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Effect of concentration of red dragon fruit (*Hylocereus costaricensis*) peels extract as a dye of Dye-Sensitized Solar Cell (DSSC) on DSSC efficiency

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Abstract. The utilization of red dragon fruit peels (*Hylocereus costaricensis*) as a DSSC sensitizer has been done to study the effect of extracted dye concentration on DSSC efficiency. DSSC has four main components, namely working electrode, sensitizer, a counter electrode, and electrolyte. One of the most essential components in DSSC is a sensitizer. In this work, variations of concentration of dye extracted were carried out to obtain an optimal concentration of dye so that TiO_2 could fully absorb molecular dyes. The dye solution was extracted by dissolving the red dragon fruit peels into methanol, acetic acid, and aquades. Variation of concentration used was 5g/20mL; 10g/20mL; 15g/20mL; 20g/20mL; 25g/20mL; and 30/20mL (b/v). Optical properties of dye solution and TiO_2/dye layer was characterized by UV-Vis spectrophotometer, functional groups of TiO_2/dye layer was characterized by Fourier Transform Infra-Red (FTIR), and current-voltage of DSSC was characterized by Keithley I-V Meter. Extracted dye results show optical absorption at a wavelength of 450 - 550 nm, which has a peak that tended to increase with increasing concentration. Meanwhile, the absorption spectrum was obtained from Fourier Transform Infra-Red (FTIR) shows the presence of functional groups O-H, C=O, C=C, C-O, and C-H aromatic. The results of DSSC current-voltage characterization obtained an efficiency of 0.047% at a concentration of 20g/20mL; this was supported by the highest absorbance of TiO_2 films which dye coated at a concentration of 20g/20mL

INTRODUCTION

Solar energy can be converted into electrical energy using solar cells. DSSC is third-generation of solar cells that dye-based as a photon absorbent (photosensitizer) [1]. DSSC are photovoltaic devices that are economical, simple to fabricate, easily obtained the materials, and have excellent conversion efficiencies [2]. DSSC consists of four components: conducting glass (e.g., FTO or ITO), semiconductor electrode (TiO_2, SnO_2 or ZnO), a counter electrode (Pt or C), dye as a photosensitizer, and electrolyte as redox mediator [3]. One of the most essential components of a DSSC is photosensitizer.

Many complex metals and organic dyes have been used as sensitizers in DSSC [4]. It has been reported that the highest efficiency of complex metals as a sensitizer was achieved from Ruthenium compounds, with a total efficiency of 11-12% [5-6]. The use of synthetic dye requires high production costs, complicated manufacturing methods, and is not environmentally friendly despite providing high efficiency. Natural organic dyes are widely available, and their manufacture is simple, non-toxic, and entirely biodegradable [7-10].

A natural dye can be extracted from plant parts, such as leaves, flowers, or fruit. One of natural dye pigments commonly used as a sensitizer is anthocyanin. Anthocyanin is a flavonoid pigment as one of the best sensitizers for broadband semiconductors [11-12]. In this study, anthocyanin pigment was used from red dragon fruit peels. Red dragon fruit is widely developed in Indonesia so that its existence can be found easily.

The amount of dye adsorbed by semiconductors can be studied by controlling the size of the semiconductor and modifying the morphological structure of the semiconductor [13]. The properties of the dye solution can also affect the number of dye molecules adsorbed by semiconductors [14]. One of the solution's features that can be easily

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controlled is the concentration of the solution. The dye solution concentration on the semiconductor is also crucial for study because of its influence in DSSC performance. In this work has been done concentration variation of extracted dye to reach the optimum concentration so that dye molecules can be absorbed on the semiconductor surface to increase the performance of DSSC.

EXPERIMENTAL

The working electrodes with TiO_2 paste were coated by screen printing. This study used UV-Visible Spectrophotometer Lambda 25 to measure the absorption spectra of dyes solution, Fourier Transform Infra-Red (FTIR) to show the functional groups of TiO_2 dye-coated and Keithley I-V Meter 2602A to measure the photoelectric conversion efficiencies. The peels of dried red dragon fruit are cut into small pieces and blended until smooth. The soft peels is dissolved into methanol, acetic acid, and distilled water solvents (25: 4: 21). The concentrations are varied by 5g/20mL, 10g/ 20mL, 15g/20mL, 20g/20mL, 25g/20mL, and 25g/20mL (b/v). The extracted dye is stirred using a magnetic stirrer at a speed of 300 rpm until all the paste dissolve. The dye solution is filtered with Whatman filter paper No.42. Working electrodes were immersed in a dye solution for 24 hours. The TiO_2/dye layer was characterized by UV-Vis Spectrophotometer and FTIR. The counter electrodes were prepared from a carbon catalyst. Fabrication of DSSCs was arranged into a sandwich structure. The electrolyte solution was injected into the cell. DSSCs were measured using IV Meter.

RESULT AND DISCUSSION

Absorption spectra of dye solutions and TiO_2/Dye layers

Figure 1 shows that each concentration has a peak at a wavelength between 450-570 nm. The absorbance at this wavelength is an characteristic of anthocyanins; its range of 450-570 nm [15]. This shows that the peels of red dragon fruit contains anthocyanin. Extracted anthocyanin pigments can appear optimally by using acid solvents. In this study, using a mixture of three solvents, namely methanol, acetic acid, and distilled water with a ratio of 25: 4: 21.

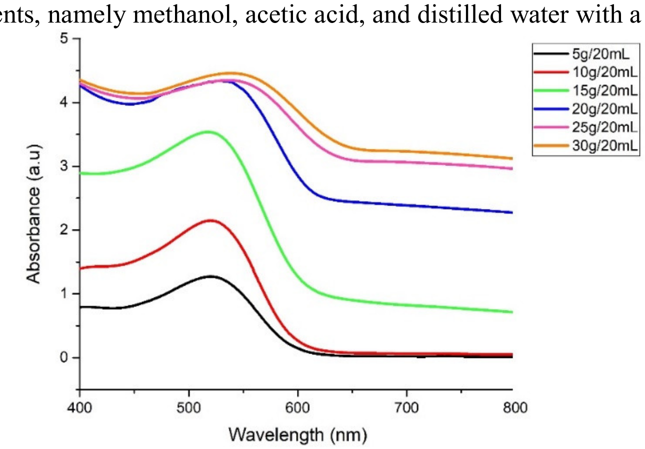

FIGURE 1. Absorbance Spectrum of Dye Solution for Red Dragon Fruit Peels with Variation of Concentration

Variation of concentration in dye solution does not affect the position of the peak but affects the absorbance value of the spectrum. The high concentration of anthocyanin dye causes dye molecules were absorbed and reflected from the photon light of UV-Vis spectrophotometer lamps. The content of this dye is equivalent to the light absorbed. This is in accordance by the Lambert-Beer law that absorbance of solutions is equivalent to the concentration in the same length of light trajectory [16]. The smaller the concentration, the lower the pigment compounds contained in the dye; therefore the optical absorption peak decreases. Thus the dye derived from an extract of H. Costaricensis peels can act as a sunlight absorber. This shows the opportunity to use this dye as a sensitizer to DSSC.

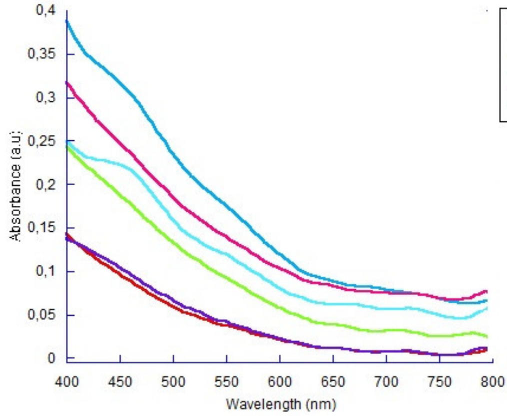

FIGURE 2. TiO_2 Layer Absorbance Curve / Red Dragon Fruit Skin Dye with Variation Concentration

Figure 2 shows the spectrum of TiO_2 layers soaked in red dragon fruit peels dye in each concentration of 24 hours. The high absorbance peak is influenced by the presence of metal ions (Titanium) which are bound by the dye so that the color of the dye is changed. The higher the absorbance value shows the more molecules absorb the photon energy, indicating a bond formed between the chromophore dye and Ti molecules. Anthocyanin molecules absorbed photons energy to transition to higher energy levels.

Figure 2 shows that a concentration of 20g/20mL owns the highest absorption. The highest absorption suggest that many dye molecules attach to the TiO_2 surface at a concentration of 20g/20mL. In this curve (Figure 2), many dye molecules were attached to the TiO_2 layer affect the absorbance value although 20g/20mL is not a highest concentration . It can be proved that TiO_2/dye adsorption decreases when the concentration is higher than 20g/20mL. Based on several previous studies, the higher dye concentration at a specific limit will be inversely equivalent to the effect of photosensitization, it is because of the photosensitizer adsorption limits on the TiO_2 surface [17]. Excessive concentrations of natural dye allow multilayer dye deposition and polymerization [18]. From the absorbance results above shows the optimum concentration of the use of dragon fruit peel as a dye in DSSC, namely at a concentration of 20g/20mL.

FTIR characterization of TiO_2/Dye Layers

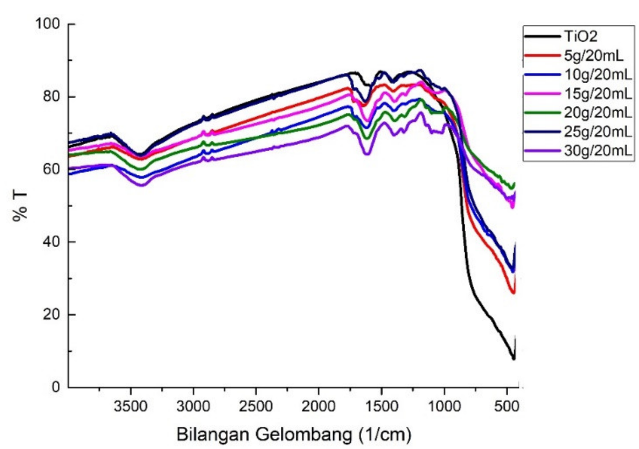

FIGURE 3. FTIR Spectrum of TiO_2 Layer/Dye of Red Dragon Fruit Peels with Variation in Concentration

In general, the existence of an O-H group at wave number 3400 cm^{-1}, C-H group in the range of wavelength 2800 cm^{-1}, C=C group at wave number 1600 cm^{-1}, and C-O group at wave number 1300 cm^{-1} with different intensities. O-H group determined on TiO_2 was produced from ethanol, which was used as a solvent when making TiO_2 paste [19].

The structure of Ti-O-Ti is identified at wave number 587.4 cm^{-1} [20]. The identification of functional groups in the TiO_2/dye layer of red dragon fruit peels at a concentration 20g/20mL is shown in Table 1.

TABLE 1. Characteristics of Functional Groups in the TiO_2/Dye Layer from Red Dragon Fruit Peels at a Concentration of 20g/20mL

Sample	Wavelength Number (cm^{-1})	The Intensity of Transmittance (%T)	Functional Group
20g/20mL	3420.90	69.98	O-H
	2882.74	76.60	C-H
	1618.35	78.53	C=C
	1393.63	83.39	C-O
	1316.47	84.53	C-O
	1099.47	85.44	C-O
	468.72	64.74	Ti-O-Ti

When anthocyanin dye was treated with concentration variations, no peak shift occurred. However, FTIR analysis showed that there was a shift in the transmittance curve of TiO_2 without soaking and after soaking in the dye. The lower transmittance shows the higher the absorbance. The shift of transmittance suggest that there is a binding of anthocyanin dye molecules on the TiO_2 surface, so that there is a contribution of anthocyanin to absorb photons and increasing the absorbance. Anthocyanin dye has a carbonyl group (C=O) and a hydroxyl group (O-H) so that the anthocyanin dye chromophore can bind to Ti from TiO_2. When anthocyanin dye in the form of cyanidin interacts with TiO_2, it replaces OH^- from the Ti (IV) structure in combination with the proton from the cyanidin group to produce H_2O. The reaction between dye anthocyanin and TiO_2 is shown in Figure 4.

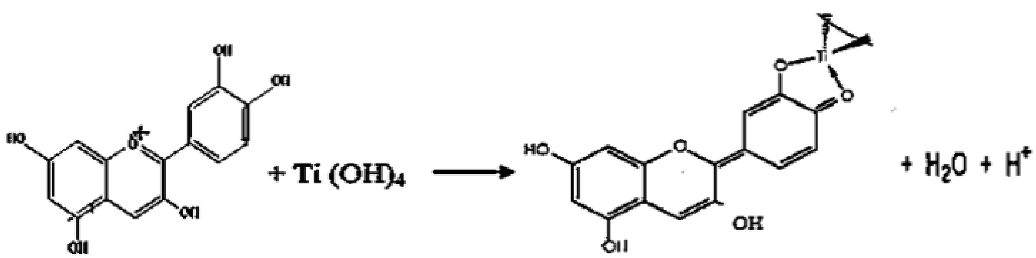

FIGURE 4. I-V DSSC Curve with Variation in Red Dragon Peels Dye Solution Concentration Variation [22]

Current–Voltage (I-V Characterization Results

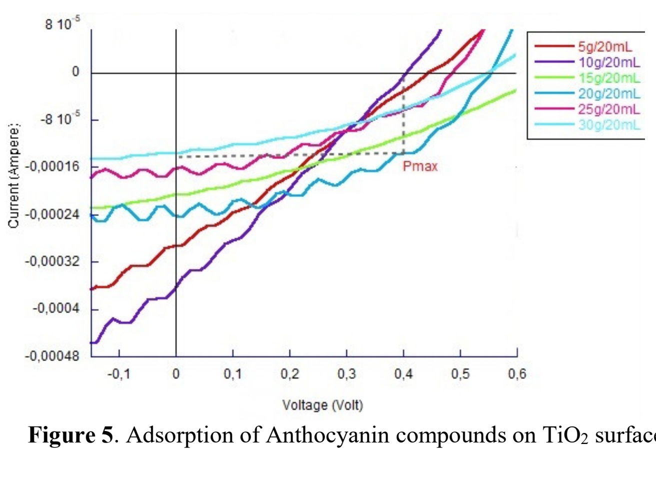

Figure 5. Adsorption of Anthocyanin compounds on TiO_2 surface

TABLE 2. DSSC Parameters from Red Dragon Peels Extracted Dye with Variation of Concentration

Sample	V_{oc} (V)	I_{sc} (A)	V_{max} (V)	I_{max} (A)	*FF*	η (%)
5g/20mL	4.85×10^{-1}	3.20×10^{-4}	2.12×10^{-1}	1.82×10^{-4}	2.49×10^{-1}	2.58×10^{-2}
10g/20mL	3.33×10^{-1}	3.17×10^{-4}	2.42×10^{-1}	1.71×10^{-4}	3.92×10^{-1}	2.77×10^{-2}
15g/20mL	6.36×10^{-1}	2.10×10^{-4}	3.33×10^{-1}	1.29×10^{-4}	3.23×10^{-1}	2.89×10^{-2}
20g/20mL	5.15×10^{-1}	2.93×10^{-4}	4.09×10^{-1}	1.74×10^{-4}	4.73×10^{-1}	4.77×10^{-2}
25g/20mL	4.54×10^{-1}	1.95×10^{-4}	4.39×10^{-1}	1.21×10^{-4}	6.01×10^{-1}	3.57×10^{-2}
30g/20mL	5.30×10^{-1}	1.18×10^{-4}	3.18×10^{-1}	8.82×10^{-5}	4.45×10^{-1}	1.87×10^{-2}

Table 2 shows that the higher the concentration of dye solution. the efficiency of DSSC increases but decreases when the concentration is enlarged to 25g/20mL and 30g/20mL. The highest efficiency was obtained at a concentration of 20g/20mL, which was equal to 0.0477%. This result is consistent with the solution of red dragon fruit peels dye with a concentration of 20g/20mL adsorbed on the surface of TiO_2, showing the highest peak of absorbance. This efficiency increase because of the widening of the wavelength range absorbed in the red dragon fruit peels dye on the TiO_2 layer. However, the efficiency of DSSC decreases at concentrations more than 20g/20mL. The precipitation of dyes on the TiO_2 electrodes can explain this result. Because of this phenomenon. some dissolution of TiO_2 by the acidic carboxylic groups of the dye can occur. The resulting Ti^+ ions form insoluble complexes with anthocyanin dyes. causing precipitation of these complexes in the pores of the film. This gives rise to inactive dye molecules on the TiO_2 surfaces [21]. Based on this work. it has been found that red dragon fruit peels dye has good interaction with the TiO_2 surface at a concentration of 20g/20mL, due to the high dye loading value without producing the significant inactive dye precipitation effect.

SUMMARY

DSSC performance with a concentration of 20g/20mL produced the highest efficiency of 0.047%; this was also supported by the highest absorption of TiO_2/dye layers at a concentration of 20g/20mL. It can be suggest that many dye molecules attach to the TiO_2 surface at a concentration of 20g/20mL. However, the efficiency of DSSC decreased when the concentrations is more than 20g/20mL, it is because of the precipitation of dye on the TiO_2 nanostructure. This raises the number of inactive dye molecules on the surface of TiO_2. preventing the electron injection processes in DSSC.

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