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Integration of photosystem I and photosystem II from tylakoid membrane of *spirulina sp*. for DSSC natural dye pigments

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Abstract. Conversion of sunlight to electron within pigment-protein complex of Photosistem I (PS I) and Photosystem II (PS II) in kloroplast's tylakoid membrane is the hearth of photosynthesis process. This process is very efficient with nearly 100% quantum efficiency. In this paper, we demonstrate the integration of PS I and PS II pigment-protein complex extracted from spirulina sp, as the natural dye for DSSC structure. The PS I and PS II was obtained by ultrasonic cell rupture followed by staggered sequential centrifugation at various g-force level to separate the tylakoid protein complex from other cell components. Contrary to typical DSSC using inorganic dyes which requires elaborate surface treatment, expensive, and employing hazardous dyes, the devices described here are straightforward and inexpensive to fabricate. The device also perform well on photovoltaic activity yielding open circuit voltage of 0.20 V, short-circuit current density of 7.60 μA, and fill factor of 35% at 1 mW/cm^2 incandescence lamp illumination.

1. Introduction

The energy profile of Indonesia is currently dominated by the use of oil. With current oil reserves and production rate it is predicted that oil would last for 9 years [1]. Similarly, the other fossil fuel of natural gas and coal would burnt out in the next 40 and 70 years respectively. This condition has prompted the government to advocate the exploration of renewable energy as the alternative energy source of the future. Located within the equator with ample sunlight all the year, Indonesia has the solar energy potential of 9,286 Mwatt. Besides, Indonesia's location along the "ring-of-fire" provides other forms of renewable energy potentials, including the biomass, wind energy, hydroenergy, and geothermal energy awaiting explorations.

Despite the various policies favoring clean energy use, to date solar energy only contributes a tiny share of Indonesia's electricity generation of less than 0.06% [1]. The relatively high cost of silicon-based solar technology has been a major impediment to the widespread implementation. On the other hand, organic solar cell, with potential to reduce the material and process costs, suffers from inferior power conversion efficiency and shorter lifetime due to degradation. Improving the efficiency of organic solar cell to the level of silicon-based module will drive down the cost of solar technology.

Recently, the implementation of engineered photosynthetic processes and their integration into opto-electronic devices have became one of the main objective in organic solar cell research. Photosynthetic in green plant and bacteria is widely accepted as one of the most efficient energy harvesting process in nature with quantum efficiency nearly 100%. The highly efficient process relies on the seamless organization of light-harvesting pigments, protein complexes and molecular

functional groups held in precise geometries, wherein the molecular electronic states are intricately arranged to enable the unidirectional flow of charges [2].

2. Literature Review

Early work on bioinspired optoelectronics system employed photosynthetic pigment as active materials in metal-chlorophyll-metal devices [3-5]. However, the device showed rather unsatisfactory performance with efficiency below 0.5%. The absence of charge acceptor moieties within the active layer was caused this low performance. The subsequent improvement on device performance was realized when n-type or p-type semiconductor material [6-7] was introduced along with chlorophyll. A modest power conversion efficiency of 2.3% is achieved when chlorophyll mixed with C70 [7]. In all of these studies the researcher failed to perceive photosynthesis as a whole interconnected system, which resulted in a modest efficiency of the system. In the natural setting of photosynthesis, light is absorbed by the antenna complex of Photosystem II (PSII) to be funneled to the photosynthesis reaction center P680. PSII antenna consists of protein-embedded chlorophyll to absorb light and carotenoids to quench excess radiation energy. The funneled energy excites the electron of P680 into an excited P680* state. The process is quickly followed by electron transfer from P680* (formed P680+) to the primary electron acceptor pheophytin, quinone molecules Q_A-Q_B, and plastoquinone to cytochrome b6f protein complex. Subsequently the charge is transferred by phthalocyanine to P700 reaction center of Photosystem I (PSI) and then ferredoxin for ATP generation. The redox process is completed when P680+ regains electron from splitting of water molecules into oxygen and protons [1].

Most recently, the biomimetic strategy has been borrowed from photosynthetic organisms utilizing the whole photosynthetic pigments and proteins to be incorporated into DSSC and photoelectrochemical devices [8-13]. Thereby, the high efficiency of the photosynthesis might be retained in the artificial devices. Adding xanthophyll to chlorophyll cosensitizer is shown to improve the efficiency by 1.5 to 2 times the efficiency of DSSC with individual dye [8]. Similarly, by using ubiquinone 10 in place of I^-/I_3^- electrolyte to mimic thephotosynthetic process, an increase of 10% in efficiency can be realized [9]. Further, by employing bacterial photosynthesis reaction center (RC)-light harvesting core complex (LH 1) immobilized onto the Gold electrode as photosensitizer, a relatively high photocurrent of 7.1 μA/cm2 had been achieved in a bio-photo-electro-chemical cell structure [10]. An improvement in photocurrent up to 10 μA/cm^2 was obtained when the protein was suspended into the supported lipid bilayer [11]. Further, the highest photocurrent response of 45 μA/cm^2 is obtained when the protein complex was densely packed via Langmuir film deposition [12]. In our previous publication, it is shown that the photocurrent can be improved further to 300 μA/cm^2 by using alfalfa leaves chlorophyl pigment-protein complexes [13]. In all of these works, it is evident that utilizing the whole sets of photosynthetic pigment-protein complexes improves the DSSC performance significantly. Herein, we demonstrated a DSSC device with positive photocurrent responses. The natural dyes was attained from thylakoid membrane pigment-protein complexes which retained the photosystem I (PS I) and photosystem II (PS II) of photosynthetic pigment-protein complexes. V_{OC} of 0.13 V and I_{SC} of 0.35 μA were achieved under 3 mW/cm^2 incandescence radiation power. The devices showed stable photocurrent responses without significant reduction in performance under continuous cycling test.

3. Method

3.1. Purification of spirulina sp. pigment-protein complexes

Freshwater *spirulina sp*. was obtained from Neoalgae Technology in Sukoharjo, Central Java in the form of wet pellet, freshly harvested on the 5th day of growth stage. The wet pellet is initially rinsed with distilled water three times and then resuspended in membrane isolation buffer (MIB), made from mixture of Tris-HCl, $MgCl_2$, $NaHCO_3$, EDTA, sucrose, and β-merkaptoethanol prepared in accordance with previously reported method [14]. Ultrasonic cell disruptor (Qsonica 125) is used to break the algae cell at 72 Watt power output, in a pulse mode of 5 s ON followed by 5 s OFF for 30

minutes. The ultrasonic process is performed at ice bath of 4 C to minimize damage to the protein complexes. Thie dye is termed "sonic". The resulting suspension is then centrifuged at 10,000 rpm for 10 minutes to remove the unbroken *spirulina sp*. cell as well as large cell debris. The dyes obtained from this process is termed "p10k" and "s10k". The supernatant solution is then re-centrifuged at 14,000 rpm for 10 minutes to remove the small cell debris and large organels. The dyes obtained from this final process is termed "p14k" and "s14k".

3.2. Fabrication of DSSC devices

A 10 mm x 10 mm DSSC devices were fabricated on patterned ITO electrode (Latech Scientific). The TiO_2 photoelectrode was made by pasting mixture of TiO_2 (SigmaAldrich) powder with ethanol by using doctor's blade technique. The photoelectrode was then sintered at 500 ^oC for 30 minutes in air. The thickness of TiO_2 film is approximately 8 µm. Further, the TiO_2 photoelectrodes were immersed in 0.5 mM thylakoid membrane solution for 24 h at room temperature and rinsed with ethanol and distilled water.

3.3. Characterization of the DSSC

Spectrophotometric characterization was performed by using OceanOptic RedTide USB650 and USB650UV on suspended solution. Film thickness was estimated by Swanopoel's emvelope method, while the optical bandgap value was exracted from the transmittance spectra by using Tauc's plot [15]. Current-Voltage measurement and DSSC characterization was performed by using Keithley SMU2430 on 100 W incandescent lamp supplying power input of 1 mW/cm^2 for the solar cell device.

4. Result and Discussion

Figure 1 (a) shows the DSSC device structure consisting of ITO anode, TiO_2 photoelectrode sensitized with various thylakoid membrane dyes, I^-/I_3^- electrolyte and Al counter electrode as cathode. Figure 1 (b) depicts the energy level diagram of the DSSC charge transfer systems. The sunlight radiation excites electrons from PS I/PS II dyes which are then transferred to TiO_2 photoelectrode towards the ITO anode. To compensate the excited electrons, the Al cathode supplies the electrons via the I^-/I_3^- redox couple electrolyte. Figure 1 (c) shows the photograph of the DSSC device prior dye immersion, after dye sensitized, and completed DSSC devices for I-V characterization

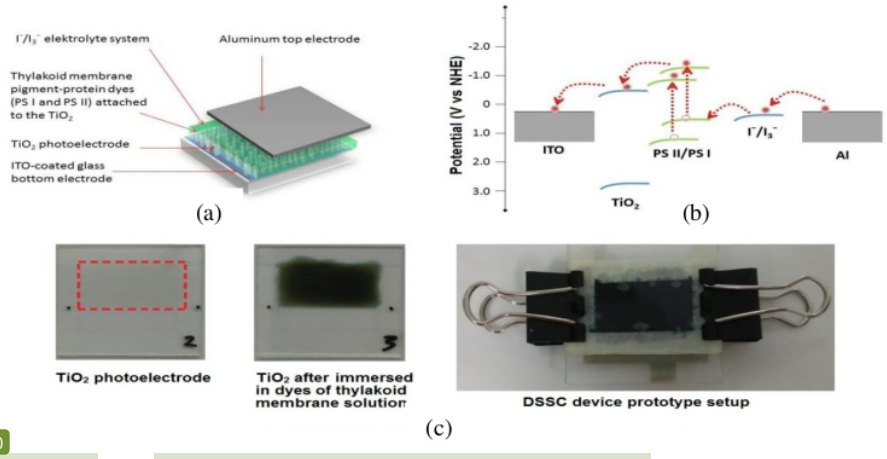
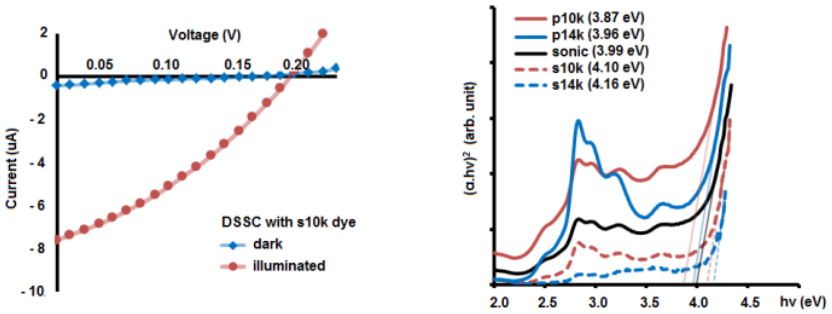


Figure 1. (a) The device structure and (b) energy band diagram of the DSSC devices with various thylakoid membrane protein dyes. (c) Photograph of the actual DSSC devices studied in this work.

Preliminary I-V characterization of the DSSC devices shows clear indication of photocurrent responses where the devices respond differently during dark and illuminated states. Figure 2 (a) shows

I-V characterization results of DSSC devices with various dyes from thylakoid membrane fractions. All of the devices show clear photovoltaic behavior with characteristic diode curve with open circuit voltage (V_{OC}) ranges from 0.20 v to 0.40 V and short circuit current (I_{SC}) ranges from 0.003 µA to 7.6 µA. The DSSC device with as sonicated thylakoid membrane protein dye shows largest V_{OC} at 0.40 V, but it has relatively low I_{SC} at 0.73 µA. The photocurrent values improved with centrifugation of the thylakoid membrane protein dyes. Centrifugation at 10,000 rpm seems to improve the photocurrent significantly, with highest I_{SC} at 7.6 µA is achieved in DSSC using s10k dye and I_{SC} of 0.76 µA is achieved for p10k dye. Further centrifugation at 14,000 rpm resulting in dyes with lower performance at I_{SC} of 0.31 µA and 0.003 µA for s14k and p14k respectively.

In terms of photovoltaic performance, the sonic dye has the highest V_{OC} of 0.40 V. The photovoltaic decreases to 0.38 V and 0.20 V for p10k and s10k dyes respectively. Further centrifugation of the dyes lower the VOC to 0.28 V and 0.20 V for p14k and s14k respectively. To have further understanding on the qualitative presence of PS I/PS II pigment-protein complexes in the samples, the optical bandgap of all samples is extrapotated by using Tauc's plot method. Figure 2 (b) shows the $(\alpha hv)^2$ vs hv plot of all samples. It can be seen that the optical bandgap of supernatant samples are unambiguously extrapolated at around 4.0 – 4.1 eV from a sharp plot. On the other hand, the optical bandgap of pellet samples are weakly extrapolated at slightly lower energy bandgap at 3.8–3.9 eV. The UV band absorption from the thylakoid membrane protein is likely due to absorption by Mn complex or Quinone in the intact PS I and PS II pigment-protein complexes [16], therefore this results suggesting that less PS I/PS II are present in the pellet samples compared to the supernatant samples.



(a) (b)

Figure 2. (a) I-V curve charaterization of DSSC sample with p10k dye extracted from *spirulina sp* and (b) the $(\alpha hv)^2$ vs *hv* plot of various dyes extracted from thylakoid membrane of *spirulina sp*.

Table 1 summarizes the photovoltaic characterization results of all samples irradiated with 1 mW/cm^2 equivalent irradiance. From the preliminary results, it can be deducted that the V_{OC} of the samples generally stable at 0.20 to 0.38 V. Whereas the I_{SC} for supernatant films are generally higher than the pellet films, with the highest I_{SC} achieved is 7.60 µA for s10k sample. This observation can be explained as the PS I/PS II pigment-protein complexes which generally weighed in the range of ~100s kDa are likely to stay in the supernatant fraction when centrifuged at 10,000 rpm.

Table 1. Characterization Results of DSSC devices with various dye combination.

Sample name	Type of dyes	V_{OC} (V)	I_{SC} (μA)	FF
Sonic	Ultrasonicated *spirulina sp.*	0.40	0.73	0.21
p10k	Pellet 10,000 rpm	0.38	1.24	0.43
s10k	Supernatant 10,000 rpm	0.20	7.60	0.35
p14k	Pellet 14,000 rpm	0.28	0.003	0.26
s14k	Supernatant 14,000 rpm	0.20	0.31	0.23

The results obtained from optical band gap analysis are corroborated the I-V characterization results of the DSSC devices measured by using I-V characterization. Therefore it can be concluded that the higher the PS I/PS II presence in the active materials is likely to enhance the photocurrent output of the solid state organic solar cell devices.

5. Conclusion

Construction and characterization of DSSC devices with thylakoid membrane pigment-protein complexes have been demonstrated. The use of organic dyes from thylakoid membrane is shown to effectively convert sunlight into electrical energy. Preliminary characterization of the solid state organic photovoltaic devices exhibit modest Isc of 7.60 μA/cm^2, V_{OC} of 0.20 Volt, and Fill Factor 0.35 when lluminated under the 1 mW/cm^2 incandescent radiation. The photocurrent response is unambiguously originated from the presence of PS I/PS II pigment protein complexes in the active materials. The higher the PS I/PS II content within the active materials enhance the photocurrent response of the devices. This encouraging result implies that incorporating the whole photosynthetic pigment-protein complex could enhance the performance of organic solar cell significantly.

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References

[1] National Energy Council 2019 *Energy Outlook Indonesia 2019* (Jakarta: Ministry of Energy and Mineral Resouces)
[2] Blankenship R E. 2002 *Molecular Mechanisms of Photosynthesis* (Hoboken, NJ: Blackwell Science)
[3] Tang C W, Albrecht A C 1975 *J Chem Phys* **63** (2) 2139-2142
[4] Segui J, Hotchandani S, Baddou D, Leblanc RM 1991 *J Phys Chem* **95** (22) 8807-8812
[5] Farag A A M 2009 *Appl. Surface Sci.* **255** (9) 4938-4943
[6] Yun J J, Jung H S, Kim S H, Han E M 2005 *Appl Phys Lett* **87** (12) 123102
[7] Wang Y W, Sasaki S, Zhuang T, Tamiaki H, Zhang J P, Ikeuchi T, Hong Z, Kido J, Wang X F 2013 *Org. Electron* **14** (8) 1972-1979
[8] Lim A, Manaf NH, Tennakoon K, Chandrakanthi RLN, Lim LBL, Sarath Bandara JMR, Ekanayake P 2015 *Journal of Biophysics* **2015** 510467
[9] Yu Z, You S, Wang C, Bu C, Bai S, Zhou Z, Tai Q, Liu W, Guo S, Zhao X 2014 *J Mater Chem A* **24** (2) 9007-9010
[10] Yaghoubi H, Lafalce E, Jun D, Jiang X, Beatty J T, Takshi A 2015 *Biomacromol* **16** (4) 1112-1118
[11] Gebert J, Reiner-Rozman C, Steininger C, Nedelkovski V, Nowak C, Wraight, C A, Naumann R L C 2015 *J Phys Chem C* **119** (2) 890-895
[12] Kamran M, Delgado J D, Friebe V, Aartsma T J, Frese R N 2014 *Biomacromol* **15** (8) 2833-2838

[13] Kusuma D Y, Soetedjo H 2017 *Journal of Neutrino*, **9** (2) 26-31
[14] Goss R, Greifenhagen A, Bergner J, Volke D, Hoffmann R, Wilhelm C, Schaller-Laudel S 2017 *Planta*, **245** (4) 793-806
[15] Caffarri S, Tibiletti T, Jennings R C, Santabarbara S 2014 *Curr Protein Pept Sci* **15** (4) 296-331
[16] Vass I, Szilard A, Sicora C 2005 43 *Adverse Effects of UV-B light on the Structure and Function of the Photosynthetic Apparatus* Handbook of Photosynthesis, (London: Taylor and Francis

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