Optical properties of natural dyes on the dye-sensitized solar cells (DSSC) performance

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Abstract. This study reported several natural dyes for application in dye-sensitized solar cells (DSSC). This study aims was to determine the effect of optical absorption properties of natural dyes on efficiency of DSSC. The sandwich structure of DSSC consist of TiO_2 as working electrode, carbon layer as counter electrode, natural dyes as photosensitizer, and electrolyte as electron transfer media. The natural dyes used in this experiment were extracted from dragon fruit anthocyanin, mangosteen peels anthocyanin, and red cabbage anthocyanin. The absorbance of dyes solutions and the adsorption of the dye on the surface of TiO_2 were characterized using UV-Vis spectrophotometer, the quantum efficiency versus wavelength was characterized using incident photon-to-current efficiency (IPCE) measurement system, and the efficiency of DSSC was calculated using *I-V* meter. UV-Vis characteristic curves showed that wavelength absorption of anthocyanin dye of red cabbage was 450 – 580 nm, anthocyanin of mangosteen peels was 400 – 480 nm, and anthocyanin of dragon fruit was 400 – 650 nm. Absorption spectra of the dye adsorption on the surface of TiO_2 which was resulted in the highest absorbance of red cabbage anthocyanin. IPCE characteristic curves with anthocyanin dye of red cabbage, mangosteen peels anthocyanin, and dragon fruit anthocyanin resulted quantum efficiency of 0.058%; 0.047%; and 0.043%, respectively at wavelength maximum about 430 nm. *I-V* characteristic curves with anthocyanin dye of red cabbage, mangosteen peels anthocyanin, and dragon fruit anthocyanin resulted efficiency of 0.054% ; 0.042% ; and 0.024%, respectively.

1. Introduction
Dye-sensitized solar cells (DSSCs) are energy devices for converting light energy into electricity [1,2]. DSSC offered the advantages as new class of low cost and easy to fabricate, and can achieve high solar energy conversion efficiency [3]. Also, they are not involve the complex technology so that can reduce of production cost and the materials are easily obtained from the environment [1]. The standard structure of a DSSC consist of transparent conducting oxide as substrate (e.g. FTO or ITO), semiconductor layer from TiO_2 or ZnO as photo anode, Pt or C as counter electrode, dye molecules as photosensitizer, and electrolyte as electron transfer media [4]. One of the main factors which affect in the DSSC performance is dye.

The dyes have been developed by the researchers, both synthetic and natural dyes. In current studies of DSSCs, synthetic dyes can reach conversion efficiency at 11 – 12% [5,6]. In generally, these kinds of synthetic dyes, such as N3 and N719. However, they have high production costs, containing the heavy metals so that create environmental pollution. Alternatively, natural days can be used as a photosensitizer for the purpose with environment friendliness. The advantages of natural dyes include widely available, cost effective, and environment friendliness. Natural dyes can be extracted from various plants, fruits, flowers, and leaves [7]. Several natural dyes pigments such as flavonoid, betacyanin, anthocyanin, chlorophyll, tannin, and β-carotene have been successfully as sensitizers of DSSCs [8]. Many research have been developed kinds of natural dyes. Chang et al. employed chlorophyll dye from wormwood and anthocyanin dye from red cabbage as sensitizer in DSSC and reported conversion efficiency of 0.9% and 1.47%, respectively [9]. Shalini et al. in the year 2015 have been successfully took extracts from leaves, seeds, flowers, fruits, vegetables, and tree barks as natural dyes. His research results showed that the best of DSSC parameters by pomegranate peel (flavonoid pigment), raspberries (betacyanin pigmen), moses-in-the-cradle (chlorophyll pigmen) [10]. A number studies have been mentioned about dyes have not many studies the optical properties of the dyes adsorption to the working electrode and related the contribution of dyes for energy conversion efficiency and quantum efficiency. The optical properties of the dye adsorption on the surface of TiO_2 is an important parameter to determine the efficiency of DSSC [11]. The dye molecules collected light and produced excitation of electrons [12]. Therefore, in this review article reported the effect of optical properties about dye absorbance for quantum efficiency and energy conversion efficiency of DSSC.

2. Methods

The used materials are natural dyes from red cabbage, mangosteen peels, and dragon fruit as photosensitizer, *Fluorine-doped Tin Oxide* (FTO) conductive glass from Dyesol was cut the size of 2cm x 2.5 cm as substrate, TiO_2 powder 21 nm as working electrode semiconductor (photoanode), carbon as counter electrode (photocathode), electrolyte solution from EL-HPE Dyesol as electron transfer media, different solvents (ethanol, methanol, acetic acid, and distilled water) as extraction solvent of dyes, graphite pencil-2B and candle as carbon for counter electrode, and filter paper to remove solid residues from the anthocyanin extracts.

TiO_2 films were coated on the FTO conductive glass by spin coating using TiO_2 pastes, annealing process of TiO_2 films by furnace, fresh dyes were milled by mortar, homogeneity of dyes solutions by magnetic stirrer hot plate. The absorbance of dyes solutions and the adsorption of the dye on the surface of TiO_2 were characterized using UV-Vis spectrophotometer (Lambda 25), the quantum efficiency versus wavelength was characterized using incident photon-to-current efficiency (IPCE) measurement system (QEX7 Serial #150), and the efficiency of DSSC was calculated using *I-V* meter (Keithley 2602A).

Red cabbage was cut into very small pieces and mashed in a mortar. It was kept in solvents of distilled water, methanol, and acetic acid for 24 hours. Mangosteen peels were milled and dried for 3 – 5 dyes. Sample of mangosteen peels powder was soaked in ethanol with stirring for 12 hours at room temperature. Fresh dragon fruit was mashed in a mortar and added solvents of distilled water, ethanol, and acetic acid. It was kept for 24 hours. The extract of anthocyanin dyes solutions were filtered using filter paper, respectively. The absorption spectra of dyes solutions were characterized by using UV-Vis spectrophotometer.

TiO_2 pastes were prepared using TiO_2 powder in ethanol. TiO_2 solution was stirred by 300 rpm for 30 minutes. TiO_2 pastes were deposited on the FTO conductive glass with an active area of 1cm x 2cm by spin coating technique. TiO_2 films were annealed in a furnace at 400ºC for 10 minutes.

Counter electrodes were prepared from carbon catalyst on the FTO conductive glass. Working electrode and counter electrode were assembled into a sandwich type arrangement. Electrolyte solution was filled the space between the two electrodes. The DSSCs were characterized using incident photon-to-current efficiency (IPCE) measurement system and *I-V* Meter.

3. Results and Discussion

3.1. *Absorption spectra of different natural dyes solutions and the dye adsorbed on the TiO_2 surface*

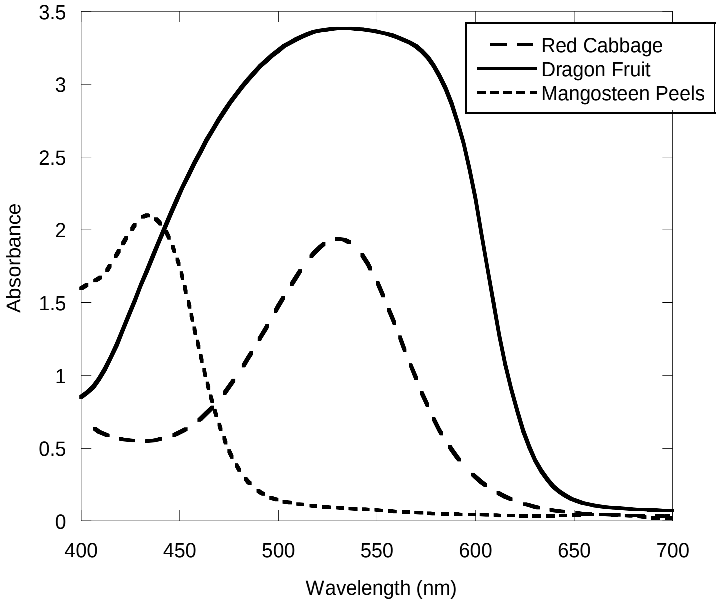

Figure 1. UV-Vis absorption spectrum of different anthocyanin natural dyes solutions

Figure 1 shows the absorption spectra of different anthocyanin dyes solutions. The absorption wavelength of anthocyanin dye of red cabbage was 450 – 580 nm, anthocyanin of mangosteen peels was 400 – 480 nm, and anthocyanin of dragon fruit was 400 – 650 nm. The results of absorption wavelength showed that the dyes solution in Fig.1 can be used as photosensitizer for DSSC because they appeared the absorption of visible region. The graph in Fig.1 showed that the dye solution of dragon fruit anthocyanin was resulted in the widest and highest of absorbance.

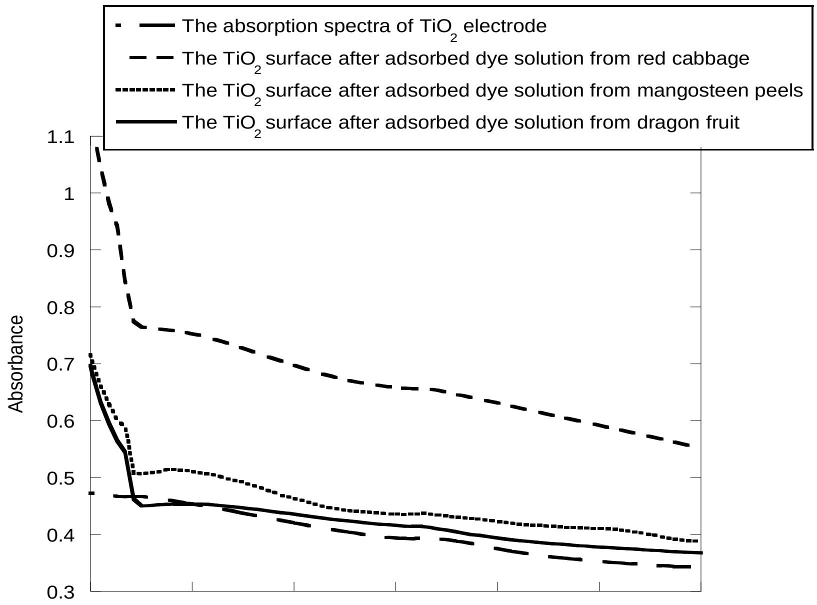

Figure 2. UV-Vis absorption spectrum of TiO_2 electrode and dye after adsorption on the TiO_2 surface

Figure 2 shows the absorption spectra of TiO_2 films can increase after the dye adsorption at wavelength above 400 nm. This result showed that the dye adsorption on the surface of TiO_2 can be used as photosensitizer for DSSCs absorbed of light in the visible region. The dye solution of dragon fruit anthocyanin was resulted in the widest and highest of absorbance, however when the dye adsorption by dragon fruit anthocyanin on the surface of TiO_2 was resulted in the lowest of absorbance. The dye adsorption by red cabbage anthocyanin on the surface TiO_2 was resulted in the highest of absorbance than the others of anthocyanin dyes were presented in Fig.2. This situation may be explained that the dye adsorption by dragon fruit anthocyanin on the surface of TiO_2 less than the dye of red cabbage anthocyanin.

3.2. Incident Photon-to-Current Conversion Efficiency (IPCE) Characterization

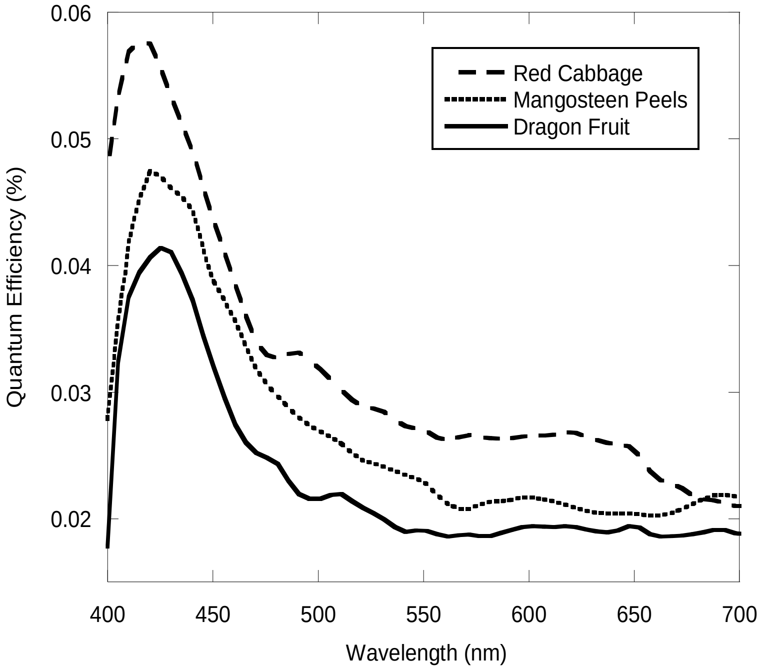

Figure 3. IPCE spectrum of DSSCs with different anthocyanin natural dyes

The IPCE versus wavelength curve obtained is shown in Figure 3. It shows that the dyes has effectively worked the wavelength in the range of 400 nm – 460 nm at wavelength maximum about 430 nm. This result shows the wavelength region contributed in highest current formation. The IPCE spectrum showed the decrease after in wavelength about 460 nm. This situation can be explained that the dye adsorption on the surface of TiO_2 was not work optimally in visible region because the back transfer of electrons excitation on the TiO_2 trapped back into the UV region, so that the photons were converted into the current would be slightly [13,14]. Most of the molecules of dyes that attached on the surface of TiO_2 has not effectively inject the electron to electrode. The result of IPCE curve was comparable with the result of absorbance curve of the dye adsorption on the TiO_2 surface (Figure 2). The dye adsorption on the surface of TiO_2 was higher as the higher contribution of photons was absorbed, so that the result of efficiency quantum was also higher. The DSSC of red cabbage anthocyanin resulted in the highest of quantum efficiency.

3.3. Photocurrent – Photovoltage Characterization

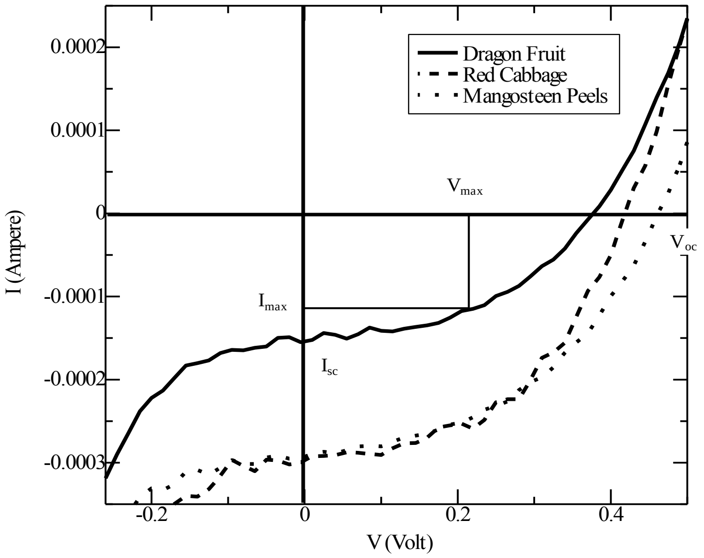

Figure 4. Current-voltage curves for the DSSCs by different anthocyanin natural dyes

For the *I-V* curves by Fig.1, the samples were illuminated with Xe light source using *I-V* Meter. The light intensity was kept constant at 1000 W/m^2 and active area of the cell exposed to light was 2 cm^2 (1 x 2 cm). From *I-V* plot can be calculated parameters of DSSCs as reported in Table 1 :

Table 1. Parameters of DSSCs with different anthocyanin natural dyes extracted from vegetable, fruit, and rind.

Dye solution	**Photos**	I_{max} **(mA)**	V_{max} **(V)**	I_{sc} **(mA)**	V_{oc} **(V)**	***FF***	***η (%)***
Hylocereus polyrhizus (Dragon Fruits)		0.17	0.28	0.23	0.34	0.63	0.024
Brassica oleracea var (Red cabbage)		0.35	0.31	0.49	0.43	0.51	0.054
Mangosteen pericarp		0.25	0.34	0.38	0.46	0.48	0.042

The conversion efficiency value of DSSCs were resulted in the highest efficiency of DSSC by red cabbage anthocyanin. This result was comparable with IPCE curve in Fig.3. The quantum efficiency was higher showed as the higher contribution of photons was absorbed, so that the conversion efficiency of DSSC was also higher. It was also supported by UV-Vis characteristic of the dye adsorption on the TiO_2 surface showed that in the highest absorbance of red cabbage anthocyanin. This study reported that the efficiency DSSC was higher as the higher adsorption of the dye on the surface of TiO_2.

Table 1 displayed that the open circuit voltage (V_{oc}) of measured DSSCs were fluctuated, while the measured short circuit current (I_{sc}) increased as the increasing of dye adsorption on TiO_2 surface. This result can be explained that the absorption of photons were converted to electrons have least. The dye adsorption on the TiO_2 surface was not dominant work in the visible region. The efficiency has a low because the output current has least. This situation effected the conversion efficiency is low.

In conclusion, the absorption spectra of dye adsorption on the surface of TiO_2 which was resulted in the highest absorbance of red cabbage anthocyanin. This result was comparable to the results of conversion efficiency and quantum efficiency for DSSCs that solar cells using red cabbage anthocyanin as sensitizers has highest values of efficiency. The efficiency was higher as the higher adsorption of the dye to the surface of TiO_2.

Acknowledgments
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