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Spectroscopy Characterization and Optoelectronic Analysis of Dragon Fruit Peels and Black Grape Blend in the Electronic Application

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ABSTRACT: This project optical characterization for natural dyes of betalains and anthocyanin in blend of dragon fruit and black grape, respectively, to function as dye sensitized solar cell DSSC. Different of solvent extracting from deionized water and methanol used to observe the absorption spectra by using UV-visible spectroscopy. Ultrasonic extraction treatment imposed to blend dye with parameters of temperature of 60 °C and time of 45 min, respectively. UV- visible absorption spectra, the blend dye extracted with methanol (Blend-Methanol), compared to deionized water (Blend-DE) has the peaks absorbance of 325, 545 nm with wide absorbing range in visible light spectrum 300-600 nm. As for the photon energy, results show an energy band gap of 2.9 eV with the higher absorption coefficient of 3.4 k.m^{-1} . FT-IR Fourier transforms infrared used to study characterize the functional groups of dye. FTIR spectra, of blend dye represented the existing of carboxyl group correspond to the C=O stretching vibration bonds which is an important functional group in the betalains dye of dragon fruit.

KEYWORDS: Anthocyanin, Betalains, Natural dyes, Optical analysis, Electronic devices.

I. INTRODUCTION

The dye sensitized solar cells were created by Michael Grätzel 1991 as an alternative in solar cell development because its specialty on simple fabrication, low cost and clean to the environment because used safer material in fabricating. The visible spectral, which is approach to ultraviolet and infrared can be generate electricity [1]. Dyes are important parameters in absorption of photon energy of sunlight and its dye molecules will sensitized the broad bandgap semiconductor to the visible spectrum [2]. Natural dye which was extracted from various natural fruits and plant contained anthocyanin, chlorophyll, carotenoid dyes and have been used in DSSC [3]. 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 nanoparticles oxide materials as TiO_2 layer [4]. The leaves of plants pigmentation in type of chlorophyll, betalains and anthocyanin, resulted from the electronic structure that can modify the wavelength due to its reactions. Anthocyanin is a dye which is responsible to give the color of the fruits, and plant in the range of purple-dark red ranges. The groups of carboxyl and hydroxyl contained in anthocyanin bound onto Titanium Oxide layer and excite electron transfer from dye to oxide layer. Lo and Chang used the extract of anthocyanin from berries as sensitizers and the efficiency showed about 0.5% and the dye blends from chlorophyll and anthocyanins represented the efficiency as much as 0.7%. The combination of dye can improve the of dye sensitized solar cell [5]. The absorption range in the visible light spectrum of betalains dye 300-600 nm are corresponding to the betacyanin and contained carboxyl group which promotes a stronger electron coupling bond. A lot of researchers developed betalains dye in their researches by the efficiencies of DSSC shows by using spinach and bougainvillea were 0.3% [6], and 0.42% [7]. Dragon fruit known is a tropical fruit existed in Southeast Asia, belongs to the climbing cacti family. Dragon fruit, also known as pitahaya fruit grow on a veining epiphytic cactus native to the tropical forest regions of South America [8]. Black Grape in scientific name called as the genus has a mostly circumpolar distribution with species in Asia. The type of solvent for extracting of natural dyes from the plant and leaves is important because different solvent give a different sensitizing performance. In this work, the blend dye of Dragon fruit and Black Grape were extracted by using methanol and deionized water DE as extract solvents. These extracted dyes were study characterized by UV-vis Spectroscopy to observe on the absorption spectrum and FT-IR spectral analysis to determine the assigned functional groups in the natural dye.



Figure1. Dragon fruit and black Grape.

II. EXPERIMENTAL PROCEDURES

1. Dye Sensitizer Solar Cells DSSC Components:

The semiconductor material such as the Titanium Oxide. The main factors in DSSC is the dye itself. A typical structure of DSSC consists of two-layer transparent glass coated with ITO to give the conductivity. The dyes should accomplish the requirement such as having an intense absorption in the visible spectrum. In addition, the dyes must have the C=O or O-H stretching vibrations to contribute with TiO₂ layer [9]. The sensitization approaches allow the generation of electricity with irradiation of energy lower than the bandgap of the semiconductor material which light absorbing dyes are adsorbed [10]. The natural dyes are used as a sensitizer, because they are cheap, renewable source, and non-toxic. Natural dyes are also easily extracted and safety materials. Anthocyanin is a dye existing in Black Grape and other red fruits utilizes as the sensitization of wideband gap semiconductor. Several colors such as purple-red range represent that anthocyanin gives colors to the fruit and other plants.

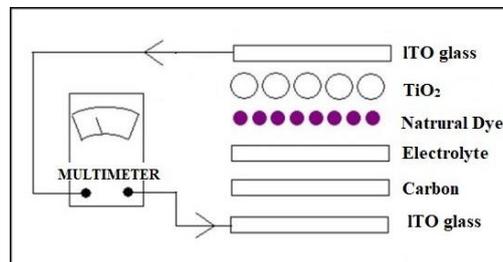


Figure2. Typical structure of dye sensitizer solar cell DSSC.

2. Natural dyes sensitizer of Anthocyanin and Betalains:

Anthocyanin is a dye which utilizes as sensitization of a wideband gap semiconductor. Several dyes in the range of purple-red represent that anthocyanin gives colors to the fruit. The carboxyl and hydroxyl groups as show in Figure.3 and excite free electron transfer from the sensitizer to the conduction band of oxide layer. Anthocyanins display an extensive absorption band in the visible light due to the electrons transitions from HOMO to LUMO energy level. Anthocyanin's adsorption onto oxide layers produces strong complexes exhibited commonly which arise from =O or O-H groups sites on semiconductor layer. Anthocyanin from various plants also gave a different sensitizing performance [11]. Besides that, by using natural dyes which have an extensive absorption band, the solar cell is able to harvest a large fraction of sunlight and its effect to have a good fill factor.

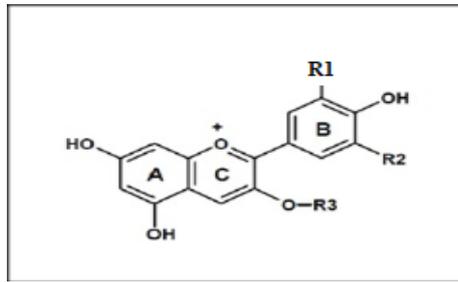


Figure3. Anthocyanin dye structure [11].

Betalains is a nature dye which has favorable light absorbing and capable of complexing metal. The existence of betalains dyes in the fruit will present the functional group of $-COOH$. Betalains dyes in Figure-4 include the purple-red betacyanin's.

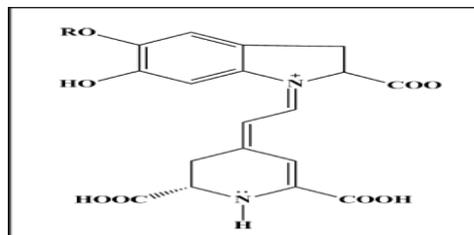


Figure4. Betalains dye structure[12].

III. MATERIALS AND METHOD: EXTRACTION METHOD OF NATURAL DYES

About 10 g of Dragon fruit and Black Grape is blended into 25 ml of Methanol solution or Deionized water (DE) at room temperature as the extract solvent. Black Grape's and Dragon fruit are mashed into paste using a mortar. The blend is cleaned by ultrasonic for 45 min with a temperature of $60^{\circ}C$ for extracting anthocyanin and betalain dyes. The procedure is shown in Figure.5(a) and Figure.5(b). After that, the solvents are entered into a centrifuge machine for 45 min with 2500 rpm.



Figure 5(a). Preparation of natural dye.



Figure 5(b). Blend-DE, Blend-Methanol.

The absorption spectrum of the dyes was performed using CECIL UV-Vis model (CE7200). A UV-vis Spectrophotometer is used to measure the absorbance range in the visible light region. The sample of dyes is refilled into place in the sample holder. The evaluation of the band gap energy for dye absorbed by the oxide layer surface is computed by using



formula in Eq. (1). Where h is the Planck's constant, ν is the frequency, λ is the wavelength and c are the light speed. The numerical values of the symbols are: $h = 6.634 \times 10^{-34}$ Js, $c = 3 \times 10^8$ m/s, photon energy E :

$$E = \frac{hc}{\text{wavelength}(\lambda)} \quad (1)$$

The absorption coefficient α determines how far into a material, light of a particular wavelength can penetrate before it is absorbed. The absorption coefficient α of the respective wavelengths is obtained by the division of the absorbance with the wavelength shown in Eq. (2) using constant of λ for the wavelength of the dyes and K is the Boltzmann constant with the value of 8.617×10^{-5} eV.

$$\alpha = \frac{4\pi k}{\text{wavelength}(\lambda)} \quad (2)$$

IV. RESULTS AND DISCUSSION

Figure.6(a), 6(b) represented the result of absorbance spectrum by using UV-Vis Spectrophotometer of the blend dyes from dragon fruit and black grape from various solvent which is methanol and deionized water DE in the visible light spectrum 400-800 nm. The blend dye extracted with blend-Methanol compared with blend-DE water has the highest absorbance with range of 325-545 nm and has the highest ability in absorbing photon energy from sunlight and was a good chosen to be employed as a pigment for DSSC dye sensitizer solar cell.

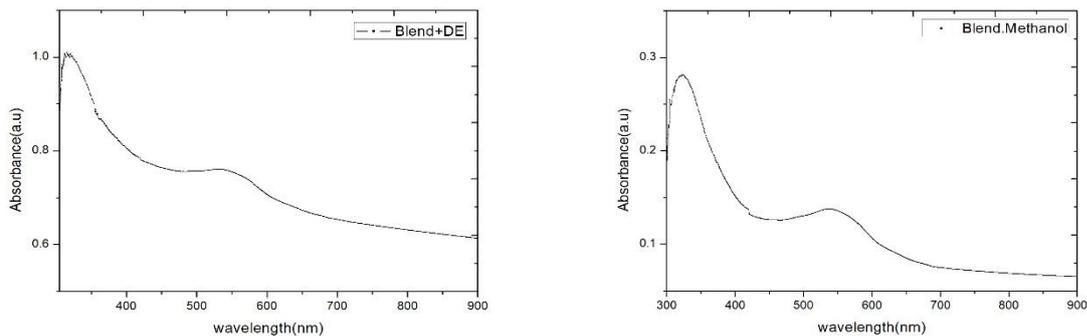


Figure 6(a). Absorption spectra of Blend-DE. Figure 6(b). Absorption spectra of Blend-Methanol.

Optical properties as shown in Table 1, the photon energy and the absorption coefficient α of the nature dyes with different extract solvent from methanol and deionized water. From Table 1, the photon energy and absorption coefficient are good values when extracted the blend dyes with Methanol solvent, which is about 2.9 eV and 3.41 km^{-1} . Figure 7(a), 7(b) shows the photon energy of blend dyes with various extract solvent used as Methanol or DE water.

Table 1. Optical Characteristic of the nature dyes.

Dyes	Solvent	Peak Absorbance (nm)	Absorption range (nm)	Photon Energy (eV)	Absorption Coefficient α (km^{-1})
Blend Dyes (Dragon fruit+ Black grape)	Deionized water	320, 540	300-600	2.88	3.0
	Methanol	325, 545	300-600	2.9	3.41

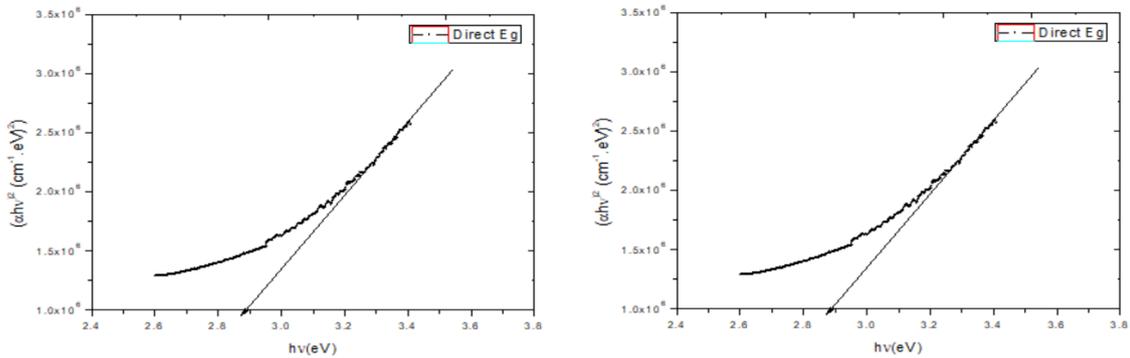


Figure.7(a).Photon energy of Blend-DE.Figure.7(b).Photon energy of Blend-Methanol.

FT-IR spectrometer model 4200 JAS.CO, was used to measure an assigned functional group for active compound depending on the peak values in the region IR-spectra. Figures. 8(a),8(b) shows the FT-IR spectrometer of blend dyes dissolved with DE water and Methanol respectively. FT-IR spectra of blend-DE shows the peak at 1639 cm^{-1} contained C=O stretching vibration. The peak at 2081 cm^{-1} represented to C=O stretching bond. The peak at 3435 cm^{-1} corresponds to the O-H stretching vibration. The peaks contained wide of stretch vibrations C=O represented the presence of carbonyl groups and O=H stands for hydroxyl groups in Betalains dye which is well showed with UV-Vis absorption spectra. For blend-Methanol, the two peaks situated at 1050 cm^{-1} are attributed to esters group which having C-O stretching vibrations. The peak at 1637 cm^{-1} contained C=O stretch represented the presence of carbonyl group. The peak 3417 cm^{-1} corresponds to the O-H stretching vibration.

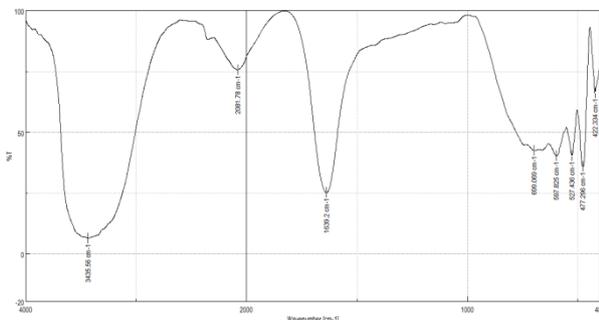


Figure.8(a).FT-IR spectrum of Blend-DE.

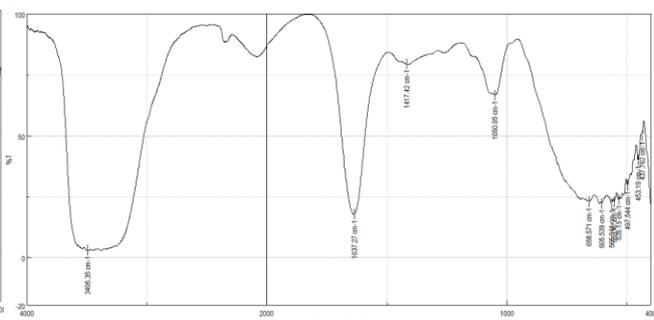


Figure.8(b).FT-IR spectrum of Blend-Methanol.

V. CONCLUSIONS

In abridger, absorption spectra UV-vis and FT-IR spectra are measured to study the optical characteristics of the ability of the dyes to absorb photon in the range of visible light region and associated the functional groups of the active components present in extracting dye. The existing of carboxyl groups has a reversible binding with high equivalence binding constant that can be established the photodetector with presence of oxides materials in the DSSC dye sensitized solar cells. The wide region of absorption spectra in the range of 300-600 nm proven that the blend dye can absorb photon in the visible light spectrum. The blend dyes which are extracted from Dragon fruit and Black Grape were successfully used as light acceptors in electronic applications of dye sensitized solar cell DSSC.

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