Performance improvement of dye-sensitized solar cells (DSSC) by using dyes mixture from chlorophyll and anthocyanin

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Abstract. This article showed the effect of single and mixture natural dyes on the DSSC performance. The single dyes extracted from moss chlorophyll and mangosteen peels anthocyanin. The dyes mixture was prepared by mixing from both chlorophyll and anthocyanin. The absorbance of dyes solution and the adsorption of the dye onto the working electrode were analyzed using UV-Vis spectroscopy. The photocurrent-photovoltage of DSSCs were measured using I-V meter. The dyes mixture has an increased absorption at visible spectrum range as compared to single dye. The adsorption of the dyes mixture onto the TiO$_2$ electrode has higher absorbance than single dye. The DSSC with single dye from moss chlorophyll and mangosteen peels anthocyanin resulted the conversion efficiency of 0.049% and 0.042% respectively. The dyes mixture of chlorophyll and anthocyanin improved the conversion efficiency of 0.154%.

1. Introduction

A dye-sensitized solar cell is the type of solar cells based on the dye of semiconductor that converts the photon energy into electricity[1,2]. Advantages of DSSC are simple and low-cost in fabrication, can be coated on the flexible substrate, and also achieve the high conversion efficiency for the future[3 – 5]. The standard structure of DSSC consists of conducting glass substrate made of Transparent Conducting Oxide (TCO). TCO usually used Fluorine doped tin oxide (FTO) or Indium doped tin oxide (ITO)[6]. Working electrodes are obtained from the semiconductor material (e.g., TiO$_2$, SnO$_2$ or ZnO)[7]. The material such as platinum (Pt) or carbon (C) are usually chosen as counter electrodes. Sensitizers can be made from synthetic and/or natural dyes, while solution of iodide/triiodide (I/I$^3$) redox couple can be used as electrolyte[8]. Many researches developed the modification of DSSC components to obtain the high efficiency and low-cost DSSC. The photosensitizer is one of the main components which are widely developed by researchers because it affects in working mechanism of DSSC. The role of the sensitizer is to absorb the light, inject the electrons into the semiconductor, and convert the energy of DSSC[9,10].

Many synthetic dyes are employed as a sensitizer for DSSC. The most common of synthetic dye used ruthenium based metal complexes like N719 and black dye[11]. They are susceptible to absorb the broad spectrum of light and can achieve the high conversion efficiency. It were reported the conversion efficiency of 11-12%[12 – 13]. However, the synthetic dyes have the demerits like...
toxicity, high cost, and poor variations of color. The natural dyes are alternatively a photosensitizer with environmentally friendly.

The advantages of natural dyes are easy to obtain, having many variations of color, easily available from the environment, low-cost, and environmental friendliness. The natural dyes can be explored from the part of plants including leaves, flowers, fruits, trunk, roots, seeds, and rind[14]. Source of plants are used as natural dyes from pigment molecule consists of chlorophyll, anthocyanin, carotene, tannin, and flavonoid[14 – 15].

The research has been successfully used pigments molecule as DSSC photosensitizer. Arifin et al. (2017) reported the efficiencies from 0.040% to 0.094% for papaya leaves as a photosensitizer in DSSC[16]. Taya et al. (2013) explored the green algae and found 0.01% efficiency[17]. Pratiwi et al. (2016) extracted the anthocyanin from dragon fruits, mangosteen peels, and red cabbage with efficiency of 0.024%, 0.042%, and 0.054% respectively[18]. Utilization of flower extract also used like Oleander, hibiscus, and Ixora with 0.59%, 1.02%, and 0.30% efficiencies, respectively[10]. Flavonoid source was extracted from Jatropha curcas and achieved 0.12% efficiency[19]. El-Agez et al. (2012) obtained the carotene source from canarium nut extract. It resulted the conversion efficiency of 0.01%[20].

The research of dye modification has been done by mixing two dyes with different region of light absorption. The mixing dyes aim to widen the wavelengths range of light absorption. The wider light absorption can enhance the conversion efficiency of DSSC. The research by Chang et al. (2013) extracted the chlorophyll dye from wormwood and anthocyanin dye from purple cabbage with efficiency of 0.54% and 0.75% respectively, while the dyes mixture from both dyes can enhance the efficiency of 1.47%[15]. Pratiwi et al. (2017) tried by mixing the natural dye from red cabbage anthocyanin with synthetic dye from N719. The mixing dyes aim to improve the efficiency of natural dye from red cabbage anthocyanin. DSSC based on red cabbage anthocyanin resulted in the efficiency of 0.024%, while by addition 20% synthetic dye improve the conversion efficiency of natural dye from red cabbage anthocyanin of 0.054%[21].

Based on previous research, the anthocyanin dye showed absorption in the visible wavelength range from 480-580 nm, while the chlorophyll dye in the range 500-600 nm and 600-700 nm. Hence, the dyes mixture from two different dyes needs to be studied to improve the DSSC performance. This article will investigate the dyes mixture on the DSSC performance.

2. Experiments

Natural dyes were extracted from moss chlorophyll and mangosteen peels anthocyanin. The dyes mixture was obtained from both chlorophyll and anthocyanin (1:1 volume ratio). The substrates used FTO glass from Dyesol with a size of 2 cm x 2.5 cm and active cell area of 2 cm². Working electrodes were coated using TiO₂ paste from Aldrich 21 nm by the spin coating technique, counter electrodes were coated using carbon, and electrolyte solution used EL-HPE Dyesol.

Moss powder was dissolved in the aceton solvent and stirred to get homogeneous solution. Its solution was filtered using filter paper. The solution of filter result was held chromatography process for moss chlorophyll extract was obtained. Mangosteen peels powder was dissolved in the ethanol solvent and stirred for 12 hour. Extract of mangosteen peels anthocyanin was filtered using whatman filter paper.

Characterization includes optical properties (absorbance) and electrical properties. Optical characterization using UV-Visible Spectrophotometer Lambda 25 to analyze the absorbance of dye solutions and dye after adsorbed onto the TiO₂ electrode. Electrical properties of the DSSCs were measured using Keithley I-V Meter 2602A.
3. Results and Discussion

3.1. Optical Characterization of Different Natural Dye Solutions and the Dye After Adsorbed onto the TiO$_2$ Electrode

Figure 1. Absorption spectra of chlorophyll extracted from moss, anthocyanin extracted from mangosteen peels, and their mixtures

Fig. 1 revealed the UV-Vis absorption spectra of single moss; mangosteen peels extract as well as their mixtures. The chlorophyll extract exhibited the first absorption spectra at wavelength 400-490 nm and the second peak at wavelength 630-700 nm. The dye solution of anthocyanin extract can absorb the light at wavelength 400-480 nm. These results represented the dyes solution of moss contain the chlorophyll pigment and mangosteen peels contain the anthocyanin pigment, so that they can be used as DSSC photosensitizers because they have the light absorption in the visible spectrum. The chlorophyll and anthocyanin dyes have the different light absorption, therefore to improve and widen the region of light absorption by mixing of both chlorophyll and anthocyanin dyes at a volume ratio of 1:1.

The result of dyes mixture from chlorophyll and anthocyanin can improve the absorbance and widen the region of light absorption. The curve in Fig.1 revealed the dyes mixture has higher absorbance than single dye. The dyes mixture performed the increase in absorbance from the single dye. It indicated the increase in the intensity of light absorption (hyperchromic effect). The result of dyes mixture has two absorption peaks at wavelength 430 nm (the contribution of anthocyanin dye) and 500 nm (the contribution of the first peak from chlorophyll dye). The second absorption peak from chlorophyll dye was not contribution the absorption peak. This situation can be caused by both chlorophyll and anthocyanin dyes used the different solvent. Each of the solvents was affected by the level of polarity. It involved the shift in the absorption peak and level of absorbance. The shape of absorption peak can be shifted to longer wavelengths (a red shift/bathochromic) and shorter wavelengths (a blue shift/hypsochromic).
The UV-Vis characteristic for absorption spectra of dye after adsorbed onto the TiO$_2$ electrode is shown in Fig.2. The curve can be observed the absorbance peak of dye after adsorbed onto the TiO$_2$ electrode increased and approached into the absorption of UV region. This situation indicated that the absorption spectra of dye after adsorbed onto the TiO$_2$ electrode was not good to absorb in the visible region.

The absorbance of TiO$_2$ electrode using dyes mixture from chlorophyll and anthocyanin performed the significant peak in absorption spectra compared with single dye. It was comparable to the UV-Vis characteristic of dyes solution that dye solution using the mixture from chlorophyll and anthocyanin has higher absorbance than single dye. The increased peak of absorbance and widened region of light absorption can improve the intensity of absorption onto the TiO$_2$ semiconductor.

3.2. $I$-$V$ Characterization

![I-V Characterization Graph](graph.png)

**Figure 3.** $I$-$V$ plot for DSSCs with chlorophyll dye, anthocyanin dye, and dyes mixture
Fig. 3 shows I-V characteristic curve for DSSC with single dye and dyes mixture from chlorophyll and anthocyanin. From I-V curve in Fig. 3 the parameters of DSSC were determined, and its values were observed in Table 1.

The conversion efficiency of DSSC significantly improved by using dyes mixture. It was due to the absorption of visible light spectrum over a wider range as compared to single dye. This result was also supported by UV-Vis characteristic of dye after adsorbed onto the TiO$_2$ electrode which dyes mixture from moss chlorophyll and mangosteen peels anthocyanin extract has higher absorbance than single dye.

Table 1. Parameters of DSSCs sensitized by chlorophyll, anthocyanin, and mixed dyes.

| Dye Source              | Photos | $I_{max}$ (mA) | $V_{max}$ (V) | $I_{sc}$ (mA) | $V_{oc}$ (V) | FF  | $\eta$ (%) |
|-------------------------|--------|----------------|---------------|---------------|--------------|-----|------------|
| Moss                    | ![Moss Image] | 0.30           | 0.32          | 0.46          | 0.39         | 0.56| 0.049      |
| Mangosteen peels        | ![Mangosteen Image] | 0.25           | 0.34          | 0.38          | 0.46         | 0.48| 0.042      |
| Moss + mangosteen peels | ![Moss + Mangosteen Image] | 0.83           | 0.37          | 1.13          | 0.60         | 0.46| 0.154      |

Table 1 represented that DSSC by the dyes mixture can achieve better performance for open-circuit voltage ($V_{oc}$), short-circuit current ($I_{sc}$), and fill factor (FF). It exhibited great adsorption of dyes mixture from chlorophyll and anthocyanin onto the TiO$_2$ electrode, the intensity of light absorption was high with over a wider range. Theoretically, more higher light absorption will increase the number of excited electron from the HOMO to the LUMO state of dye. Thus, the measured currents will also increase. Therefore, the efficiency DSSC based on dyes mixture from chlorophyll and anthocyanin also improved.
4. Conclusion
The performance of dye-sensitized solar cells based on the single and mixture narutal dyes has been reported in this article. The dyes mixture from chlorophyll and anthocyanin extract has higher light absorption at visible spectrum range as compared to single dye. Moreover, the adsorption of the dyes mixture onto the TiO$_2$ electrode has higher absorbance than single dye. The DSSC based on dyes mixture performed an open-circuit voltage ($V_{oc}$), short-circuit current ($I_{sc}$), and conversion efficiency of 600 mV, 1.13 mA, and 0.154%, respectively. It suggest, the dyes mixture can improved the DSSC performance.

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