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Potential of Purple Cabbage, Coffee, Blueberry and Turmeric as Nature Based Dyes for Dye Sensitized Solar Cell (DSSC)

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Abstract

Natural dyes extracted from purple cabbage, coffee, blueberry and turmeric were used as sensitizers to fabricate dye sensitized solar cells (DSSC). The dyes were extracted by using an ultrasonic extraction method by setting parameter of 30 °C at 30 minutes and 37 Hz. UV-Vis spectrophotometer is used to measure the absorbance of cocktail dyes which consist of purple cabbage and blueberry, turmeric and coffee that were extracted using ethanol and distilled water. From the result, the broadest spectrum between the extracted dyes is the cocktail dye from purple cabbage and blueberry which is in the range of 550 nm and having the lowest photon energy of 1.85 eV compare to the later. The result shows that, the combination of purple cabbage and blueberries as cocktail dye have good potential in future development of DSSC.

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Keywords: natural dyes; ultrasonic; extraction; spectrum; photon energy; purple cabbage; coffee; blueberry; turmeric

1. Introduction

Dye-sensitized solar cells (DSSC) are photoelectrochemical devices that convert visible light into electrical energy based on sensitization of wide band gap semiconductor. The typical configuration of DSSC consists of nanocrystalline titanium dioxide (TiO_2), dye molecule, an electrolyte which contains iodide/triiodide (I^-/I_{3-}) and counter electrode which acts as a catalyst for electron regeneration. Dye-sensitizer is important in absorbing sunlight and transforming it into electrical energy. The important parameters in enhancing the

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efficiency of DSSC are the absorption spectrum of the dye and its anchoring group that promotes efficient electron injection into the conduction band of TiO_2 which increases the conversion efficiency of DSSC [1].

So far, synthetic inorganic compound dyes such as Ruthenium (II) complex with carboxylated polypyridyl ligands are used as sensitizers in DSSC [2] and the conversion efficiency so far achieved is 11%-12% [3]. But due to expensive and tedious synthesizing method, nature based dyes from fruits and leaves are considered as a viable option to dye-sensitized due to low cost, abundant in resources and safe material handling. Dyes contain an important compound that forms a pigment which are essential in the DSSC efficiency calculation. Pigments from carotenoids, betalains, anthocyanins and chlorophyll are one of the major contributors to a pigment coloring. The highest DSSC efficiency for nature based dye by using mangosteen pericarp as much as 1.17% [3]. The single dye has less tendency to absorb all the light from the visible spectrum, so as an alternative is by mixing two different dyes to absorb in the lower and higher wavelength regions [14]. The combination of chlorophyll dye and anthocyanin dye brought better absorbability compared to N719 because different dyes give a different absorption wavelength due to the differences in composition and promotes conversion efficiency of DSSC [5].

Anthocyanin is a watery soluble substance and is commonly found in flowers, fruits and plants. The presence of carbonyl (C=O) and a hydroxyl group (OH) contained in anthocyanin can attach the dye with TiO_2 surface and stabilize the excited states and resulted the maximum absorption by having lower energy. Anthocyanin exhibit broad region of the visible light spectrum and attributed to charge transfer transitions [6].

Betalains represented the red-violet betacyanins and the yellow-orange betaxantins and one of water-soluble nitrogen which contained pigments. Most of Caryophyllales family contained betalains pigments which are in flowers, fruits and vegetative tissues of plants [7]. Betalains pigments absorb in the range of 476 nm to 600 nm in visible light spectrum and gained its color by reflecting red color wavelength [8].

The types of solvent in extracting the pigments from fruits and plants are important. Different types of solvents have been studied due to the effect of the absorption spectrum of the dyes as well as the bonding between the dyes and TiO_2 surface [9]. Ethanol as extract solvent in extracting nature based dyes shows a higher efficiency than using water as much s 0.71% and 0.52% [10]. Previous studies also have reported that by using ethanol and methanol as extraction solvents for C. fruticosa and P. Amaryllifolius leaves promotes a broad range of wavelength in between of 410 nm and 700 nm with three main peaks located at 530, 605 and 660 nm in visible light spectrum [9]. It is because of anthocyanin is more soluble in ethanol solution and less aggregation of the dye molecules compared to water. Water brings high dielectric constant because of bipolar and amphiprotic solvents which depends on its chain length [10]. So, the influence of extraction solvents has been investigated in this paper.

In this paper, four types of natural dye were extracted from purple cabbage, blueberry, coffee and turmeric. These extracted dyes from different extract solvent were characterized by UV-Vis Spectrophotometer to see the absorption spectra. Additionally, cocktail dyes from the combination of purple cabbage and blueberry as well as coffee with turmeric were also investigated. The photon energy of each dyes and absorption coefficient was studied.

2. Experimental details

2.1 Extraction of natural dyes

10 g of Blueberry's fruit is mixed in 15 ml of distilled water (DI) or 15 ml of ethanol at room temperature as the extract solvent. Blueberry's fruit is crushed using a mortar into small size. Place it into the ultrasonic cleaner for 15 minutes with the frequency of 37 Hz using Degas mode with the temperature of 30 ^{O}C for

extracting anthocyanin process. The extraction temperature should be below 50 ^{O}C because if the temperature more that, the stability of anthocyanin will be decreased because of the losses of glycosyl moieties and α-diketone formation [11]. After that, enter the solvents into a centrifuge machine for 25 minutes with 2500 rpm, shown in Fig. 1. 1.2 g of turmeric and coffee is mixed in 15 ml of distilled water (DI) or 15 ml of ethanol at room temperature as the extract solvent. Turmeric is crushing using mortar into small size. Place it into the ultrasonic cleaner for 15 minutes with the frequency of 37 Hz using Degas mode for extracting pigment from turmeric and coffee. After that, enter the solvents into a centrifuge machine for 25 minutes with 2500 rpm, shown in Fig. 2.

Fig. 1: Preparation of extraction of anthocyanin pigment for purple cabbage and blueberry

Fig. 2: Preparation of extraction of pigment in turmeric and coffee

2.2 Characterization and Measurement

The absorption spectra of the dyes were performed using Evolution 201 UV-Vis Spectrophotometer. UV-Vis spectrophotometer is used to measure the absorbance rate in visible light spectrum. The determination of the band gap of dye absorbed by TiO_2 surface is calculated by using formula in (1). Where h is the Planck's constant, v is the frequency, λ is the wavelength and c is the speed. The numerical values of the symbols are h = 6.63 x 10^{-34} Js, c = 3.0 x 10^{8} m/s, 1eV = 1.60 x 10^{-19} J and E stands for photon energy.

$$E = hv \qquad (1)$$

$$= \frac{hc}{\lambda}$$

The absorption coefficient determines how far into a material, light of a particular wavelength can penetrate before it is absorbed. The absorption coefficient of the respective wavelengths is obtained by the division of the absorbance with the wavelength shown in (2) using K boltzman constant;

$$absorption\ coefficient = 4\pi k/\lambda \quad (2)$$

3. Result and Discussion

3.1 Effect of solvent on extraction

Figs. 3 and 5 are shown the effects of solvents on the absorption spectra of purple cabbage (PC), blueberry (B), coffee (C), turmeric (T) and cocktail dyes from purple cabbage with blueberry (PC+B) and coffee with turmeric (C+T) extracted by using ethanol (Etha) and distilled water (DI). Form Fig. 5, the absorbance of PC and B shows a broad range of wavelength between 500 nm and 600 nm, which is located in the visible range spectrum with the peak value located at 550 nm and 520 nm. PC+B shows a broadest spectrum region compared to PC and B in the range of 450 to 650 nm. From the peak absorbance, this is good agreement in the presence of anthocyanin pigments showed in Fig. 4. The existence of a carbonyl group (C=O) and a hydroxyl group (OH) in anthocyanin can improve the conversion efficiency of dye-sensitized solar cell based on natural dye [12]. B-Etha has the highest peak absorbance compared to B-DI. PC-DI has the highest peak absorbance compared to P-Etha. PC, B and PC+B with ethanol have the highest absorption intensity compared with DI water. It is proven that the selection of the appropriate solvent is important in developing broad absorption spectrum and automatically can enhance the efficiency of DSSC [10]. Anthocyanin pigments having chemical adsorption that can be accepted to occur in the condensation of alcoholic-bound protons with a hydroxyl group on TiO_2 surfaces [3] and can enhance the conversion efficiency of DSSC. The surface of TiO_2 will be stabilizing from this bounding and the shift towards the lower energy of maximum absorption. Anthocyanin pigments also are water-soluble plant pigment that does not show their brilliant colors until they are accumulated in the acidic vacuoles and also absorb light at the longest wavelength.

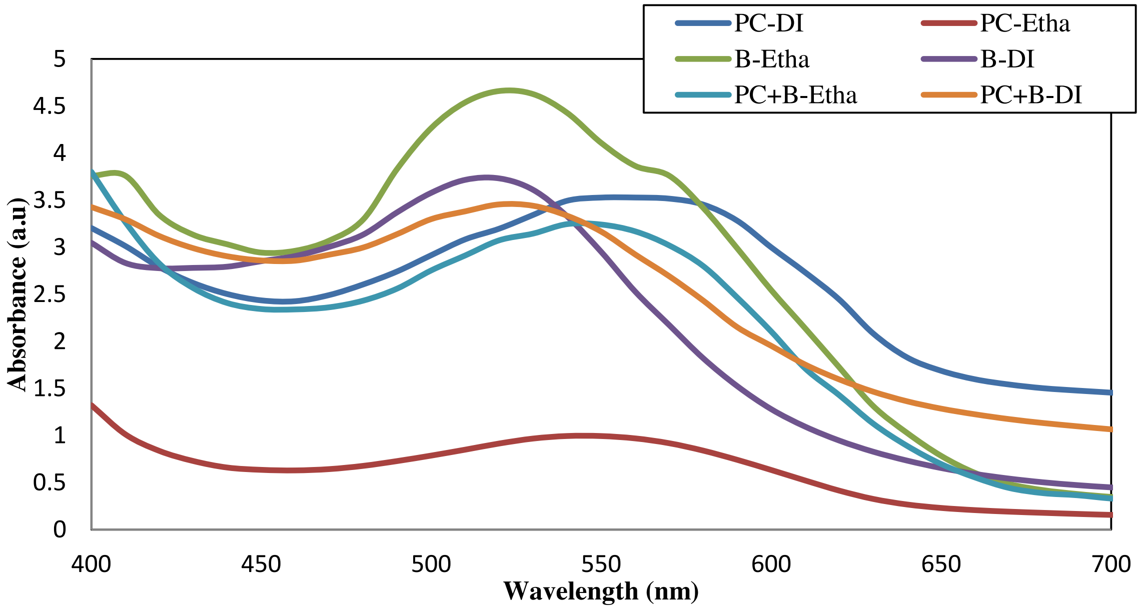

Fig. 3. UV-Vis absorption spectra of purple cabbage and blueberry extracted with ethanol and deionized water

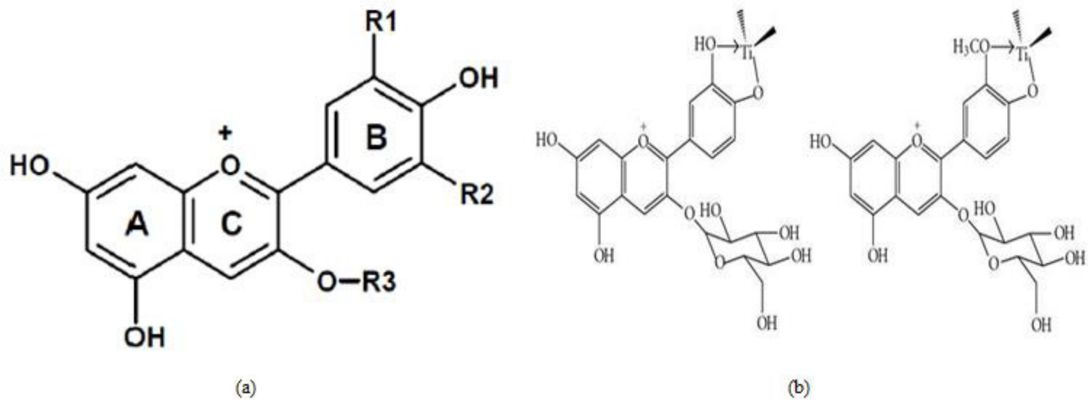

Fig. 4. (a) Structure of anthocyanin pigments; (b) The binding between anthocyanin molecule and TiO_2 particle [6]

Fig. 5 shows the UV-Vis absorption spectra of T, C and a mixture of both dyes (C+T) in ethanol and distilled (DI) water solution. From Fig. 7, absorption peak at T-DI and T-Etha can be seen at a wavelength of 480 nm with absorption range between 400 to 550 nm. The absorption peak of C-DI and C-Etha shows at the 480 nm and 450 nm. The highest peak of absorbance is obtained by cocktail dyes (C+T) located at 450 nm compared to single dyes with broad spectrum region between 400 to 550 nm. Single dyes are having a low absorbance rate, which means it can only utilize the light of several part of visible light spectrum.

From the peak absorbance which presented by T, C and C+T, the presence of betalains pigment have been proven. The betalains pigments shown in Fig. 6 include the red-purple betacyanins, (betanin (I) and betanidin

(II), which present the maximum absorptivity at λ_{max} about 535 nm, and the yellow betaxanthins with λ_{max} near 480 nm [13].

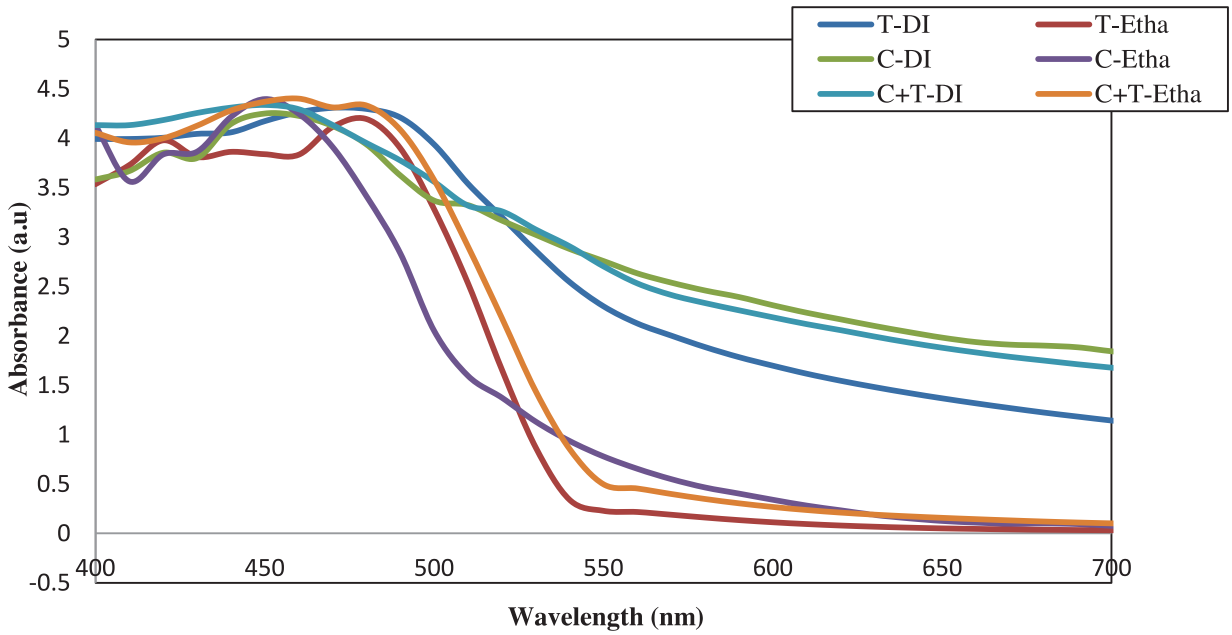

Fig. 5. UV-Vis absorption spectra of turmeric, coffee and cocktail dyes from turmeric and coffee extracts

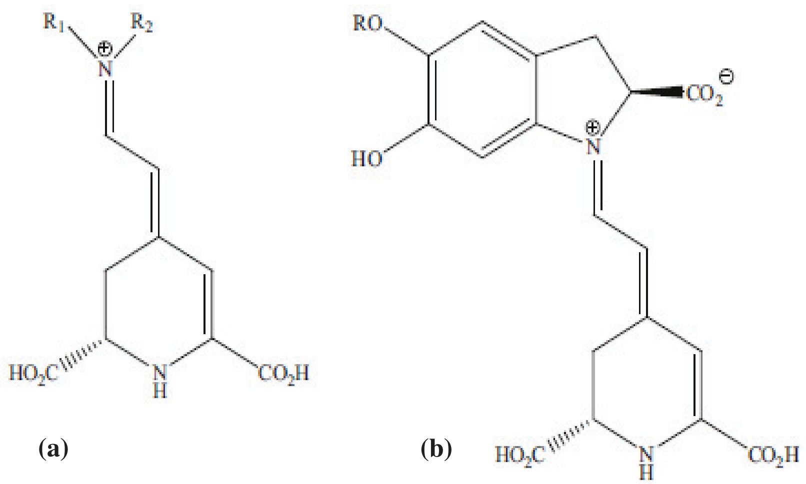

Fig. 6. General structures of the main betalains (a)betaxanthins (R1 = H and R2 = amine or amino acid group); (b) betacyanin (R = b-D-glucose) [14].

Fig. 7 show the suitable extract solvent for each dye. From this absorbance graph, all pigments can absorb light photons and lead to production of excited electrons which allows the TiO_2 conduction band with acceptable performance to increase the conversion efficiency of dye-sensitized solar cell [9]. Dyes which contained anthocyanin pigment have enough hydroxyl groups to bind with TiO_2 tightly and being able to inject electrons into the TiO_2 conduction band when excited with visible light [15].

The major problem of DSSC is low efficiency. It is due to the lack of available bonds between the dye and TiO_2 molecules which electrons can be transported from the excited state molecules in the TiO_2 film [16]. So, using these dyes will help the interaction between sensitizer and TiO_2 molecules are related in developing high conversion efficiency of DSSC.

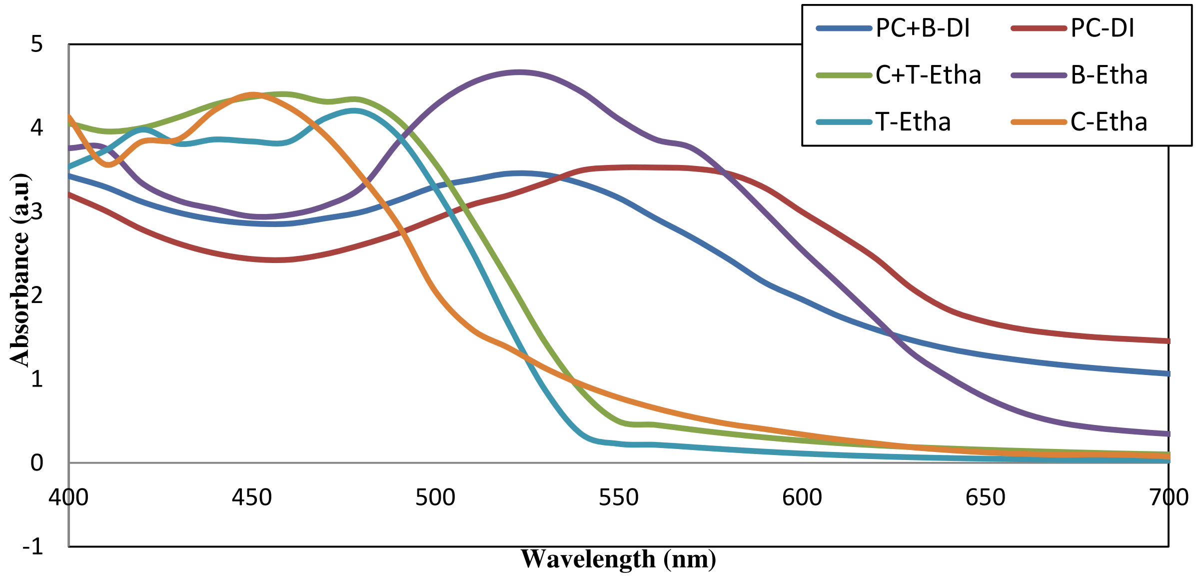

Fig. 7. Suitable extraction solvents for each dye

3.2 Bandgap estimation and absorption coefficient of the dyes

Between the conduction band and valence band, there is an energy difference which is called as energy band gap and used for analyzing the performance of DSSC which related to solar energy absorbed. Table 1 demonstrates the ethanol and DI water as extract solvents for each dye. For purple cabbage, blueberry, turmeric and cocktail dye from turmeric and coffee shows photon energy of 2.26, 2.39, 2.59 and 2.76 eV. Coffee extracted with DI water shows low photon energy of 2.59 eV compared to ethanol as high as 2.76 eV. The cocktail dyes from purple cabbage and blueberry extracted with ethanol has the lowest photon energy of 2.26 eV compared to DI water 2.35 eV.

Fig. 8 has shown the dependence of the absorption coefficient on the wavelength of the visible light spectrum for the dyes. The lowest photon energy was resulted from using cocktail dyes from purple cabbage and blueberry. These two dyes were mixed together and then was tested using UV-Vis Spectrophotometer to see the absorbance of dyes in the visible light spectrum and the result displayed peak absorbance of 550 nm and absorption coefficient of 1.97 k m^{-1}. A lowest band gap of dye helps the electron move fast from the valence band to the conduction band and only need less energy to the recombination of electrons. Cocktail dyes from purple cabbage and blueberry also have a broader region of the visible light spectrum compared with other dyes between the ranges of 450 to 650 nm, which mean it can absorb photon from sunlight at entire region. This is because of synergistic sensitization by the dye mixture extracted from single natural resources [15]. Two different dyes can enhance the absorption range due to composition and improve the photoelectric conversion efficiency [5].

Table 1. Photon energy and absorption coefficient (α) of the dyes

Dyes	Extract solvent	Peak Absorbance (nm)	Absorption range (nm)	Photon energy (eV)	Absorption coefficient (α) k m^{-1}
Purple cabbage	Ethanol DI water	550	500-600	2.26	1.97
Blueberry	Ethanol DI water	520	500-600	2.39	2.08
Cocktail dye (Purple Cabbage and Blueberry)	Ethanol DI water	550 530	450-650	2.26 2.35	1.97 2.04
Coffee	Ethanol DI water	450 480	400-550	2.76 2.59	2.41 2.26
Turmeric	Ethanol DI water	480	400-550	2.59	2.26
Cocktail dye (Turmeric and Coffee)	Ethanol DI water	450	400-550	2.76	2.41

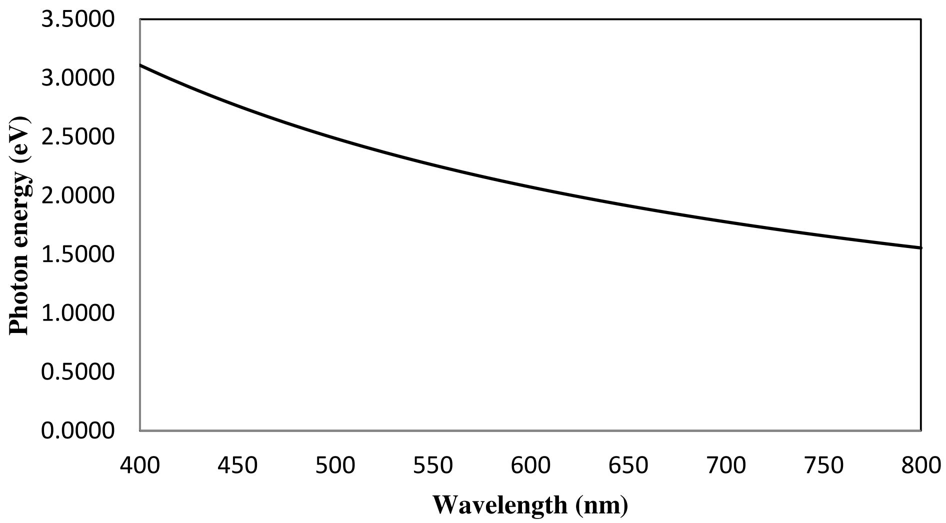

Fig. 8. Dependence of absorption coefficient on the wavelength of the dyes.

4. Conclusion

In this work, the adsorption characteristic for harvesting sunlight was investigated by using nature based dyes from purple cabbage, blueberry, turmeric and coffee using two different solvents of ethanol and DI water. As a result, cocktail dyes from purple cabbage and blueberry dissolved in ethanol showed a broader region of spectrum in the range of 450 nm to 650 nm respectively compared to DI water. This result may come from the fact that anthocyanin contained in the blueberry and purple cabbage more soluble in ethanol and less aggregation of the dye molecules compared to water. The lowest bandgap of cocktail dyes from purple cabbage with blueberry presented as 2.26 eV and well match with the wide bandgap semiconductors that used as photoanode in DSSC. A lowest band gap of dye helps the electron move fast from the valence band to the conduction band and only need less energy to the recombination of electrons and enhances the efficiency of DSSC respectively.

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