Efficiency enhancement of dye-sensitized solar cells (DSSC) by addition of synthetic dye into natural dye (anthocyanin)

D D Pratiwi¹, F Nurosyid¹, A Supriyanto¹ and R Suryana¹
¹Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Sebelas Maret, Jl. Ir. Sutami 36A Kentingan Jebres Surakarta 57126, Indonesia
²Department of Physics, Graduate Program, Universitas Sebelas Maret, Jl. Ir. Sutami 36A Kentingan Jebres Surakarta 57126, Indonesia

E-mail: nurosyid@yahoo.com

Abstract. This article reported combination of anthocyanin and synthetic dyes in dye-sensitized solar cells (DSSC) applications. This study aims was to improve the performance of DSSC by addition of synthetic dye into anthocyanin dye. Anthocyanin dye was extracted from red cabbage and synthetic dye was obtained from N719. We prepared anthocyanin and synthetic dyes at 2 different volume, anthocyanin dye at volume of 10 ml and combination dyes with anthocyanin and synthetic dyes at volume of 8 mL : 2 mL. The DSSCs were designed into sandwich structure on the fluorine-doped tin oxide (FTO) substrates using TiO₂ electrode, carbon electrode, anthocyanin and synthetic dyes, and redox electrolyte. The absorption wavelength of anthocyanin dye of red cabbage was 450 nm – 580 nm, the combination of anthocyanin and synthetic dyes can increase the absorbance peak only. The IPCE characteristic with anthocyanin dye of red cabbage and combination dyes resulted quantum efficiency of 0.081% and 0.092% at wavelength maximum about 430 nm. The DSSC by anthocyanin dye of red cabbage achieved a conversion efficiency of 0.024%, while the DSSC by combination dyes achieved a conversion efficiency of 0.054%, combination dyes by addition synthetic dye into anthocyanin dye enhanced the conversion efficiency up to 125%.

1. Introduction
Dye-sensitized solar cells (DSSCs) are solar cells based on dye molecules that can absorb the light and convert light energy into electricity [1,2]. The advantages of DSSCs are low cost materials, simple to fabricate, easily obtained the materials, good conversion efficiencies, and many colour design [3]. The DSSC device consists of five components: conducting glass made of transparent conducting oxide as substrate (e.g. FTO or ITO), semiconductor electrode (TiO₂, SnO₂ or ZnO), counter electrode (Pt or C), dye as photosensitizer, and electrolyte as redox mediator [4]. One of the most important components of a DSSC is photosensitizer.

The research have been developed the synthetic and natural dyes. The synthetic dyes based on Ru with metal complexes such as N3, N749, and N719 which later be achieved efficiency up to 8.2%, 10.4%, and 10.1%, respectively [5-7]. However, synthetic dyes have expensive production and basic materials cost. They also contain heavy metals which make environmental pollution. There is alternatively towards the used of natural dyes as environment friendliness photosensitizer. The natural dyes are organic materials, they can be widely available, low cost, environment friendliness, various colors modified, and studied [8]. The pigments of natural dyes are present in the various part of the plant, vegetable, fruits, flowers, and leaves. Natural pigments containing betalains, carotenoids, chlorophyll, and flavonoids have been successfully as photosensitizer in DSSCs [9]. Many researchers
have been developed in the various natural dyes. Teoli et al. in the year 2016 have been successfully extracted anthocyanin from blueberry and reported highest efficiency of 1.13% [10]. Chang et al., Taya et al., Syafinar et al., and Hasoon et al. developed the chlorophyll dye from spinach and it has given 0.016%-0.29% [11-14]. The study took extracts from Bougainvillea flowers and carotenoid pigments from Sponge gourd reporting conversion efficiency of 0.325% and 0.13% [5,16]. Chang et al. used chlorophyll dye from wormwood and anthocyanin dye from purple cabbage as natural dyes, the conversion efficiency of DSSCs were 0.54% and 0.75%, respectively and then after mixing the extracted wormwood chlorophyll and purple cabbage anthocyanin at volume ratio of 1:1, the conversion efficiency of DSSC was increased to 1.47% [17]. This result can be explained that it has widening of visible light absorption range, thus increasing the excitation of electrons were transmitted to TiO$_2$ semiconductor to enhance the photocurrent of DSSC. The novelty of this research is to improve the performance of natural dye with addition of synthetic dye, so that the good performance and low-cost DSSCs were obtained. The natural dye used red cabbage anthocyanin and synthetic dye was obtained from ruthenium complex N719. The addition of synthetic dye aims was to increase the efficiency of natural dye. The function of dye absorbed the light energy to produce excitation of electrons [18]. Selection of dye in DSSC plays vital role in improving the absorption of photons, so that the great efficiency was obtained.

2. Experimental

The dyes used by this study was extracted from red cabbage anthocyanin, while synthetic dye was obtained from ruthenium complex N719, fluorine-doped tin oxide (FTO) from Dyesol as substrate, the semiconductor layer from TiO$_2$ powder 21 nm as working electrode, carbon layer as counter electrode, the solution of PEG 400, potassium iodide, and iodine as redox electrolyte.

The working electrodes with TiO$_2$ paste were coated by spin coating. This study used UV-Visible Spectrophotometer Lambda 25 to measure the absorption spectra of dyes solution, incident photon-to-current efficiency (IPCE) Measurement System QEX7 Serial #150 to measure the quantum efficiency versus wavelength of DSSCs, and Keithley I-V Meter 2602A to measure the photoelectric conversion efficiencies.

Red cabbage was cut into small pieces and added them in solvents of distilled water, methanol, and acetic acid. It was kept for 24 hours. The extract of red cabbage anthocyanin dye solution was filtered using filter paper. The absorption spectra of anthocyanin dye solution was characterized by using UV-Vis spectrophotometer. An active area of 2 cm$^2$ FTO conductive glass was deposited with TiO$_2$ paste using spin coating technique. The TiO$_2$ films were annealed at 400ºC for 10 minutes. The TiO$_2$ films were soaked for 24 hours in solution containing the anthocyanin dye of red cabbage at volume of 10 ml and combination dyes with anthocyanin and synthetic dyes (N719) at volume of 8 ml : 2 ml.

The counter electrodes were prepared from carbon catalyst. Fabrication of DSSCs were arranged into a sandwich structure. Electrolyte solution was injected into the cell. The DSSCs were measured using incident photon-to-current efficiency (IPCE) and I-V Meter.

3. Results and Discussion

3.1. Absorption spectra of dyes solutions

The absorption spectra in Figure 1 shows the UV-Visible result of synthetic dye (N719) solution at wavelength in the range of 500 nm – 600 nm. The absorption wavelength anthocyanin dye of red cabbage was 450 nm – 580 nm at wavelength maximum about 530 nm. The curve by Figure 1 known that red cabbage evidently has absorbance in the visible light zone, so it can be used as photosensitizer for DSSC, but it has absorbance lower than the absorbance of synthetic dye (N719).

The UV-Visible result of anthocyanin dye of red cabbage with addition of 2 ml synthetic dye (N719) was not show the expansion visible light absorption range, but it can increase the absorbance peak only at wavelength maximum about 530 nm. This result showed that synthetic dye contributed to enhancement the absorbance peak of anthocyanin dye of red cabbage.
3.2. **IPCE Characterization Results**

**Figure 1.** Absorption spectra of anthocyanin dye, combination of anthocyanin and synthetic dyes, and synthetic dye solutions

**Figure 2.** IPCE spectrum of DSSCs with anthocyanin dye and combination of anthocyanin and synthetic dyes
The IPCE spectrum by Figure 2 showed that quantum efficiency value of anthocyanin dye with addition of 2 ml synthetic dye (N719) increase quantum efficiency at wavelength about 430 nm. The absorption of photons occurred optimally of absorption wavelength in the range of 400 nm – 450 nm at wavelength maximum about 430 nm. This result shows the contribution of photons to the dye yielded high energy and photocurrent. The IPCE spectrum showed the decrease in the visible light zone, thus the absorption of photons appear to be decreasing. The reason is that the adsorptions of dyes on the TiO2 surface were relatively small because the absorption abilities of dyes were not too dominant [19]. The decrease of absorbance can also happen because great enhancement in the exciton recombination, so that the electrons excitation would be slightly and electrons transfer from dye into the conduction band of semiconductor was not work effectively. The dye can be considered as a negative contributor (contributed the only slightly) to the overall of photocurrent when irradiated in the visible light zone. [20].

3.3. Current – Voltage (I-V) Characterization Results

![Current-voltage curves for the DSSCs by anthocyanin dye and combination of anthocyanin and synthetic dyes](image)

**Figure 3.** Current-voltage curves for the DSSCs by anthocyanin dye and combination of anthocyanin and synthetic dyes

The I-V curves of the DSSCs based on anthocyanin and combination dyes are shown in Fig.3 and their photoelectrical parameters are listed in Table 1:
Table 1. Photoelectrical parameters of DSSCs by anthocyanin dye and combination of anthocyanin and N719 dyes

| Red cabbage : N719 | $I_{\text{max}}$ (mA) | $V_{\text{max}}$ (V) | $I_{\text{sc}}$ (mA) | $V_{\text{oc}}$ (V) | FF | $\eta$ (%) |
|-------------------|----------------------|---------------------|---------------------|------------------|----|-----------|
| 10 ml : 0 ml      | 0.17                 | 0.28                | 0.23                | 0.34             | 0.63 | 0.024     |
| 8 ml : 2 ml       | 0.35                 | 0.31                | 0.49                | 0.43             | 0.51 | 0.054     |

The conversion efficiency of DSSC by combination dyes at volume of 8 ml : 2 ml can achieve better conversion efficiency. This result was comparable with quantum efficiency by IPCE curve in Fig.2. The quantum efficiency was higher, then the conversion efficiency of DSSC was also higher.

As known from the photoelectrical parameters results shown in Table 1, open-circuit voltage ($V_{\text{oc}}$), short-circuit current ($I_{\text{sc}}$), and conversion efficiency by the combination dyes at volume of 8 ml : 2 ml has the better performance than the volume of 10 ml : 0 ml. The reason for this result was that the combination dyes with red cabbage anthocyanin and synthetic (N719) dyes at volume of 8 ml : 2 ml can increase light absorption. The higher light absorption can absorb the greater photons, thus the electrons in excited state were also increased to enhance the measured photocurrent. The DSSC with combination of synthetic (N719) and natural dyes was obtained the photocurrent increased. The photocurrent was increased, so that the conversion efficiency of DSSC by addition of 2 ml synthetic dye into red cabbage anthocyanin can increase the efficiency up to 125%. Composition variations of dyes can increase the efficiency of natural dye, as a result the low cost DSSCs were obtained.

4. Conclusion

In conclusion, the results showed that the absorption wavelength of anthocyanin dye of red cabbage was 450 nm – 580 nm, while the combination of red cabbage anthocyanin and synthetic dyes can increase the absorbance peak only. The IPCE characteristic with anthocyanin dye of red cabbage and combination of anthocyanin and synthetic dyes resulted quantum efficiency of 0.081% and 0.092% at wavelength maximum about 430 nm and they contributed in the highest current formation of absorption wavelength in the range of 400 nm – 450 nm. The I-V characteristic with anthocyanin dye of red cabbage anthocyanin and combination of anthocyanin and synthetic dyes resulted efficiency of 0.024% and 0.054%, the DSSC efficiency by addition synthetic dye into anthocyanin dye significantly enhanced the conversion efficiency up to 125%.

Acknowledgment

This work is supported by Directorate of Research and Community services, Ministry of Research, Technology, and Higher Education and Institute for Research and Community services, Sebelas Maret University by PUPT Grant Program. (Contracts Number : 353/UN27.21/PN/2016)

References

[1] Grätzel M 2003 J.Photochems. Photobio 4 145-153
[2] Grätzel M 2005 Inorg. Chem. 44 6841-6851
[3] Dodoo-Arhin D, Howe RCT, Hu G, Zhang Y, Hiralal P, Bello A, Amaraturega G and Hasan T 2016 Elsevier Ltd. 105 2016 33-41
[4] Sharma S, Jain KK, and Sharma A 2015 Mater. Sci. Appl. 6 1145-1155
[5] Nazeeruddin MK, Zakeeruddin SM, Humpry-Baker R, Jirousek M, Liska P, Vlachopoulos N, Shklover V, Fischer C-H, and Grätzel M 1999 Inorg. Chem. 38 6298-6305
[6] Nazeeruddin MK, Spilvallo R, Liska P, Comte P, Grätzel M 2003. Chem. Commun. 9 12 1456
[7] Robertson N 2006 Angew. Chem.Int. Ed. 45 15 2338–2345
[8] Bose S, Soni V, and Genwa KR 2015 Int.J.Scientific and Research Publications. 5 4 2250-3153
[9] Bhogaita M, Shukla AD, and Nalini RP 2016 Sol. Energy. 137 2016 212-224
[10] Teoli F, Lucioli S, Nota P, Frattarelli A, Matteocci F, Di Carlo A, Caboni E, and Forni C 2016
[11] Chang H, Lo Y-J 2010 Sol. Energy. 84 1833–1837
[12] Taya SA, El-Agez TM, El-Ghamri HS, and Abdel-Latif MS 2013 Int.J.Mater.Sci.Appl. 2 37–42
[13] Syafinar R, Gomesh N, Irwanto M, Fareq M, and Irwan YM 2015 Energy.Procedia.Elsevier B.V. 11 584
[14] Hasoon S, Al-haddad RMS, Shakir OT, and Ibrahim IM 2015 Int.J.Sci.Eng.Res. 6 2229–5518
[15] Godibo DJ, Anshebo ST, and Anshebo TY 2015 J.Braz.Chem.Soc. 26 92–101
[16] Maurya IC, Srivastava P, and Bahadur L 2016 Opt.Mater.(Amst.). 52 150–156
[17] Chang H, Kao M, Chen T, Chen C, Cho K, and Lai X 2013 J.Photoenergy. 2013 8
[18] Chiba Y, Islam A, Watanab Y, Komiya R, Koide N, and Han L 2006 Japanese.J.Appl.Phys. 45 1638–1640
[19] Hoffmann MR, Martin ST, Choi W, and Bahnemann DW 1995 Chem.Rev. 95 69-96
[20] Brennan LJ, Milton FP, Salmeron AS, Zhang H, Govorov AO, Fedorov AV, and Gun’ko YK 2015 Nanoscale Research Letters. DOI 10.1186/s11671-014-0710-5