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(Research Article)

Analysis performance of dye-sensitized solar cells (DSSC) of single and double mixed natural dye as photosensitizers

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Abstract

The performance of DSSC with single and double mixed dyes as photosensitizers were studied. The selected dyes were extracted from water hyacinth (*Eichhornia crassipes*) leaves and Malabar fruit (*Melastoma malabathricum* L.). There were three kinds of dyes applied in the DSSC (crude chlorophyll of water hyacinth, crude anthocyanin of Malabar fruit, mixture of chlorophyll and anthocyanin). The single dye of chlorophyl and anthocyanin had bandgaps energy of 1.75 eV and 1.99 eV, respectively, and the bandgap energy of the mixed dye was 2.25 eV. The mixed dyes resulted in a broader spectrum of absorption wavelength which allows more absorption of sunlight to produce energy. The efficiency values of single dye of chlorophyll, anthocyanin, and the mixed dye were $3x10^{-3}$ %, and $2.4x10^{-2}$ %, and $4.9x10^{-2}$, respectively.

Keywords: Anthocyanin; Bandgap energy; Chlorophyll; Efficiency

1. Introduction

One of efforts to reduce dependence on fossil energy is seeking alternative renewable resources. Of the various renewable resources, solar energy has proven to be an alternative source of choice due to the energy supply is abundant and sustainable, amounting to 3.8 million EJ/year. From the perspective of energy management and environmental security, the use of the visible light spectrum through solar cells is able to convert it into electricity directly from sunlight (1).

Silicon-based solar cells currently dominate the photovoltaic energy market, reaching 93% of total solar power generation. Single crystal silicon based solar cells have achieved an efficiency of 26.7% which is close to the maximum theoretical efficiency limit of 31% (2). However, the silicon material needed to make these solar cells must be very pure, which requires high costs and is very dangerous for the environment.

These constraints encourage the development of alternative photovoltaic technology that has low fabrication and material costs. Dye sensitized solar cells, which were first introduced by O'Regan and Grätzel in 1991, which were then called Dye Sensitized Solar Cells, are an attractive alternative because of their properties, such as low production costs, a wide choice of substrates that can be used, and do not require high purification. and low impact on the environment (3).

Organic dyes commonly used in DSSC were chlorophyll, anthocyanin, and carotene (4). Chlorophyll is found in the leaves of every plant. Chlorophyll is able to absorb red, blue, and purple wavelengths of light. The peak absorption wavelengths

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of chlorophyll are in the range of 400-450 nm and 650-700 nm (5). Anthocyanins are red, purple, and blue pigments which belong to the flavonoid group and can be used as dyes (6). Furthermore, anthocyanin has a wavelength absorption band in the range of 490-550 nm (7). Carotene has a peak absorption band in the light wavelength range of 400-600 nm. Carotene is a yellow-orange to red pigment that comes from plants (8) (9).

Natural dye has a narrow wavelength absorption; therefore, mixed dyes are used to increase the absorption area (10). Dye mixtures with two or more dyes with different absorbance is an effective technique to increase the wavelength absorption of DSSC (11). Dye mixture can increase the efficiency and stability of DSSC. Using dyes with different absorbances can improve performance better than a single dye. This research was to analyze the performance of DSSC on single and double mixed natural dyes as photosensitizer.

2. Materials and Methods

2.1. Dye extraction

The extraction of dye from water hyacinth leaves and Malabar fruits were carried out by crushing the fresh leave and fruit by addition of aquadest. The ratio of solid sample and aquadest was 1:20. The mixture was filter through a Whatman filter paper. The filtrate was used as dye for a photosensitizer.

2.2. Preparation of Photoelectrodes, and Working Electrodes

The capacitive touch screen used had a dimension of 25 mm x 25 mm. The working electrode glass was placed in a conductive position upwards, is then glued with four layers of tape equivalent to a thickness of 0.494 mm. Next, TiO_2 paste was deposited on the working electrode using the doctor blade method. TiO_2 paste that has been deposited on conductive glass was placed in an oven at 105aC for 5 minutes. After cooling, then put it in the dye solution for 24 hours and store it in a dark place. After the dye was adsorbed, the working electrode was air dried.

2.3. DSSC assembly

The DSSC was assembled with a glass working electrode and a reference electrode stacked like a sandwich cell in a sequence consisting of conductive glass at the top, dye-sensitized TiO_2 photoelectrode, electrolyte, reference electrode, and conductive glass. Then the two electrodes were clamped using two clips on both sides. The two offset sides of the electrode are connected with jumper cables and clamped using crocodile claws. The DSSC components that have been assembled were then dripped with 0.5 mL electrolyte solution into the offset gap.

2.4. Absorption spectra of dye

UV-Vis spectrophotometric measurements were carried out to analyze the light absorbance ability and the peak value of the UV-Vis wavelength absorption. The absorption spectra of dyes were recorded in the range of 400 nm to 700 nm.

2.5. Electrical properties measurement

DSSC efficiency was determined from the results of measurements of current-voltage and power-voltage curves. A 10 kΩ potentiometer and digital multimeter (Fluke 77 III and Heles UX-369C) were used to obtain the maximum output voltage value. The I-V and P-V curves are used to determine the values of short-circuit density (Isc), open circuit voltage (VOC), maximum power (P_{max}) and fill factor (FF). The fill factor (FF) and efficiency (η) of DSSC were calculated using equations as stated in equation (1) and (2).

$$FF = \frac{V_{max} \times I_{max}}{V_{oc} \times I_{oc}} \quad \text{................}(1)$$

$$\eta(\%) = \frac{P_{max}}{P_{in}} \times 100\% \quad \text{................}(2)$$

2.6. Bandgap Energy Calculation

The Tauc plot method was usually used to determine the bandgap value of dye extraction by measuring the absorbance of dye by using a UV-Vis spectrophotometer absorbance data to calculate the energy bandgap value. The bandgap value of the material was determined by plotting a linear curve of the relationship $(\alpha hv)^2$ $(m\text{-}1\ eV)^2$ on the y-axis to hv (eV) on the x-axis. The equation was formulated as follows (12).

$$(\alpha hv)^2 = (hv - Eg) \quad \text{(3)}$$

where:
α = absorption coefficient (cm^{-1})
hv = energy photon (eV)
Eg = *bandgap* energy (eV)

When $(\alpha hv)^2$ is zero, there will be an intersection of the curve on the x axis (hv (eV)) and the intersection value is the band gap value of the material.

$$0 = \quad 0 = (hv - Eg) \quad \text{(4)}$$

$$Eg = hv \quad \text{(5)}$$

3. Results and Discussion

3.1. Single and Double Mixed Dye absorbance

The absorbance of dyes was analyzed in the wavelength range 400 nm to 700 nm by using a UV-Vis spectrophotometer. Absorbance measurements was plotted in graphs as seen in Figure 1.

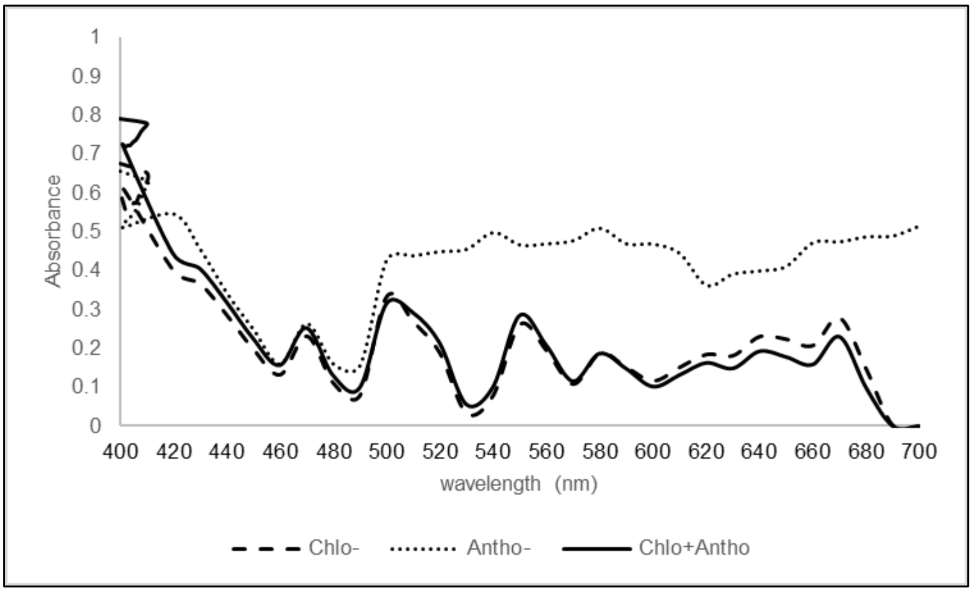

Figure 1 Absorbance of chlorophyll, anthocyanin and mixed chlorophyll and anthocyanin

The absorbance of single dye either chlorophyll of water hyacinth or anthocyanin of Malabar fruit showed a fluctuated values in the range of 500 nm to 700 nm. On the other hand, the absorbance of mixed dyes showed a relatively constant absorbance values. The consistent absorbance value would result in a larger efficient in the performance of DSSC.

3.2. Bandgap Analysis

Bandgap energy is the energy difference between the conduction band and the valence band in a semiconductor material (5). This energy difference determines the material's ability to absorb light and convert it into electrical energy. The smaller the bandgap energy value, the longer the wavelength of light that can be absorbed by the material, which can increase energy conversion efficiency (13).

The natural colorant anthocyanin from Malabar fruit, chlorophyll from water hyacinth leaves and the mixture of anthocyanin and chlorophyll which were used as photosensitizers in this study have varying bandgap energies. This variation affects the dye's ability to absorb different light spectra and its conversion efficiency. The ideal bandgap energy must be large enough for electron excitation to occur, but not too large so as not to reduce energy conversion efficiency (13). Bandgap energy for a single natural dye and a mixture of two dyes are presented in **Table 1**.

Tabel 1 *Bandgap* energy of chlorophyll, anthocyanin and mixed dyes

Dye	**Bandgap Energy (eV)**
Chlorophyll	1.75
Anthocyanin	1.99
Chlorophyl and anthocyanin	2.25

Chlorophyll and anthocyanin produced different energy bandgaps which affected the efficiency of absorption and transfer of light energy. There are some factors that can affect the bandgap energy derived from natural dyes. For example, chlorophyll extracted from different leaves might produce different bandgap energy, the affecting factors includes the type of chlorophyll and the amount of chlorophyll. Syafinar (4) reported that chlorophyll extracted from spinach has a bandgap energy of around 1.83 eV which allows the absorption of light at a wavelength of 439-663 nm. Meanwhile, research conducted by Rahayu et al. (14) on the anthocyanins of the Malabar fruit has a smaller bandgap energy compared to chlorophyll, around 2.1 eV, which allows the absorption of light at 532 nm. The bandgap energies obtained from chlorophyll of water hyacinth leaves and anthocyanin of Malabar fruits were slightly lower that those reported by previous findings. However, this research found that the mixture of chlorophyll of water hyacinth leaves and anthocyanin of Malabar fruits resulted in higher bandgap energy at 2.25 eV compared to a single dye as a photosensitizer. This indicated that the combination of chlorophyll and anthocyanin could resulted in a broader absorption spectrum which allows more absorption of sunlight to produce energy. The broader of the absorption wavelength can reduce the energy for the excitation of the electrons to the conduction band, therefore, the mixture of two dyes allows increasing the absorbance coefficient of the photosensitizer.

3.3. Measurement of current-voltage

The performance of DSSC of single and double mixed dyes as shown in **Tabel 2**. The greatest efficiency of single dye was found in anthocyanin (Malabar fruit) as amount of 0.024%. Fill factor which is a dimensionless indicator showed the ratio of the maximum power produced by a solar cell to the product of V_{oc} and I_{sc}, the result was inversely proportional to the efficiency produced with the largest fill factor value for natural dye of chlorophyl of water hyacinth leaves of 0.2739. then sequentially 0.2701 and 0.2529. The greater the fill factor value of a solar cell, the better the stability of the solar cell will be. Sanjay et al. (2018) stated that increasing the absorption range of the light spectrum is directly proportional to the efficiency of the energy produced.

Tabel 2 Performance of *DSSC* for single and double mixed dyes

Dye	**V_{oc} (V)**	**I_{sc} (mA)**	**I_{max} (mA)**	**V_{max} (V)**	**P_{max} (mW)**	**FF**	**Ef (%)**
Chlorophyll	285	0.0210	0.0113	145	1.6390	0.2739	0.003
Anthocyanin	621	0.0762	0.0380	315	11.970	0.2529	0.024
Chloro+antho	415	0,1977	0,1114	199	22,163	0.2701	0.049

4. Conclusions

A photosensitizer of single dye resulted in a lower bandgap energy and higher efficient value compared to mixed dyes (1.75 eV, 1.99 eV, 2.25 eV, respectively for chlorophyll, anthocyanin and mixed chlorophyl and anthocyanin). A broader absorption wavelength obtaining from mixed dyes allowed more absorption of sunlight to produce more energy. The efficiency values of single dye of chlorophyll and anthocyanin, and the mixed dye were $3x10^{-3}$%, and $2.4x10^{-2}$%, and $4.9x10^{-2}$, respectively.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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