Effect of composition of chlorophyll and ruthenium dyes mixture (hybrid) on the dye-sensitized solar cell performance

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Abstract. The fabrication of dye-sensitized solar cell (DSSC) has been conducted by varying the composition of natural dye from moss chlorophyll (Bryophyte) and synthesis dye from ruthenium complex N719. The sandwich structure of DSSC consists of the working electrode using TiO₂, dye, electrolyte, and counter electrode using carbon. The composition of chlorophyll and synthesis dyes mixture were 100% and 0%, 80% and 20%, 60% and 40%, 40% and 60%, and 20% and 80%. The UV-Vis absorption spectra of moss chlorophyll showed the first peak in the wavelength range of 450-500 nm and the second peak at wavelength of 650-700 nm. The peak value of absorbance at wavelengths of 450-500 nm was 6.1004 and at wavelengths of 650-700 nm was 3.5835. The IPCE characteristic curves showed the absorption peak of photon for DSSCs occurred at wavelength of 550-650 nm. It considered that photon in this wavelength can contribute dominantly to produce the optimum electrons. The I-V characteristics of DSSCs with composition of chlorophyll and synthesis dyes mixture of 100% and 0%, 80% and 20%, 60% and 40%, 40% and 60%, and 20% and 80% resulted the efficiency of 0.0022; 0.0194; 0.0239; 0.0342; and 0.0414, respectively. It suggested that the addition of a little composition of the ruthenium complex dye into moss chlorophyll dye can increase the efficiency significantly.

1. Introduction

Organic solar cell is a type of photovoltaic that uses light energy (photons) from the sun. It also called renewable energy or alternative energy. It converts solar energy into eco-friendly electrical energy. One of the solar cell development is dye-sensitized solar cell (DSSC) by Grätzel. DSSC is solar cell based on a dye that can absorb the incident sunlight and uses the light energy to produce electrons transfer reaction. The advantages of DSSC are the simple and low cost to fabricate, the materials also easily obtained, and good performance for the future [1-3].

DSSC components include semiconductor layer on the Transparent Conductive Oxide (TCO) substrate as the anode, a catalyst on the counter electrode as the cathode, the dye as a photosensitizer, and redox electrolyte. One of the components that affect the performance of DSSC is the dye. The dye such as synthesis from complex compounds or natural pigments from the parts of a plant [2,4].

The researchers have been developed the synthetic and natural dyes in the DSSCs application. The type of synthesis dye is generally uses the ruthenium complexes. It can result the high efficiency, but it has high cost production, difficult to synthesize, and contains heavy metals that are not eco-friendly.
Therefore, the natural dye is alternatively as eco-friendly dye. Natural dye can be extracted from the parts of plant such as leaves, flowers, or fruit [5-11].

The research has been conducted in Japan used plant pigments as photosensitizer in the dye sensitized solar cell application. The research proved that natural dye can provide the photovoltaic effect. The pigments of plant parts consist of chlorophyll [12], anthocyanin [13-15], carotenes [16] or betalains [17,18].

This research used natural dye of chlorophyll extract from moss (Bryophyte) mixed with synthesis dye of ruthenium complex N719. The dyes mixture (hybrid) aim to improving the efficiency of DSSC. Chlorophyll is the main pigment in the photosynthesis of green plant which absorbs the maximum wavelength at 670 nm. Therefore, chlorophyll is an attractive natural pigment as photosensitizer in the visible spectrum [12].

The moss was used in this experiment because it easy to obtain in the land, water, or damp places. The moss plant can live with the minimum sunlight, but it can carry out own photosynthesis. The moss plant certainly has chlorophyll because it performs photosynthesis, so that it contains the many chloroplasts. This article will discuss the composition of dyes mixture on the I-V and Incident Photon to Current Conversion Efficiency (IPCE) characteristics of DSSC. The composition of dyes mixture plays vital role in the DSSC application. The function of dye absorbs the photons to produce the electrons excitation.

2. Experimental
Natural dye was extracted from moss chlorophyll (Bryophyte), while synthesis dye was obtained from ruthenium complex N719. The dyes mixture (hybrid) was obtained from both chlorophyll and synthesis. Concentration between chlorophyll and synthesis dyes were 100% and 0%, 80% and 20%, 60% and 40%, 40% and 60%, and 20% and 80%. The substrates used Fluorine-doped Tin Oxide (FTO) glass from Aldrich with a size of 2.0 cm × 2.5 cm and active cell area of 1.0 cm × 2.0 cm. The working electrodes were coated using TiO2 nanopowder 21 nm from Aldrich by the spin coating method, the counter electrodes using carbon produced from pencil and candle soot. Electrolyte solution was made by mixing the KI and I2 in the Polyethylene glycol (PEG) solution.

Characterization included UV-Visible Spectrophotometer Lambda 25 to determine the wavelength of dye absorbance, Keithley I-V meter to determine the efficiency of the DSSC prototypes, and Measurement System QEX7 Serial #150 to determine the Incident Photon to Current Efficiency (IPCE) of the DSSC prototypes.

3. Results and Discussion

3.1. Optical Characterization of Chlorophyll Dye Solution
The absorption spectra of chlorophyll dye solution use UV-Vis spectrophotometer. The result of UV-Vis characterization is shown in Fig.1. The absorption spectra of moss chlorophyll show the first peak in the wavelength range of 450-500 nm and the second peak at wavelength of 650-700 nm. The peak value of absorbance at wavelengths of 400-500 nm is 6.1004 and at wavelengths of 550-700 nm is 3.5835. These correlates with the pigment in the moss chlorophyll, it absorbs color spectrum of greenish blue (400-500 nm) and red (610-800 nm). It indicates that chlorophyll dye can be used as a photosensitizer of DSSC due to its absorbance in the visible spectrum.
3.2. Incident Photon-to-Current Efficiency (IPCE) Characterization in the DSSC Application

IPCE characterization is used to determine the absorption of dye that produces the current in the DSSC devices. The IPCE characteristic shows a graph with quantum efficiency (QE) percentage versus wavelength (\(\lambda\)). QE is the comparison of electrons (currents) and photons which is given in the sample of certain wavelength. Figure 2 is the graph of absorbance and QE versus wavelength of chlorophyll dye.

**Figure 1.** Absorption peak of moss chlorophyll dye

**Figure 2.** The graph of absorbance and quantum efficiency versus wavelength of moss chlorophyll dye
Figure 2 shows that the quantum efficiency (QE) is higher at the wavelength of 550-650 nm than the other wavelengths. It means that at the wavelength range of 550-650 nm, the absorption produces more current than another wavelength. It happens because the absorption produces the exciton (hole-electron pairs) and current. In the wavelength range of 450-500 nm, QE is lower than in the wavelength range of 550-650 nm in spite of its high absorbance of chlorophyll dye solution. It is considered when chlorophyll dye is exposed the light, it’s not overall wavelengths can excite the electrons of the dye in DSSC.

![Graph showing quantum efficiency at different wavelengths](image)

**Figure 3.** IPCE characteristics of DSSCs with the composition of moss chlorophyll and ruthenium dyes mixture

Figure 3 shows that DSSC with 100% moss chlorophyll dye has the lowest quantum efficiency. Peak absorbance of all DSSC prototypes occur at the wavelength of 550-650 nm. It exhibits that photon is absorbed by the dye in this wavelength produces high energy and photocurrent. The DSSC with more concentration of ruthenium dye increase the photons contribution, accordingly the efficiency is bigger. The efficiency will increase when the chlorophyll dye is added ruthenium dye. It can be seen in the green curve with sample of 100% chlorophyll dye has lowest QE, while the red curve shows that the efficiency increases at sample of 80% chlorophyll dye (20% ruthenium dye). The QE is higher as comparable to the addition of ruthenium dye into chlorophyll dye.
3.3. I-V Characterization

![Figure 4. I-V characteristics of DSSCs with the composition of moss chlorophyll and ruthenium dyes mixture](image)

Figure 4 is the I-V characteristics of DSSC prototypes with composition of moss chlorophyll and ruthenium dyes mixture. All curves show the diode characteristics correlating the p-n junction. The p-n junction consists of electron donor (n-type) and electron acceptor (p-type). Electron donor is dyes mixture, while electron acceptor is TiO₂ semiconductor. It is shown that ruthenium concentration affects the performance of DSSC. Concentration of 100% moss chlorophyll (0% ruthenium) has lowest current, while chlorophyll and ruthenium dyes mixture have higher currents. It indicates that chlorophyll and ruthenium dyes mixture absorb the photons dominantly as compared to moss chlorophyll dye. In addition, concentration of ruthenium dye will increase the DSSC efficiency.

Previous study [19] we have demonstrated how to obtain the open circuit voltage ($V_{oc}$), the current short circuit ($I_{sc}$), the voltage maximum ($V_{max}$), the current maximum ($I_{max}$), the fill factor (FF), the power maximum($P_{max}$) and efficiency ($\eta$) from the I-V curves in Fig. 4. Table 1 represents those values for composition of moss chlorophyll and ruthenium dyes mixture.

| Characteristics | Ratio of moss chlorophyll dye : ruthenium dye (%) |
|-----------------|-----------------------------------------------|
|                 | 100 : 0 | 80 : 20 | 60 : 40 | 40 : 60 | 20 : 80 |
| $V_{oc}$ (Volt)  | 0.1200  | 0.3202  | 0.3603  | 0.3602  | 0.3802  |
| $I_{sc}$ (mA)    | 0.0458  | 0.3120  | 0.3410  | 0.5200  | 0.6120  |
| $V_{max}$ (Volt) | 0.1000  | 0.1604  | 0.2203  | 0.2403  | 0.2202  |
| $I_{max}$ (mA)   | 0.0400  | 0.2410  | 0.2170  | 0.2850  | 0.3760  |
| $P_{max}$ (mW)   | 0.0045  | 0.0387  | 0.0478  | 0.0684  | 0.0829  |
| FF               | 0.7278  | 0.3877  | 0.3892  | 0.3656  | 0.3560  |
| $\eta$ (%)       | 0.0022  | 0.0194  | 0.0239  | 0.0342  | 0.0414  |
Table 1 shows that DSSC prototypes with increasing composition of ruthenium dye will improve the efficiency value. Addition of 20% ruthenium dye into chlorophyll dye, the efficiency of DSSC is increasing significantly. The DSSC with 100% chlorophyll dye has the lowest efficiency of 0.0022%. Then, it is added by 20% ruthenium dye can increases its efficiency of 0.0194 or up to 780%. Furthermore, the addition of composition of ruthenium dye (40%, 60%, and 80%) does not significantly increase the efficiency. It is only 20-25%. It proves the addition of a little ruthenium dye can improve the efficiency of moss chlorophyll dye. As an another important aspect, it provides low production cost for DSSC application due to substitute dominants of ruthenium dye with concentration of natural dye (like moss chlorophyll).

4. Conclusion
In this research, the composition of chlorophyll and ruthenium dyes mixture (hybrid) has successfully increased the efficiency of DSSCs. Addition of a little ruthenium complex N719 dye of 20% into natural dye (moss chlorophyll) increased the efficiency significantly. As a result, the DSSC with 100% chlorophyll dye resulted the efficiency of 0.0022%, while addition of 20% ruthenium dye into chlorophyll dye, the efficiency increased 0.0194% or up to 780%.

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