Solid state organic photovoltaic devices using *spirulina* sp thylakoid membrane films as active material

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Abstract. Efficient light-to-energy conversion in Photosynthesis proceeds with quantum efficiency near unity. However, solar cell devices which incorporates chlorophyll such as DSSC generally requires elaborate fabrication process and complex device structure with liquid electrolyte. In this work, a solid state organic solar cell device is presented. The device employs simple structure of ITO/Thylakoid membrane/Al layer in a solid state structure without require liquid electrolyte. As the active materials, Thylakoid membrane layer contains the whole photosynthetic pigment-protein complexes including Photosystem I and Photosystem II. Preliminary characterization of the solid state organic photovoltaic devices exhibits modest *I*_SC of 0.44 μA, *V*_OC of 0.17 V, and Fill Factor of 0.250 when illuminated under the 1 mW/cm² incandescent radiation power. Plot of *(αhν)* against the *(hν)* for thylakoid membrane active materials reveals major optical band-gap values of 4.0–4.1 eV which corresponds to the absorption from the PS I and PS II light harvesting complexes. This encouraging result implies that incorporating the whole photosynthetic pigment-protein complex can enhance the performance of organic solar cell significantly.

1. Introduction

Since its conception in 1991 by O’Regan and Gratzel [1], the Dye-Sensitized Solar Cell (DSSC) has gained tremendous interest due to its economical base materials and simple solution-processing advantages. Typical simple DSSC device can be constructed from Indium-doped Tin Oxide/Fluorine-doped Tin Oxide (ITO/FTO)-coated glass and Titanium dioxide (TiO₂) photoelectrode. TiO₂ compounds are commonly used as pigments in wall paints, sunscreens, toothpaste, sensors and memory devices. Ruthenium (Ru) dyes coupled onto inorganic molecules are currently the most efficient dyes for DSSC with efficiency ranging from 8% to 14% [2]. However Ru is not abundant in nature and are very expensive. In the quest of achieving more economical DSSC devices, natural pigments such as chlorophyll [3], carotenoids [4], anthocyanin [5] or xanthophyl [6] are incorporated into the dyes. Furthermore, there are growing interest on engineered photosynthetic processes and their integration into the photovoltaic devices rather than using simple molecular dyes. Most recently, the biomimetic strategy has been borrowed from photosynthetic organisms utilizing the whole photosynthetic pigments and proteins to be incorporated into the man-made photocurrent devices [7-10]. By employing bacterial photosynthesis reaction center (RC)-light harvesting core complex (LHC) immobilized onto the Gold electrode, a relatively high photocurrent of 7.1 μA/cm² had been achieved in a bio-photo-electro-chemical cell structure [7]. An improvement in photocurrent up to 10 μA/cm² was obtained when the protein was suspended into the supported lipid bilayer [8]. The highest photocurrent response of 45 μA/cm² is obtained when the protein complex was densely packed via...
Langmuir film deposition [9]. Most of these works were conducted in a DSSC devices which required electrolyte solution and must be confined and sealed. Up to now, only few works reported the solid-state bio-photovoltaic device albeit the inferior device performance [10-11].

The DSSC structure uses transparent conductive electrode to collect charges while allowing sunlight to pass through. The most used transparent conducting electrode are Fluorine-doped Tin Oxide (FTO) and Indium-doped Tin Oxide (ITO). On top of the transparent conducting electrode, a dye-photoelectrode semiconductor system, usually organic or inorganic dyes immobilized onto TiO$_2$ or ZnO photoelectrode is employed. The dye molecule absorbs sunlight radiation and transfers its electrons to the photoelectrode and transparent conducting electrode respectively. To balance the charges, a counter electrode (usually platinum or graphite thin film) supplies the electrons back to the dye molecules via liquid electrolyte system, the most commonly is used aqueous I$^-$/I$_3^-$ electrolyte system. One major problem for DSSC is on the device lifetime due to the use of liquid electrolyte, which is prone to leakage or chemical decomposition.

Herein, we demonstrated a solid state organic photovoltaic devices with promising photovoltaic responses. The device employs simple structure of ITO/Thylakoid membrane/Al layer in a solid state structure without requiring liquid electrolyte. Thylakoid membrane photosynthetic pigment-protein complexes including Photosystem I (PS I) and Photosystem II (PS II) is employed as active materials. Preliminary characterization of the solid state organic photovoltaic devices exhibit modest $I_{SC}$ of 44.5 uA/cm$^2$, $V_{OC}$ of 0.13 V, and Fill Factor of 0.301 when illuminated under the 3 mW/cm$^2$ incandescent radiation power. The optical bandgap for thylakoid membrane shows major absorption at 3.2 eV which corresponds to the absorption from the pigment-protein light harvesting complexes.

2. Materials and Method

2.1 Isolation of spirulina sp. pigment-protein complexes
Saltwater spirulina sp. was obtained from Nogotirto Algae Park in Gamping, Sleman, D.I. Yogyakarta 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-merkaptopethanol prepared in accordance with previously reported method [12]. 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 oC to minimize damage to the protein complexes. This 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 form this process are termed “p10” and “s10”. 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 are termed “p14k” and “s14k”

2.2 Fabrication of Solid State Organic Solar Cell devices
Solid state organic solar cell device was fabricated with the ITO/Thylakoid membrane protein/Al structure. Thylakoid membrane pigment-protein complexes was dropcasted onto ITO-coated glass substrate (Latech Scientific) and are allowed to dry at room temperature. Thickness measurement of the active material reveals the film thickness in the range of 8-10 μm. Finally metallic Al electrode was deposited on top of the active layer by using Vacuum Evaporator.

2.3 Characterization of the Organic Solar Cell device
Spectrophotometric characterization was performed by using OceanOptic RedTide USB650 and USB650UV on suspended solution. The optical bandgap value was extracted from the absorbance spectra by using Tauc’s plot [13]. 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.
3. Result and Discussion

Figure 1 (a) shows the device structure of the Solid State Organic Solar Cell (SSO) device incorporating pigment-protein complexes as active material. The SSO devices shows simple structure of Metal-Insulator-Metal (MIM) sandwich structure without the need of electrolyte. Figure 1 (b) shows the energy level diagram of the photovoltaic devices. Sunlight radiation excite charges in PS I and PS II from its HOMO to LUMO states. The excited state is then separated into electron-hole pairs, where the electron is transferred to the ITO transparent conducting electrode as anode. The lost charge is then replenished by the Aluminum electrode as the cathode. Prior to device fabrication, the active material of thylakoid membrane pigment-protein complexes from spirulina sp. is optically characterized by using UV-Vis spectrophotometer. Figure 1 (c) summarized the absorption spectra of all samples. The absorption band at 436 nm and 670 nm is indicative of chlorophyll, both free molecule forms and pigment-protein binded form. The broad absorption band at ~600 nm is characteristics of carotenoid and xanthophyl. The UV absorption at 256 nm and 275 nm is specific to the antenna complex of PS I and PS II [14]. From Figure 3 (c), it is clearly seen that the supernatant samples of s10k and s14k contain more carotenoid and xantophyll than chlorophyll as deducted from the ratio of absorption band at 436/670 nm compared to ~600 nm. On the other hand, the pellet samples of p10k and p14k contains more chlorophyll than carotenoid. In all samples, the absorption band of 256 nm and 276 nm indicates that intact PS I and PS II pigment-protein complexes are presents in both pellet and supernatant samples. Preliminary characterization of Solid State Organic Solar Cell device is performed with satisfactory results. Figure 1 (d) shows the typical I-V curve of the devices during dark and illuminated states, indicating that the photovoltaic activity is clearly present in all samples.

![Figure 1](image)

**Figure 1.** (a) The device structure and (b) energy band diagram of Solid State Organic Solar Cell devices. (c) Absorption spectrum of various active layer samples from thylakoid membrane of spirulina sp. (d) Typical I-V curve results of the device under 1 mW/cm² incandescent illumination.

Table 1. summarizes the preliminary I-V characterizations of all samples under 1 mW/cm² incandescent illumination. From the preliminary results, it can be concluded that the open circuit
voltage ($V_{OC}$) of the samples generally stable at 0.13 to 0.17 V, except for p10k sample which is relatively low at 0.06 V. Whereas the short circuit current ($I_{SC}$) for supernatant films are generally higher than the pellet films, with the highest $I_{SC}$ achieved is 0.44 μA for s14k sample. This observation can be explained as the PS I/PS II pigment-protein complexes are likely to stay in the supernatant fraction when centrifuged at 14,000 rpm. Generally, The PS I and PS II pigment-protein complexes are weighed in the range of ~100s kDa.

| Sample name | Active Materials Layer | $V_{OC}$ (V) | $I_{SC}$ (μA) | FF |
|-------------|------------------------|--------------|---------------|----|
| Sonic       | Ultrasonicated spirulina sp. | 0.17         | 0.16          | 0.21 |
| p10k        | Pellet, centrifuged at 10,000 rpm | 0.06         | 0.12          | 0.24 |
| s10k        | Supernatant, centrifuged at 10,000 rpm | 0.15         | 0.29          | 0.24 |
| p14k        | Pellet, centrifuged at 14,000 rpm | 0.16         | 0.26          | 0.25 |
| s14k        | Supernatant, centrifuged at 14,000 rpm | 0.13         | 0.44          | 0.24 |

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 extrapolated by using Tauc’s plot method. Figure 2 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 3.5–3.6 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 [15]. Therefore, this results suggests that less PS I/PS II are present in the pellet samples compared to the supernatant samples.

**Figure 2.** $(\alpha hv)^2$ vs $hv$ plot of various active materials layer of: (a) sonicated sample, (b) pellet 14,000 rpm sample, (c) pellet 10,000 rpm sample, (d) supernatant 14,000 rpm sample, and (e) supernatant 10,000 rpm sample.

The results obtained from optical band gap analysis are corroborated the I-V characterization results of the solid state organic solar cell 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.

4. Conclusion
Construction and characterization of solid state organic solar cell devices have been demonstrated. The use of active material from thylakoid membrane is shown to effectively convert sunlight into electrical energy. Preliminary characterization of the solid state organic photovoltaic devices exhibit modest $I_{sc}$ of 0.44 μA/cm$^2$, $V_{oc}$ of 0.13 Volt, and Fill Factor 0.24 when illuminated under the 1 mW/cm$^2$ incandescent radiation. The unambiguous photocurrent response originates 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 enhances the photocurrent response of the devices. This encouraging result implies that incorporating the whole photosynthetic pigment-protein complex can enhance the performance of organic solar cell significantly.

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