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COCKTAIL DYES FROM BLUEBERRY AND DRAGON FRUIT IN THE APPLICATION FOR DSSC

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ABSTRACT

This paper optically characterized anthocyanins and betalains pigments in blueberry and dragon fruit, respectively, to function as a dye sensitizer in dye-sensitized solar cell (DSSC).Ultrasonic extraction treatment was enforced to cocktail dye with a temperature, time and frequency rating of 30 ºC, 30 minutes and 37 Hz, respectively. Different extracting solvent from ethanol and distilled water were used to observe the absorption spectra by using UV-Vis absorption spectroscopy. Fourier transforms infrared (FT-IR) were used to characterize the functional components of dyes. From FT-IR spectra, cocktail dye represented the existing of carboxyl group correspond to the CO=OH stretching vibrations which is an important functional group in betalains pigment. From UV-Vis absorption spectra, the cocktail dye extracted with ethanol (M-Etha), compared to DI- water (M-DI) has the peak absorbance of 500 nm with broader absorbing range in visible light spectrum (450-600 nm). As for the photon energy, results show a narrow energy gap of 2.49 eV with higher absorption coefficient of 2.17 km^{-1}.

Keywords: anthocyanins, betalains, cocktail dye, carboxyl group, photon energy.

INTRODUCTION

Dye-sensitized solar cells was invented by MichealGratzel in 1991 as an alternative in solar cell development because of its specialty on simple fabrication, low cost and clean to the environment because used safer material in fabricating. Visible spectrum, which is near to ultraviolet and infrared can be captured and generate electricity (Gomesh *et al.* 2014). Dyes are important parameters in absorption of a photon of sunlight to generate electricity and its dye molecules will sensitize the wide-bandgap semiconductor (TiO_2) to the visible radiation (Hemalatha *et al.* 2012).

Natural dye which was extracted from various fruits and plant contained anthocyanin, chlorophyll, carotenoid and xanthophyll pigments and have been used in DSSC (Kim*et al.* 2013). Generally, dye sensitizer from Ru-containing complex will result in efficiency up to 11-12 % (Zhou *et al.* 2011) but due to high cost and long term unavailability, natural based dyes from fruits and leaves is proposed as an alternative to reduce the cost, high light-harvesting, simple fabrication, but at the same time is friendly to nature because it is free from contamination and natural dyes from fruits, plants and leaves have been used as an alternative to overcome this problem.

The dyes use as sensitizer influence the performance of DSSC from its absorption spectrum and the anchorage of the dye of the semiconductor surface. The presence of carboxyl and hydroxyl group in the dye would bind strongly onto TiO_2 surface due to the structure of the pigment will attach strongly to the TiO_2 surface (Al-Alwani *et al.* 2015).

Plant pigmentation such as anthocyanin, betalains and chlorophyll resulted from the electronic structure that can modify the wavelength due to its reactions. From the maximum absorption wavelength (λ_{max}), the pigment of natural based dye can be described (Ludin *et al.* 2014).

Anthocyanin is a pigment which is responsible to give the color of the fruits, plant and leaves in the range of purple-red ranges. Carbonyl and hydroxyl group contained in anthocyanin pigment bound onto TiO_2 surface and excite electron transfer from dye molecules to TiO_2 surface. Different sensitizing performance occurs due to extracted different plant. Chang and Lo used the extracts of anthocyanin from mulberry as sensitizers and the conversion efficiency showed about 0.548% and the dye cocktails from chlorophyll and anthocyanins represented the efficiency as much as 0.722%. The combination of dye can improve the conversion efficiency of DSSC (Chang and Lo, 2010).

Betalainsbelongs to the family of Caryophyllales which is the main chromophore is the betalamic acid. Betalamic acid has been categorized into the reddish to violet betacyanins and the yellow to orange betaxanthins (Oprea *et al.* 2012). The range of absorption in the visible light spectrum of betalains pigment in between 476 nm and 600 nm are corresponding to the betacyanins and betaxanthins and contained carboxyl group which promotes a stronger electron coupling bond. Several researchers developed betalains pigment in their researches by and the conversion efficiencies shows by using wild Sicilian prickly pear extract, basella alba rubra spinach and bougainvillea spectablilis were 1.26% (Calogero *et al.* 2010) 0.38% (Gokilami *et al.* 2015) and 0.46% (Hernandez *et al.* 2012).

Dragon fruit known as Hylocereusundatus is a tropical fruit popular in Southeast Asia, belongs to the climbing cacti (Cactaceae) family. Dragon fruit contained a lot of vitamin C and is said to aid digestion. Dragon fruit, also known as Pitaya or pitahaya grow on a veining epiphytic cactus (Hylocereus sp.) native to the tropical forest regions of Mexico and Central and South America (Merten, 2003). Blueberry on in scientific name called as the genus Vaccinium has a mostly circumpolar distribution with species in North America, Europe, Asia, and Africa. Blueberry on in scientific name called as the genus

Vaccinium has a mostly circumpolar distribution with species in North America, Europe, Asia, and Africa.
The type of solvent for extracting natural pigment from the plant is important because different solvent give a different sensitizing performance. The absorption spectrum and the pigment extracted from the plant are affected by the solvent.

In this paper, Cocktail dye (M) was extracted by using distilled water (M-DI) and ethanol (M-Etha) as extract solvents. These extracted dyes were characterized by UV-Vis Spectrophotometer to observe on the absorption spectra and FT-IR spectral analysis to determine the functional group in the nature dye.

Figure-1. (a) Dragon fruit, b) Blueberry.

DSSC components

The typical configuration of DSSC consists of two transparent glass coated with ITO (Indium Tin Oxide) to give the conductivity to the glass. The semiconductor material which is the TiO_2 (Titanium Dioxide), iodide/tiiodide (I^-/I_3^-) and the counter electrode. The main parameter in DSSC is the dye itself. The dyes should fulfill the requirement such as having an intense absorption in the visible light spectrum. Besides, the dyes must possess the =O or OH stretching vibrations to help the TiO_2 surface chelate with the Ti(IV) sites (Narayan, 2012).

Sensitizer

Sensitizer is used to absorb light and the electrolyte contains the iodide/tri-iodide redox-couple to provide electrons for the regeneration of oxidized sensitizer (Garcia *et al.* 2003). The sensitization approach allows the generation of electricity with irradiation of energy lower than the bandgap of the semiconductor which light absorbing dye molecules are adsorbed (Wongcharee *et al.* 2007). DSSC use ruthenium (II) polypyridinic complexes sensitizers of wide band gap semiconductors but due to costly and complicated in sensitizing the complexes also contain heavy metal and produce environmental pollution. So, natural dyes are used as a sensitizer, because they are cheap, renewable, non-carcinogenic, non-toxic and no associated disposal problems. Natural dyes are also abundant, easily extracted and safe materials. Anthocyanin is a pigment contained in Blueberry utilizes the sensitization of wide band gap semiconductor. Several colors such as purple-red range represent that anthocyanin gives colors to the flowers, fruit and leaves of plants. The carbonyl and hydroxyl groups will be bounded to TiO_2 surface and excite electron transfer from the sensitizer to the conduction band of TiO_2 surface.

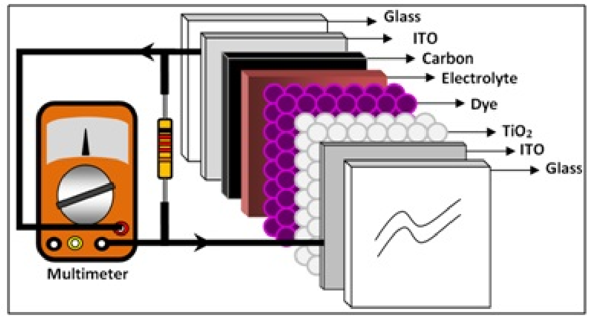

Figure-2. Cross section of DSSC.

Natural dye sensitizer

Anthocyanin

Anthocyanin is a pigment which utilizes the sensitization of wide band gap semiconductor. Several colors such as purple-red range represent that anthocyanin gives colors to the flowers, fruit and leaves of plants. The carbonyl and hydroxyl groups will be bonded to TiO_2 surface (Figure-3) and excite electron transfer from the sensitizer to the conduction band of TiO_2 surface (Figure-4).Anthocyanins display a broad absorption band in the visible region due to charge transfer transitions from HOMO (Highest occupied molecular orbital) to LUMO (Lowest unoccupied molecular orbital). Anthocyanin's adsorption onto TiO_2 surface produces strong complexes displayed prevalently the quinonodial form which ascends from –OH (or =O) groups and Ti(IV) sites on semiconductor Nano crystalline layer. Anthocyanin from various plants also gave a different sensitizing performance. Besides that, by using dyes which have a broad absorption band, the solar cell is capable to harvest a large fraction of sunlight and its effect to have a good fill factor.

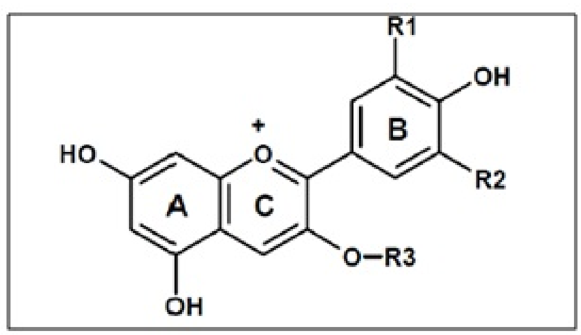

Figure-3. Structure of anthocyanin pigments (Alhamed *et al.* 2012).

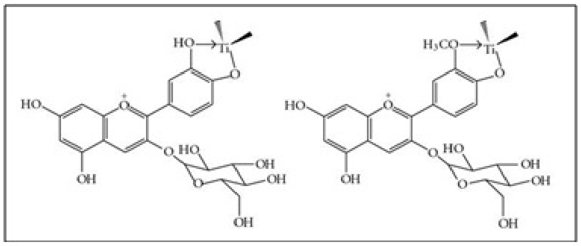

Figure-4. The binding between anthocyanin molecule and TiO_2 particle (Alhamed *et al.* 2012).

Betalains pigment

Betalains is a pigment which has favorable light absorbing and capable of complexing metal. The existence of betalains pigments in the fruit will present the functional group of (-COOH) to bind with TiO_2 surface. The betalains pigments (Figure-5) 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.

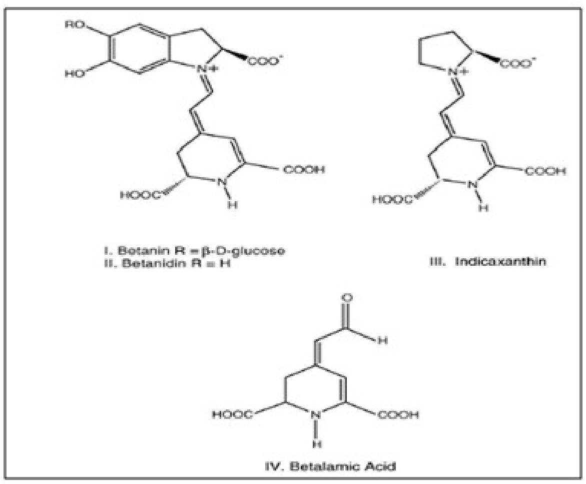

Figure-5. Betalain pigments (Zhang *et al.* 2008).

Previous research on Natural dye as sensitizer

Natural dyes from fruits, plant and leaves have the potential to be used as sensitizer for DSSC. Recently, H. Chang *et al.* reported that by using spinach as sensitizer, the conversion efficiency is about 0.131% and ipomea conversion efficiency is higher compared to spinach which is 0.278% (Chang *et al.* 2010). En Mei Jin *et al.* found by using wormwood as natural sensitizer, the efficiency achieved is 0.9% compared to bamboo only 0.7% and maple is 0.4% (Jin *et al.* 2010). Ho Chang *et al.* employed purple cabbage as sensitizer and efficiency achieved is 0.75% (Chang *et al.* 2013). A. I. Babatunde *et al.* investigated extract from Lonchocarpuscyanescens as natural sensitizer produced conversion efficiency of 0.37% (Babatunde *et al.* 2012). S. Tekerek *et al.* discovered by using Black Carrot as natural dye, the efficiency is 0.25% higher than Rosella and Black Rasberry which is only 0.16% (Tekerek *et al.* 2011). M. Tripathi *et al.* used Punicagranatum as natural sensitizer, and the performance of conversion efficiency shows 1.86% compared to chlorophyll, bixin, and anthocyanin (Tripathi *et al.* 2013). G. Calogero *et al.* showed when using wild Sicilian prickly pear, the conversion efficiency is 1.26% much lower compared to red turnip is 1.7% (Calogero *et al.* 2010). A. R. Hernandez-Martinez *et al.* investigated that using purified Bougainvillea Glabra obtained conversion efficiency as much as 0.49% compared to Violet Bougainvillea spectabilis which is only 0.35% [Hernandez *et al.* 2011).

MATERIALS AND METHOD

Extraction method of natural dye

10 g of Blueberry's fruit and dragon fruit is mixed into 15 ml of Distilled water (DI) or 15 ml of ethanol with the ration of 1:1 at room temperature as the extract solvent. Blueberry's fruit and Dragon fruit are mesh using a mortar into paste. 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 and betalains pigment process. All the procedure has shown in Figure-6 and Figure-7. After that, enter the solvents into centrifuge machine for 25 minutes with 2500 rpm. All complete dyes have shown in Figure-8(a) and Figure-8(b).

Figure-6. Preparation of natural dye.

Figure-7. Preparation of natural dye.

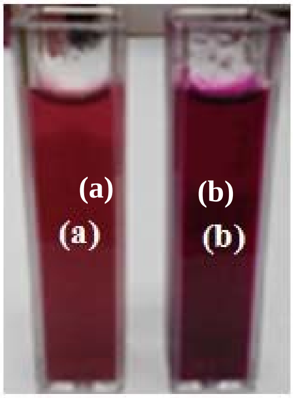

Figure-8. a) M-DI b) M-Etha.

Characterization and measurements

The absorption spectra of the dyes were performed using Evolution 201 UV-Vis Spectrophotometer has shown in Figure-10. UV-Vis spectrophotometer is used to measure the absorbance rate in visible light spectrum. The sample of dyes is refilled into cuvette and place in sample holder. The procedures to test the liquid sample are stated on (Gomesh *et al.* 2014). The determination of the band gap of dye absorbed by TiO_2 surface is calculated by using formula in Eq. (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.

$$E = \frac{hc}{\lambda} \tag{1}$$

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 Eq. (2) using K boltzman constant; where λ stands for the cutoff wavelength of the dyes and K is the Boltzman constant with the value of 8.617 3324×10^{-5} eV.

$$Absorption\ coefficient = \frac{4\pi K}{wavelength\ (\lambda)} \tag{2}$$

RESULTS AND DISCUSSION

FT-IR Spectra

Identification of the functional group for active compound is measured by using FT-IR spectra based on the peak values in the region of IR radiation. Figure-9 shows the FT-IR spectra of cocktail dyes diluted with ethanol (M-Etha) and distilled water (M-DI). For M-Etha, the two peaks located at 1090 and 1047 cm^{-1} are attributed to esters group which having C-O stretching vibrations. The peak at 1442 cm^{-1} corresponds to alkanes group contained H-C-H bend. The peak at 1667 cm^{-1} contained C=O stretch represented the presence of carbonyl group. The peak at 2990 cm^{-1} represents the alkanes group which having H-C-H asymmetric and symmetric stretch. The peak at 3417 cm^{-1} corresponds to the O-H stretching vibration.FT-IR spectra of M-DI shows the peak at 1661 cm-1 contained C=O stretch. The peak at 3415 cm-1 corresponds to the O-H stretching vibration. The present of C=O which is carbonyl group and O=H stands for hydroxyl group in cocktail dye represented the carboxylic acid group in Betalains pigment which is well matched with the UV-Vis absorption spectra.

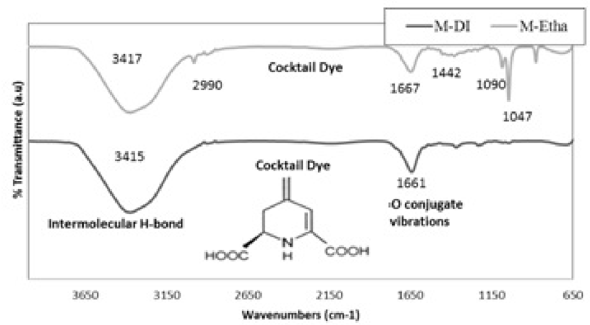

Figure-9. FTIR spectrum of M-DI and M-Etha.

Absorption Spectra

Figure-10 represented the result of absorbance spectra by using UV-Vis Spectrophotometer of the cocktail dyes from blueberry and dragon fruit from different extract solvent which is ethanol and distilled water in the visible light spectrum (400-700 nm). The cocktail dye extracted with ethanol (M-Etha) compared to DI water has the highest absorbance with the range of 450-650 nm and has the highest ability in absorbing photo from sunlight and was chosen to be employed as a dye for DSSC.

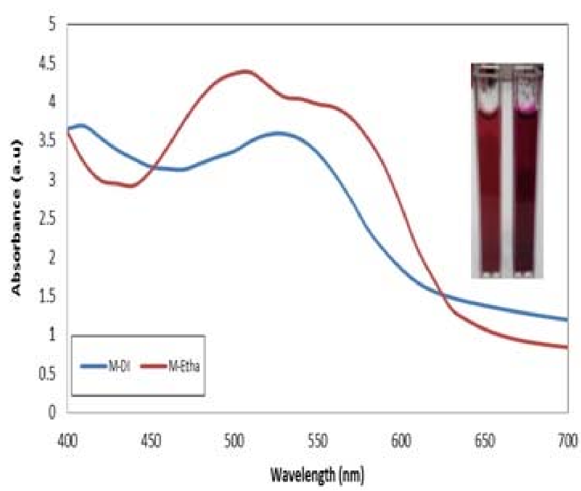

Figure-10. Absorption spectra of M-DI and M-Etha.

Optical Characteristic Nature Dyes

Table-1 shows the photon energy and the absorption coefficient (α) of the dyes with different extract solvent from DI water and ethanol. From the table, the photon energy and higher absorption coefficient (α) is when extracted the cocktail dyes with ethanol, which is about 2.49 eV and 2.17 k m-1. Figure-10 shows the dependence of the absorption coefficient on the wavelength of the dye.

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

Dyes	Extract solvent	Functional group of dye	Peak Absorbance (nm)	Absorption range (nm)	Photon energy (eV)	Absorption coefficient (α) k m^{-1}
Cocktail dyes	Ethanol	CO=OH	500	450-650	2.49	2.17
	Distilled water		530	500-600	2.35	2.04

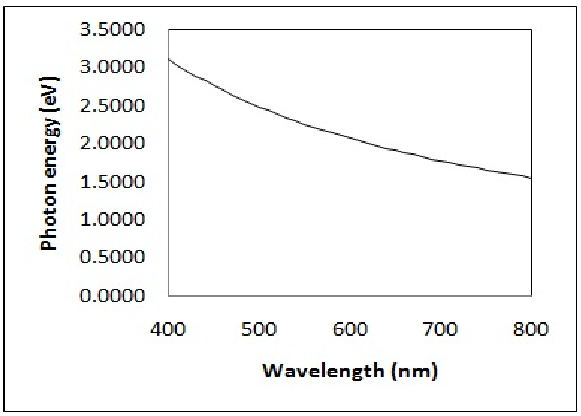

Figure-11. Dependence of absorption coefficient on the wavelength of dye.

CONCLUSIONS

In summary, the cocktail dye which is extracted from Blueberry and Dragon fruit was successfully used as light harvesters in Dye-sensitized solar cell (DSSC). The result from UV-Vis absorption spectra and the FT-IR spectra are measured to characterize the ability of the dye to absorb photon in visible light spectrum and identify the functional group of the active components present in extracting dye. The existing of carboxylic acid group has a reversible binding with high equilibrium binding constant that can establish the photosensitizer with TiO_2 surface in DSSC. The broad region of absorption spectra in the range of 500-600 nm proven that the cocktail dye can absorb photon in the visible light spectrum.

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