

Effect of Solvents on Natural Dyes Extraction from Mangosteen Waste for Dye Sensitized Solar Cell Application

I Nyoman Setiawan^{1*}, Ida Ayu Dwi Giriantari², Wayan Gede Ariastina³ and I B. Alit Swamardika⁴

¹Doctoral Study Program of Engineering Science, Faculty of Engineering, Udayana University
Kampus Sudirman, Denpasar-Bali, Indonesia.

^{2,3,4} Study Program of Electrical Engineering, Faculty of Engineering, Udayana University
Kampus Bukit Jimbaran, Badung-Bali, Indonesia

*Email: setiawan@unud.ac.id.

Abstract— Natural dyes are economically and environmentally superior to ruthenium-based dyes because they are cheap and non-toxic. In this study, natural dyes were extracted from mangosteen peel waste. Color extraction was carried out with three types of solvents (distilled water, methanol and ethanol) which had been acidified with 10% citric acid and with a ratio of material: solvent (1: 4, 1: 6, 1: 8 w / v). The photochemical properties are studied by UV-Vis spectrophotometer and FTIR spectroscopy. The absorption peak of the three types of solvent occurs at different wavelengths. The presence of carbonyl (C = O) and hydroxyl (OH) groups contained in anthocyanins can attach coloring to the surface of TiO₂. Ethanol solvents with a ratio of 1: 8 produce the lowest photon energy at wavelength and absorption coefficient of 539.00 nm and 2,008 km⁻¹ respectively. The lowest band gap of the dye helps electrons move rapidly from the valence band to the conduction band and only requires less energy for electron recombination which will increase the performance of the DSSC.

Index Terms— *Dye Sensitized Solar Cell , natural dyes, mangosteen peel, band gap*

I. INTRODUCTION

Solar cells are power plants capable of converting sunlight into electric current. Solar energy is the most promising energy source because the amount is very large and sustainable. The sun is an energy source that is expected to be able to overcome the problem of energy needs, after various conventional energy sources are reduced in number and are not environmentally friendly. The amount of sunlight energy is so large, making solar cells an alternative promising future energy source. Solar cells also have advantages such as being able to be installed modular in each location so that it does not require transmission. Various technologies have been developed in the process of making solar cells to reduce production prices to be more economical. Dye Sensitized Solar Cell (DSSC) has received considerable attention in the field of solar energy because of its simple fabrication, good efficiency, and low production costs. Dye Sensitized Solar Cell are photoelectrochemical devices that convert visible light into energy electricity based on the sensitivity of a wide band gap semiconductor. Fig.1 shows a typical configuration of DSSC consisting of FTO

glass coated with nanocrystalline titanium dioxide (TiO₂) as a photoanode, a dye molecule, an electrolyte containing iodide / triiodide (I⁻ / I₃⁻) and another FTO glass coated with carbon or platinum called the electrode counter which acts as a catalyst for electron regeneration [1]. Dye-sensitizer functions to absorb sunlight and convert it into electrical energy.

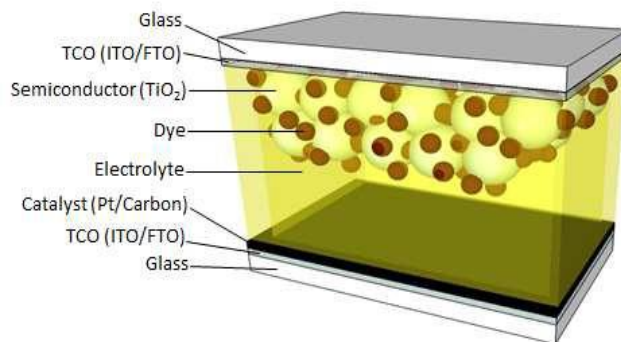


Fig. 1. Structure of Dye-sensitized Solar Cell

Dyes have an important role in DSSC to absorb sunlight. The use of synthetic dyes as sensitizers has provided better DSSC efficiency and high durability, but has disadvantages such as higher costs, the tendency to experience degradation and the use of toxic materials and difficult to be synthesized [2]. As an alternative, the use of natural dyes is very attractive for DSSC applications because it is cheap, available in large quantities in Indonesia, and sustainable [3]. Natural dyes from leaves, flowers, fruits, and roots have been investigated by researchers for DSSC [4-5]. In this study the characteristics of mangosteen peel waste (*Garcinia mangostana* L.) for DSSC were carried out. Mangosteen fruit is generally consumed by the flesh while the peel is removed as garbage which will pollute the environment. This is very unfortunate because an increase in the economic value of mangosteen can be done by utilizing the peel. Mangosteen peel contains natural anthocyanin dyes [6]. Extraction of red natural dyes (anthocyanin) is strongly influenced by several factors, namely the type of solvent, the ratio of materials to solvents and the atmosphere of acidity (pH) [7]. The effects of solvent variations and solvent comparisons on DSSC performance were studied in this study. The use of waste as a natural dye extract will be cheaper, and increase added value. Besides that the use of fruit peel can minimize waste production which begins to increase as the population increases and consumes.

II. MATERIALS AND METHODS

A. Extraction of natural dyes

Mangosteen peel samples are separated from the flesh, then cut into small pieces. After cutting, a sample was dried in the laboratory room at room temperature. After that, the samples were crushed with a blender to produce a fine powder. The study was conducted by randomize block design with 2 factors namely type of solvent (such as distilled

water, ethanol, and methanol) which was acidified with 10% citric acid and ratio of material:solvent (1:4, 1:6, 1:8 w/v). Making dyes is done by meseration method. Maseration is carried out for 24 hours using three solvents until all the powder settles. The extract is filtered using filter paper is shown in Fig. 2. Characterization of dyes was carried out using Fourier transform infrared (FTIR) and ultra violet-visible (UV-Vis).

B. Characterization and Measurement

The dye absorption spectrum was carried out using UV-Vis Spectrophotometer (UV-1800 Shimadzu). UVVis spectrophotometers are used to measure the rate of absorbance in the visible light spectrum. The band gap of the dye absorbed by the surface of TiO_2 is calculated using the formula in (1). Where h is Planck constant, ν is the frequency, λ is the wavelength and c is the speed. The numerical value of the symbol is $h = 6.63 \times 10^{-34}$ Js, $c = 3.0 \times 10^8$ m / s, $1\text{eV} = 1.60 \times 10^{-19}$ J and E stands for photon energy [8].

$$E = h\nu \quad (1)$$

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

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 Boltzman constant;

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



Fig. 2. The process of extracting natural dyes from mangosteen peel waste.

III. RESULT AND DISCUSSION

The characterization results of spectrum absorbance of the three types of solvents have different absorbance power as shown in Fig. 3. The absorbance peak for distilled water, ethanol and methanol occurs at wavelengths 513.5, 539.0, and 531.5 nm respectively. The absorption peak at these wavelengths indicates the presence of anthocyanin in dye, which is usually identified in the wavelength range of 500-600 nm [9-12].

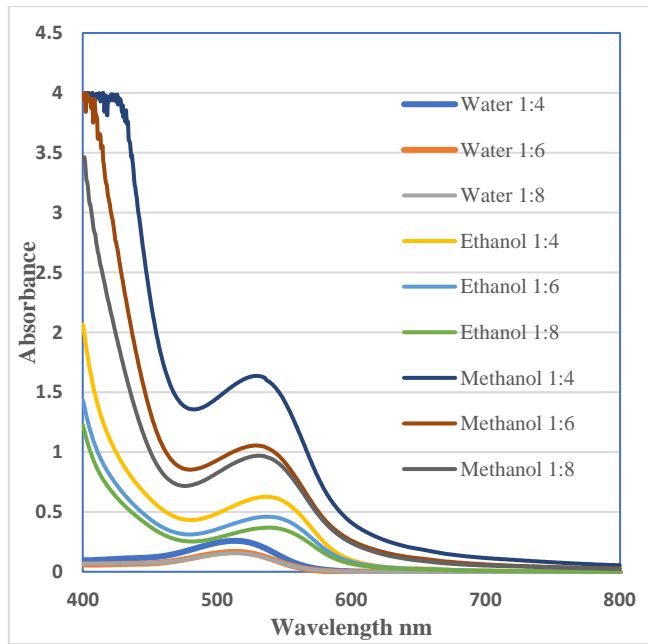


Fig. 3. Spectrum UV-Vis of dye mangosteen peels

The infrared absorption spectrum of the material has a distinctive pattern which makes it possible to identify the existence of the main functional groups in the material structure. If visually observed a spectrum of variations in dye solution concentration looks similar but there is still a difference between the intensity and maximum absorbance between the spectra as shown in Fig.4. Variations in the concentration of dye solutions generally do not change the functional group. The C-H and O-H function group is a carbonyl and hydroxyl group that constitutes the anthocyanin structure. This hydroxyl group is useful as an adhesive between pigment compounds and TiO₂ layers at FTO.

A. Band gap estimation and dye absorption coefficient

The energy difference between the conduction band and the valence band, is called the band gap energy and is used to analyze the performance of DSSC associated with the absorbed solar energy. The spectrum absorption characterization results from the three types of solvents have different absorbency, photon energy and absorption

coefficient (α) as shown in Table 1.

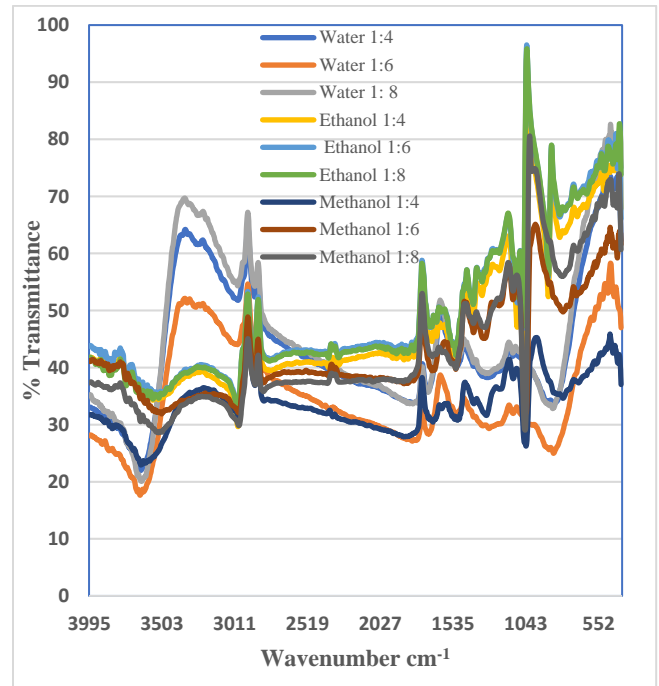


Fig. 4. Spectrum FTIR of dye mangosteen peels

Table 1. Photon Energy and absorption coefficient of dye.

Solvent	Ratio of solvent	Wavelength (nm)	Photon Energy (eV)	Absorption coefficient (α) (km ⁻¹)
Water	1:4	513.5	2.421	2.108
	1:6	513.5	2.421	2.108
	1:8	513.0	2.423	2.110
Ethanol	1:4	535.5	2.321	2.021
	1:6	535.5	2.321	2.021
	1:8	539.0	2.306	2.008
Methanol	1:4	529.0	2.350	2.046
	1:6	529.5	2.348	2.044
	1:8	531.5	2.339	2.036

Fig.5 has shown the dependence of the absorption coefficient on the visible wavelength of the spectrum for dyes. The lowest photon energy is produced from ethanol solvents with a ratio of 1: 8 at a wavelength of 539.00 nm and a absorption coefficient of 2,008 km⁻¹. The lowest band gap of the dye helps electrons move rapidly from the valence

band to the conduction band and only requires less energy for electron recombination.

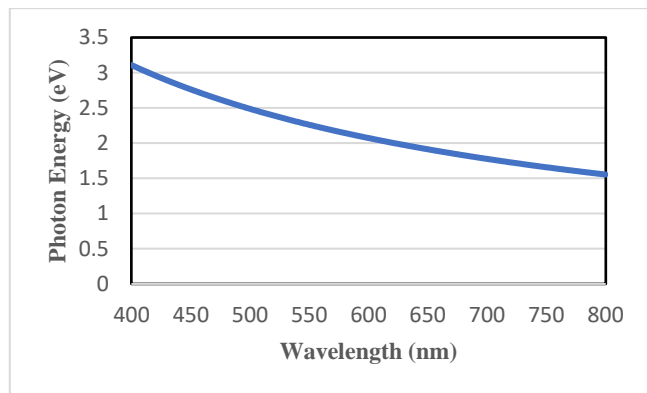


Fig. 5. Dependence of absorption coefficient on the wavelength of the dyes

IV. CONCLUSION

The absorption characteristics for harvesting sunlight were investigated using natural dyes from mangosteen peel waste. The dye extraction was carried out with three different types of solvents, distilled water, ethanol and methanol. The characterization results of spectrum absorbance of the three types of solvents have different absorbance power. Variations in the concentration of the dye solution do not change the functional group. The lowest bandgap dyes are presented as 2.321 eV with ethanol solvents and are suitable for the wide band gap semiconductors that used as photoanode in DSSC. The lowest dye band gap helps electrons move rapidly from the valence band to the conduction band and only requires less energy for electron recombination.

ACKNOWLEDGMENT

The authors are grateful for Financial support from the Directorate of Research and Community Service of Directorate General for Research and Development of the Ministry of Research, Technology and Higher Education in accordance with the Research Contract No : 171.20/UN14.4.A/LT/2018 through Research and Community Service Institute of Udayana University.

REFERENCES

- [1] Setiawan, I.N, Ida Ayu Dwi Giriantari, W.Gede Ariastina and IB Alit Swamardika, Characterization of Titanium Dioxide (TiO₂) thin films as materials for Dye Sensitized Solar Cell (DSSC), *IEEE Xplore*, 2017, DOI: 10.1109/ICSGTEIS.2016.7885786
- [2] Shalini, S., R. Balasundara prabhu, S. Prasanna, Tapas K. Mallick, S. Senthilarasu, 2015. Review on natural dye sensitized solar cells: operation, materials and methods, *Renewable and Sustainable Energy Reviews*, Vol. 51 (2015), doi:10.1016/j.rser.2015.07.052.
- [3] Setiawan, I.N, I. A. D. Giriantari, W. G. Ariastina, I. B. Swamardika, A. S. Duniyaji and N Satya Kumara, Natural Dyes from Fruit Waste as a Sensitizer for Dye Sensitized Solar Cell (DSSC). *Journal of Electrical, Electronics and Informatics*, Vol. 1 No.1, 2017
- [4] Abdel-Latif, Monzir S., Mahmoud B. Abuiriban, Taher M. El-Agez, and Sofyan A. Taya, Dye-Sensitized Solar Cells Using Dyes Extracted From Flowers, Leaves, Parks, and Roots of Three Trees, *INTERNATIONAL JOURNAL of RENEWABLE ENERGY RESEARCH*, Vol.5, No.1, 2015
- [5] Maabong, K, C. M. Muiva, P. Monowe, T. S. Sathiaraj, M. Hopkins, L. Nguyen, K. Malungwa and M. Thobega. Natural Pigments as Photosensitizers for Dye-Sensitized Solar Cells with TiO₂ Thin Films, *INTERNATIONAL JOURNAL of RENEWABLE ENERGY RESEARCH*, Vol.5, No.1, 2015
- [6] Cheok, C.Y, N.L. Chin, Y.A. Yusof, R.A. Talib, C.L. Law. Optimization of total monomeric anthocyanin (TMA) and total phenolic content (TPC) extractions from mangosteen (*Garcinia mangostana* Linn.) hull using ultrasonic treatments, *Industrial Crops and Products* 50 (2013) 1– 7. <http://dx.doi.org/10.1016/j.indcrop.2013.07.024>
- [7] Puspawati, G.A.K.D, PT. Ina, IM Wartini, dan IARP Pudja, Ekstraksi Komponen Bioaktif Limbah Buah Lokal Berwarna Sebagai Ekstrak Pewarna Alami Sehat, *Prosiding Seminar Nasional Hasil Penelitian Sebagai Aktualisasi Pelaksanaan Tri Dharma Perguruan Tinggi*, Inna Grand Bali Beach Sanur-Bali, 27-28 Februari 2014
- [8] R. Syafinar, N. Gomesh, M. Irwanto, M. Fareq, Y.M. Irwan, Potential of Purple Cabbage, Coffee, Blueberry and Turmeric as Nature Based Dyes for Dye Sensitized Solar Cell (DSSC) *Energy Procedia* 79 (2015) 799 – 807
- [9] Hao, S., Wu, J., Huang, Y., and Lin, J., Natural dyes as photosensitizer for dye-sensitized solar cell. *Elsevier Journal of Solar energi*, 80, 209-214, 2006..
- [10] Hemalatha, K., Karthick, S., Raj, C. J., Hong, N. Y., Kim, S. K., and Kim, H.J. Performance of *kerria japonica* and *rosa chinensis* flower dyes as sensitizers for dye-sensitized solar cells. *Elsevier Journal of Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 96, 305-309, 2012
- [11] Yusoff, A., Kumara, N.T.R.N., Lim, A., Ekanayake, P., & Tennakoon, K. U. Impacts of temperature on the stability of ropical plant pigments as sensitizers for dye sensitized solar cells. *Journal of Biophysics* Volume 2014, Article ID 739514, 8 pages <http://dx.doi.org/10.1155/2014/739514>
- [12] Zhao, D.Q., Tang, W.H., Hao, Z.J., Tao, J., Identification of Flavonoids and Expression of Flavonoid Biosynthetic Genes in Two Coloured Tree Peony Flowers. *Biochemical and Biophysical Research Communications* Volume 459, Issue 3, 10 April 2015, Pages 450-456