

Optical properties of anthocyanin dyes on TiO₂ as photosensitizers for application of dye-sensitized solar cell (DSSC)

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Abstract. Dye-sensitized solar cell (DSSC) is one of the alternative energy that can convert light energy into electrical energy. The component of DSSC consists of FTO substrates, TiO₂, electrolyte, dye sensitizer, and counter electrode. This study aim was to determine the effect of optical properties of anthocyanin dyes on efficiency of DSSC. The dye sensitizer used can be extracted from anthocyanin pigments such as dragon fruit, black rice, and red cabbage. The red cabbage sensitizer shows lower absorbance value in the visible range (450-580 nm), than dragon fruit and black rice. The chemical structure of each dye molecules has an R group (carbonyl and hydroxyl) that forms a bond with the oxide layer. Red cabbage dye cell has the highest efficiency, 0.06% then dragon fruit and black rice, 0.02% and 0.03%.

1. Introduction

Dye-sensitized solar cell is a dye-based solar cell that converts photons energy into electrical energy by using semiconductor materials that have the wide band gap energy [1 – 4]. A DSSC is composed of a transparent conductive oxide substrate, a wide semiconductor, dye sensitizers, a counter electrode, and an electrolyte [5, 6]. The dye sensitizer plays a key role in developing the high performance of DSSC. It has been the subject of more recent studies as the efficiency of DSSC depends mainly on its properties such as the absorption spectrum, dye-to-TiO₂ charge transfer and the anchorage of the dye to the surface of TiO₂ [7 – 10].

One of the natural dyes used as a dye sensitizer is anthocyanin. Anthocyanin absorbance spectrum in the visible ranges (450-580 nm). Anthocyanin is a pigment that is red, blue, and purple on the fruits, flowers, and leaves. Pratiwi *et al.* using dragon fruits, red cabbages, and mangosteen peels as the dye sensitizer. Dragon fruit extract gave the lowest efficiency, despite the highest absorbance value [1]. This is due to the chemical structure of electrons reaction between the dye and TiO₂, which the difference is not well understood.

In this study, the dye sensitizer used can be extracted from anthocyanin pigments such as dragon fruit, black rice, and red cabbage. This study is expected to find the composition of the dye compounds in order to absorb light better and generate more efficient electrical energy.



2. Experimental

The materials used are natural dyes from dragon fruit, red cabbage, black rice, and spinach leaves. The anthocyanin dyes were dissolved in acetic acid: quads: methanol solvents. The substrates used Fluorine-doped Tin Oxide (FTO) glass with a size of 2.0 cm x 2.0 cm and active cell area of 1.0 cm x 1.0 cm. The working electrodes was coated using TiO₂ nanopowder by the spin coating method. The counter electrode was prepared from platinum on the FTO conductive glass.

Characterization by using UV-Visible Spectrophotometer 1601 PC to determine the wavelength of dye absorbance, Fourier Transform Infrared Spectrophotometer Shimadzu Prestige 21 to know the chemical bond of dye. The working electrode and counter electrode were assembled into a sandwich type arrangement. The electrolyte solution has filled the space between the two electrodes. *I-V* meter *Keithley* 2602A to determine the efficiency of the DSSC prototypes.

3. Results and Discussion

3.1. Optical Characteristics of Anthocyanin Dyes

The absorption characteristics of each sample using a spectrophotometer UV-Vis 1601 PC. Figure 1 show the plots of absorbance spectra from the anthocyanin dyes. Figure 1 is that the red cabbage shows lower absorbance in the visible range (450-580 nm), than the other dye. The absorption characteristics is a very important properties in DSSC as it directly reflects the optical transitions probability[11]. Anthocyanin dyes show absorption in the visible region, 450-580 nm. Anthocyanin can absorb light and transfer that the light energy by resonance energy transfers to the anthocyanin pair in the reaction center of the photosystems. Anthocyanin absorbs strongly in the red and violet regions of the absorption spectrum. The absorption peaks for anthocyanin dye solution from red cabbage, black rice, and dragon fruit are 533.5 530.5 nm; 526.5 nm; and 533.5 nm with the absorbance is 0.3091 a.u; 0.6259 a.u; and 0.3857 a.u, respectively. The absorbance value is influenced by the anthocyanin compound absorbed on the surface of TiO₂, where the anthocyanin compound is proportional to the absorbed light.

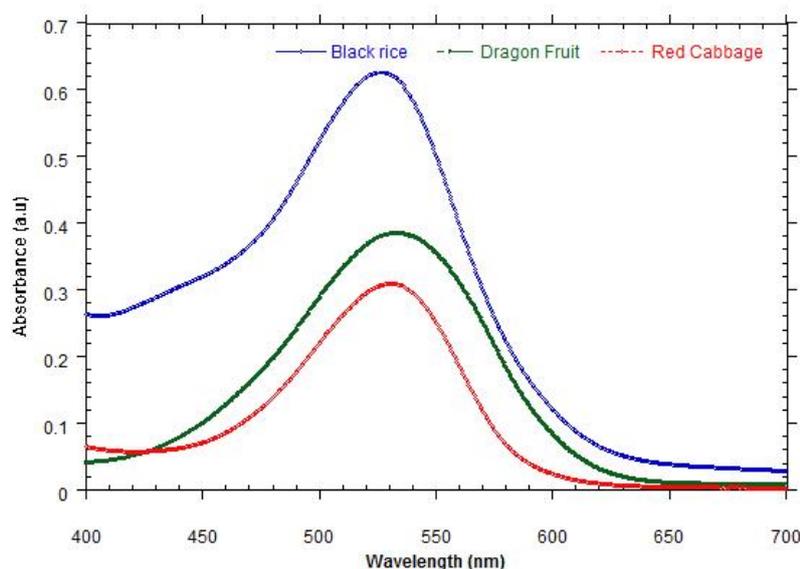


Figure 1. Absorbance spectra of anthocyanin dyes

3.2. Fourier Transform Infrared (FTIR) Characterization of Anthocyanin Dyes

Figure 2 shows the FTIR analysis to determine the functional groups on TiO₂ and TiO₂-dye. The spectra of TiO₂-dye red cabbage adsorption widened at wave number 3200-3600 cm⁻¹ is the stretching vibration of OH groups on the surface of TiO₂. The intensity dye of red cabbage had 92.3% than the other TiO₂-dye. This is due to the presence of hydroxyl groups forming intermolecular and intramolecular hydrogen

bonds. The dye of anthocyanin adsorbed on the surface of TiO_2 . The spectrum of FTIR shifted absorption wave numbers of TiO_2 and TiO_2 -dye are presented in Table 1. The intensity of TiO_2 nanoparticle is 57% thus the vibration of -OH stretching. The intensity of dye adsorbed on the surface of TiO_2 is 92.3% of red cabbage, 84.4% of black rice, and 76.1% of dragon fruit. The intensity of TiO_2 -dye occurred in the group of Ti-O-Ti are 67.8%, 38.89%, 35.8%, 38.4%, and 29%. This is due to the dye adsorbed on the surface of TiO_2 .

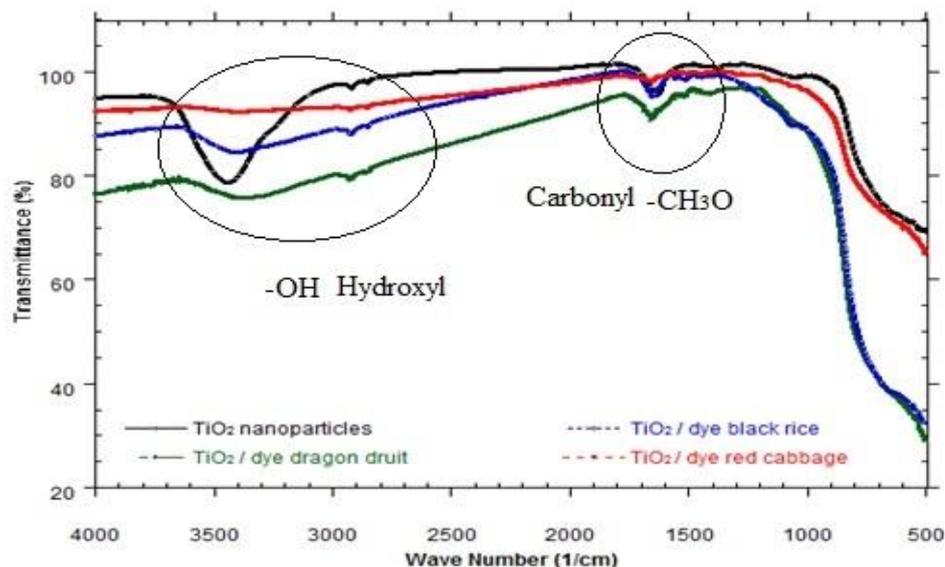


Figure 2. FTIR spectra of the dye from (a) TiO_2 nanoparticle, (b) TiO_2 -dye red cabbage, (c) TiO_2 -dye dragon fruit, and (d) TiO_2 -dye black rice

Table 1. Characterization of FTIR from anthocyanin dye and TiO_2

TiO_2		Absorption frequency (cm^{-1})				Assignment and remarks		
Peak	T (%)	Red Cabbage	Black Rice	Dragon Fruit				
Peak	T (%)	Peak	T (%)	Peak	T (%)	Peak	T (%)	
3444	57	3400	92.3	3415	84.4	3281	76.1	Ti-O-H
		2927	92.7	2924	88	2924	79.2	C-H
		2856	93.1	2855	89.4	2855	80.5	C=O
		1655	97.9	1654	95.17	1654	90.9	C=O
				1560	98.7			C=O
1640	89.2			1511	98.4	1512	95.2	C=C
						1410	95.7	C-H
		1290	99.3					C-O
		1152	98.3	1065	89.6	1017	89.1	
		709	74.1	656	38.5	584	35.4	
672	53.7	546	67.8	566	35.8	502	29	Ti-O-H

The result of spectra showed the different functional groups between the TiO_2 and TiO_2 -dye. The new absorption in TiO_2 -dye indicated the absorption from the dye adsorbed on the surface of TiO_2 . In the wave number at 3000-2700 cm^{-1} is a vibration of C-H stretching, which has two bonds and the wave number at 1655 cm^{-1} and 1654 cm^{-1} is the absorption of C=O stretching. The highest in spectra of FTIR is TiO_2 -dye red cabbage because this is due to the dye adsorbed on the surface of TiO_2 . The chemical structure of the dye of anthocyanin consisting of 7 hydroxyl flavyllium cations, these molecules function

in the absorption of light and form the natural. Anthocyanin color formed in the hydroxyl group (-HO) at position R₃ and always connected to the glucose molecule required for thermal equilibrium and the position of R₅ is one or more hydroxyl group or methoxyl (-CH₃O) in ring of B. The variety of colors shown by anthocyanin depends on the number and position of the group[12]. The widening of absorption occurs due to the reduction between the already-formed spectra. The reduced spectrum causes the breaking of the bonds of the reduced chains which then join the other bonds. Based on the result of a UV-Vis spectrum and FTIR spectrum it is concluded that the compounds are extracted of anthocyanin pigments.

3.3. I-V Characterization of DSSC

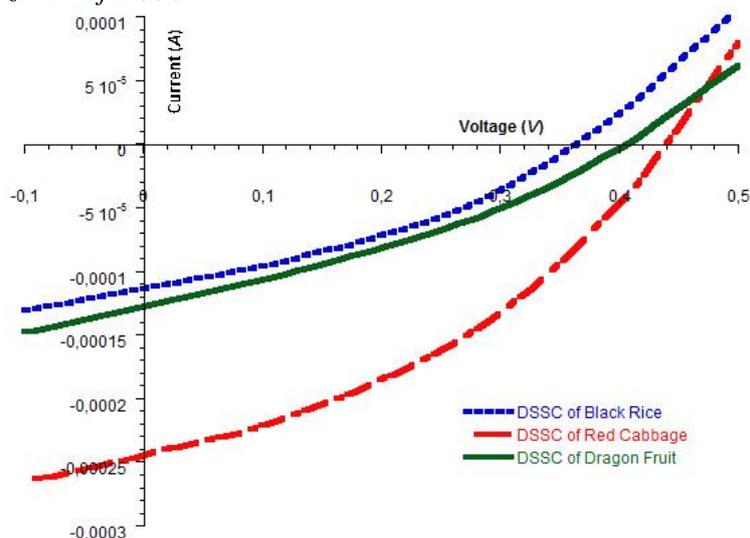


Figure 3. I-V characteristics of DSSCs with the anthocyanin dye

Table 2 and Figure 3 shows it can be seen that DSSC sensitized with black rice the lowest measured V_{oc} of 0.57 V. The black rice gave current densities value of 0.14 mA, this is the lowest value than the other dyes. The difference in the current densities of the cells may be attributed to the difference in the structure of the dyes, and how fast the charge is injected into the conduction band of the TiO₂ film[10]. The photo-energy conversion efficiency of red cabbage, black rice, and dragon fruit are 0.06%; 0.03%, and 0.02%, respectively. Red cabbage extract gave the highest efficiency, despite the lowest absorbance value. This may be the analysis of the chemical properties of the dye and electrons reactions between the dye and TiO₂. High efficiencies may be attributed to rich adsorption of dye molecules onto the TiO₂ particle. A nanoparticle of TiO₂ provided paths for the electrons while maintaining a low surface area for dye absorption. Therefore, availability of bonds between the dye and TiO₂ molecules through which electrons can transport from the excited dye molecules to the TiO₂ film has been reported to result in high efficiencies [9]. Table 2 show the I-V curve of a DSSC based on TiO₂-dye under irradiation of 1000 W/m², these include I_{sc} , V_{oc} , FF , dan η .

Table 2. Parameters of DSSCs with different anthocyanin natural dyes

Dyes	V_{oc} (V)	I_{sc} (mA)	FF	η (%)
Red Cabbage	0.6	0.21	0.46	0.06
Black Rice	0.57	0.14	0.3	0.03
Dragon Fruit	0.6	0.15	0.3	0.02

4. Conclusion

The dye of anthocyanin was used to make dye-sensitized solar cells. The absorption of dyes and attached to TiO₂ thin films in the visible region, 450-580 nm. The red cabbage extract gave the highest efficiency, despite the lowest absorbance value. The R groups in spectra of FTIR indicate that the presence of carbonyl and hydroxyl groups of substances. High efficiencies may be attributed to rich adsorption of dye molecules onto the TiO₂ particle.

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