes for Dye-Sensitized Solar Cell: *A Review. Renewable and Sustainable Energy Reviews*. 2017; 69: 705-718.
[17] R Syafinar, N Gomesh, M Irwanto, M Fareq, YM Irwan. Cocktail Dyes from Blueberry and Dragon Fruit in the Application of DSSC. *ARPN Journal of Engineering and Applied Sciences*. 2015; 10 (15): 6348-6353.
[18] R Syafinar, N Gomesh, M Irwanto, M Fareq, YM Irwan. Optical Characterization Using Nature Based Dye Extracted from Hibiscus's Flower. *ARPN Journal of Engineering and Applied Sciences*. 2015; 10(15): 6336-6340