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Studies on the Optical and Photoelectric Properties of Anthocyanin and Chlorophyll as Dihybrid Sensitizer in Dye Sensitized Solar Cell (DSSC)

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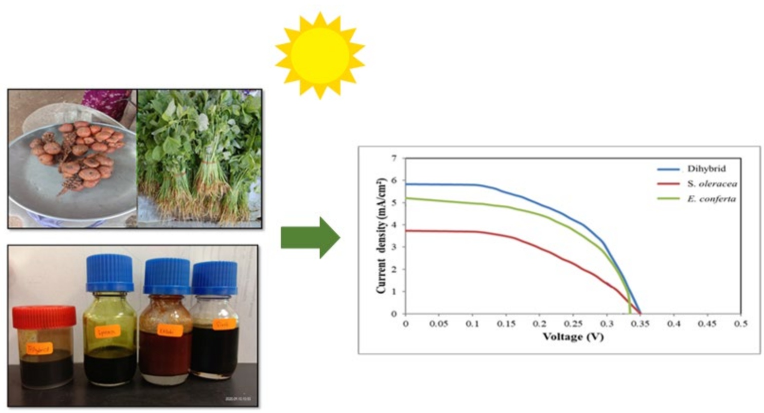
The production costs and energy conversion efficiency of dye-sensitized solar cells (DSSC) is strongly influenced by the types of dyes used to harvest photons. Natural dyes extracted from different pigments are emerged as a potential dye to enhance the efficiency of DSSC due to their merit properties such as low cost, biodegradable and less environmental concern. Natural pigments were derived from *Eleiodoxa conferta (E. conferta)* and *Spinacia oleracea (S. oleracea)* and formation of a mixture of these extracts in (1:1) volume ratio. The dihybrid extract displayed a diverse UV-vis absorption spectrum of 530–550 nm with maximum absorption at ~539 nm. The optical features of the harvested dyes and the photovoltaic productivity of the cells have been explored. The photovoltaic output of the dihybrid delivered the best findings with open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), fill factor (FF) and energy conversion efficiency values of 0.35 V, 5.83 mA/cm^2, 0.63 and 1.29 % respectively.

Graphical abstract



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1. Introduction

Nowadays, many options in seeking renewable energy sources to substitute fossil fuels today due to the increases in the current energy supply. Wind, water, biomass, and geothermal energy are examples of renewable energy. However, many of these sources cannot be used widely due to high production costs and unable to sustain the environment due to the pollution that have been generated by these sources. Therefore, to overcome these issues, solar energy was selected for being able to address domestic concerns related with energy demand. Due to the low cost solar cell technology [1-6], dye-sensitized solar cells (DSSCs) are getting more attentions. Simple preparation procedure, eco-friendly [7], good performance under diffuse light conditions, reasonably good power conversion efficiency [8-9], colourful natures, and low production cost [10-12] are the factors that gain attentions to investigate more of DSSCs.

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Sensitizers plays important roles in DSSC for capturing photons and converting to electricity. In sensitizers, absorption of dye and the pigment binds to photoanode is the most important criteria to investigate. Ruthenium dye (N719) is one of the examples using metal compounds and organic dyes for sensitization. However, the complexing of the synthesis process and high production cost contributed to the finding of new sensitizers using natural resources [13-14]. Natural dyes have been selected widely due to their potentials such as harmless, easy to fabricate and biodegradable.

In this research, Eleiodoxa conferta (E. conferta) and Spinacia oleracea (S. oleracea) that represent contain anthocyanin and chlorophyll pigments, respectively, have been used as the source of sensitizers. Different types of plant species produced different chemical composition of pigments and affect to the binding energy towards ZnO surface [15].

Even though, natural dyes are one of alternating ways to decrease to production cost, performance of DSSC photovoltaic properties still smaller than other solar cell generations. To overcome these issues, natural dyes from different plant resources were selected as sensitizers and modify the Lowest Unoccupied Molecular Orbital (LUMO) and Highest Occupied Molecular Orbital (HOMO) that match with the conduction band (CB) of ZnO. Moreover, natural dye also is easy to fabricate, low cost and able to sustain our environment. Another important thing needs to be considered is CB must match with lowest excited state of the sensitizer for effective electron transportation from molecule excited state to the semiconductor conduction band for efficient charge transportation and prevent for recombination tends to happen [16].

2. Results and Discussion

Based on Figure 1a, *E. conferta* result showed the presence of anthocyanin pigment that similar with another researcher [17-19]. Broad absorption peak at 3335 cm^{-1} indicated -OH peak that contains in anthocyanin pigment of *E. conferta*. At peaks 2974 cm^{-1} and 2930 cm^{-1} indicated the $-CH_3$ and $-CH_2$ stretching vibrations. At peak 1719 cm^{-1} showed that C=O and 1379 cm^{-1} was classified the deformation of -CH group. Meanwhile, at peaks 1395 cm^{-1} and 1271 cm^{-1} due to the C-O vibrations.

Figure 1b shows the existence of chlorophyll in spinach extracts. The wide broad peak at 3323 cm^{-1} indicated the OH bending mode due to the ethanol involvement. At peaks 2972 cm^{-1}, 2927 cm^{-1}, 1379 cm^{-1} and 1045 cm^{-1}, respectively belongs to $-CH_3$ elongation of aliphatic groups, $-CH_2$ elongation absorptions, $-CH_3$ deformation vibrations, twisting modes of the C–OH alcoholic group and C–O single bond excitations respectively.

C-O absorption band appeared at peaks 1044 cm^{-1} and 1272 cm^{-1} while C=O bending mode at peak 1718 cm^{-1} in Figure 1c. These functional groups indicated the presence of anthocyanin and chlorophyll pigments [20]. The wide band at peaks 3326 cm^{-1} was credited to -OH stretching. CH bending configurations were appointed at peaks 2973 cm^{-1} and 2927 cm^{-1} and at peak 1380 cm^{-1}, uneven CH displacement functionalities of the CH_3 group was shown.

Based on FTIR results, the existence of -OH and C=O functional groups in dyes pigments can be bounded to the ZnO particles. The bonding between ZnO and these functional groups might be either single or double dent formation [21].

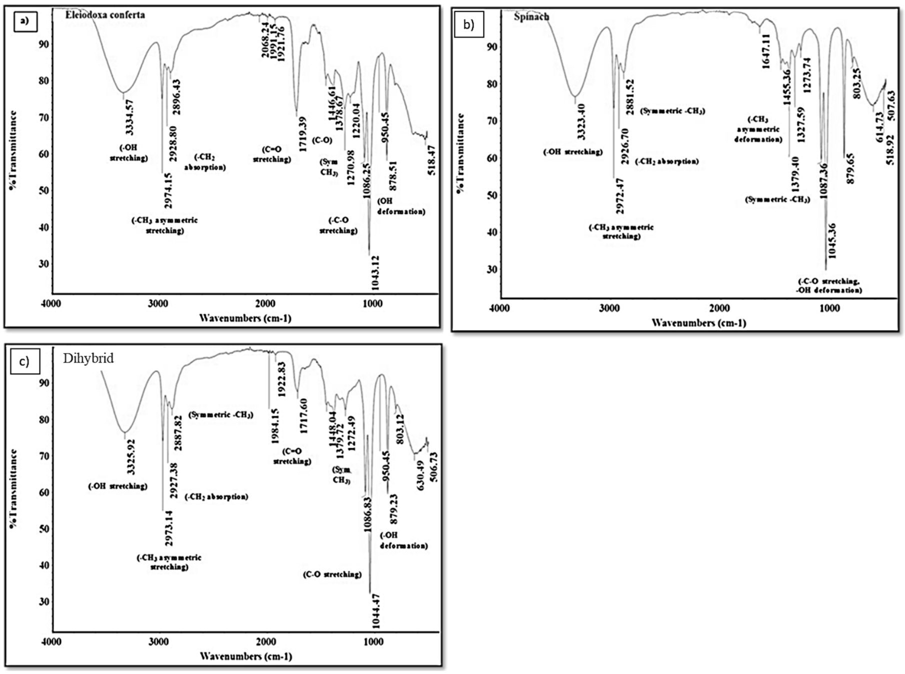

Fig. 1. FTIR analysis of a) *E. conferta*, b) *S. oleracea*, and c) Dihybrid.

Figure 2 shows the absorption spectrum of *S. oleracea, E. conferta* and dihybrid dyes solutions, respectively. *E. conferta* shows the maximum absorption at 542 nm in blue-green-red range. The variation of anthocyanin colors does not express until the extraction are concentrated in the acidic vacuoles and capture illumination at the highest absorbance [22]. Therefore, the different of anthocyanin absorption is dependent on composition of anthocyanin [23].

Minimal energy required to change the electron transfers from HOMO to LUMO to enhance the huge absorption array in the ultraviolet spectrum [24]. Meanwhile, for *S. oleracea* extract (chlorophyll dye), maximum absorption peak was detected at 541 nm. The combination of anthocyanin and chlorophyll pigments exhibited the maximum absorption at 540 nm. The broad absorption window of dihybrid dye may affect the absorption in photon energy at wider wavelengths which can generate more photoelectrons and enhanced the properties of photovoltaic. Anthocyanin is an important composition of some natural dyes. Due to its color which range from red to blue, it is prospected to become an efficient sensitizer for wide band gap semiconductors [19].

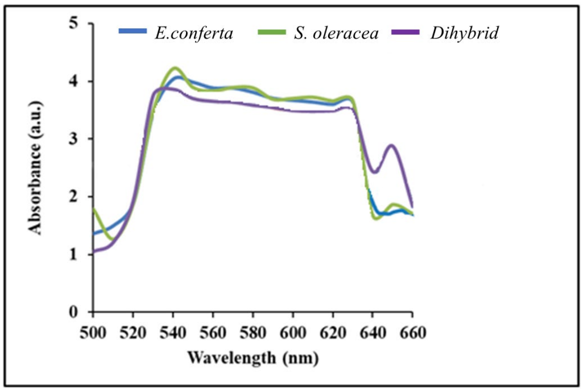

Fig. 2. Absorption spectrum of natural dyes.

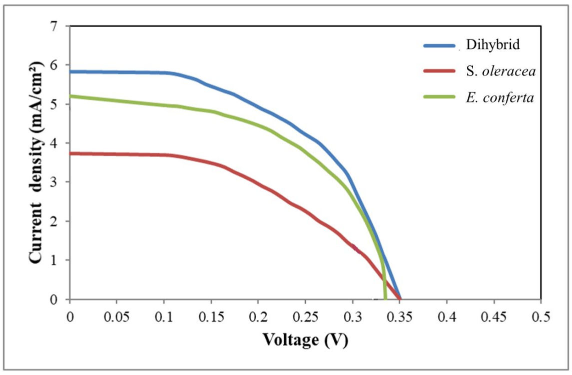

Fig. 3. J-V curves with different sensitizers.

Figure 3 indicated the performance of *J-V* for dihybrid, *E. conferta* and *S. oleracea* sensitizers. Table 1 shows the performance of photovoltaic and the mixed pigments (dihybrid) contributed the highest efficiency (η) of 1.29 % given an open circuit voltage (V_{OC}) of 0.35 V, a short circuit current density (J_{SC}) of 5.83 mA/cm^2 and a fill factor (FF) of 0.63. Meanwhile *E. conferta* that contain anthocyanin pigment achieved V_{OC} = 0.33 V, J_{SC} = 5.2 mA/cm^2, FF = 0.58 and η = 1.00 % and *S. oleracea* indicated the lowest result which are V_{OC} = 0.33 V, J_{SC} = 3.74 mA/cm^2, FF = 0.47 and η = 0.58 %. The J_{SC} is the of the important aspect in photovoltaic parameters. The high J_{SC} reflects the enhancement of electron injection and transport based on the shifted conduction band minimum (CBM) and improved the electron conductivity. Therefore, the enhancement of charge carriers in the conduction band increases the conductivity and increases the J_{SC} value and η of this mixed pigment compares to others. Recombination in dihybrid lowered compared to *E. Conferta* and *S. Oleracea* due to improvement of FF and $V_{OC.}$ However, compared to synthetic dyes (N719) natural dyes produced lower η results. It is because the attachment between bonding of natural dye and the anchoring group (interaction dye with ZnO) affected the efficiencies. Due to the long chain structure with R group, it hinders the bonding of the pigment with the ZnO surface and prevented to array effectively on the ZnO film [29-31]. *S. Oleracea* contributed to the lowest η might be the dye could not interact with ZnO surface for proper electron injection and poor interactions between the ZnO and dye molecules. The coverage of the dye molecule determines the η of the device. When the dye molecules are not fully covered onto ZnO surface, poor interaction between electron injection and tri-iodide ion.

Table 1. Photovoltaic parameters with different sensitizers

Dye source	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	η (%)
Dihybrid	5.83	0.35	0.63	1.29
E. conferta	5.2	0.33	0.58	1.00
S. oleracea	3.74	0.33	0.47	0.58

3. Material and Methods

Two types of plants were selected, which are *E. conferta* and *S. oleracea*. The samples were dried at 40 °C after washed with purified water and grinded into granulated powder. These specimen powders were quantified by weighing balance at 70 g each until and placed into three separate beakers. 700 ml of ethanol (1:10) was put into each beaker and stirred until solution became homogenous. The solutions were kept into 24 hours in dark location. To isolate the solid substances found in the extraction, all formulated extractions were filtered using three separate filter papers into three distinct beakers, and the filtrates were purified again using liquid-liquid extraction to produce pure natural dyes. Later, the natural dye solutions were condensed for 4 hours with a rotary evaporator at 78 °C. The concentrated pigments were stored in a dark bottle to shield it from direct light exposure. At last, the resulting two different pigment solutions were mixed together at 1:1 ratio to create diihybrid dye.

1 g of ZnO powder and 0.2 g Polyethylene glycol (PEG) were mixed until homogeneous mixture of ZnO paste was produced. Next, 5 ml of ethanol was added into the paste and stirred until homogeneous and deposited onto ITO glasses and sintered at 400 °C for 30 min. Carbon paste was formed by blended the activated carbon powder with ethanol and agitated around 1 hour and was spread onto ITO glasses. The carbon counter electrodes were sintered for 30 minutes at 250 °C.

ZnO coated glass must be immersed in natural dyes for 24 hours, respectively. Redox electrolyte (Iodolyte HI-30 with a concentration of 30mM (Solaronix) and acetonitrile as solvent) was cast on the surface of the sensitized photoanodes. ZnO working electrode with a cell active area of 6.5 cm^2 was then clipped with the counter electrode and sealed with slurry tape.

The absorption spectra of all samples were determined using UV–vis (HP 8453). Shimadzu FTIR spectrometer (IRAffinity-1) in the wave number range of 4000–500 cm^{-1} with a maximum resolution of 0.5 cm^{-1} were used to measure dye extraction. The photocurrent–voltage (J–V) curves of DSSCs were recorded with a computer-controlled digital source meter (Keithley 2400) under an irradiation of 100 mWcm−2. The HOMO and LUMO level were analyzed by electrochemical impedance spectroscopy (EIS, GamryREF 3000, USA).

4. Conclusions

As a conclusion, natural sensitizers were successfully extracted from *E. conferta* (anthocyanin) and *S. oleracea* (chlorophyll). Dihybrid dye produced the best results amongst other sensitizers. The value of optical band gap decreased for when the sensitizers were mixed and produced the highest photovoltaic properties values compare to the individual extraction. Even though the efficiencies of natural dyes still lowered compared to the synthetic dyes, but these results will be served as references for future studies in natural dyes. Modification of other layers in DSSC such as photoanode, counter electrode and electrolyte able to enhance the properties of photovoltaic using natural dyes as sensitizers.

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Author Contributions

Conceptualization, Hidayani Jaafar; Logashini Magesvaran; Nadiah Ameram.;Investigation, Hidayani Jaafar; Logashini Magesvaran; Nadiah Ameram.; Resources, Hidayani Jaafar; Logashini Magesvaran; Nadiah Ameram.; Data curation, Hidayani Jaafar; Logashini Magesvaran; Nadiah Ameram.; Writing—original draft preparation, Hidayani Jaafar; Logashini Magesvaran.; Writing—review and editing, Hidayani Jaafar; Logashini Magesvaran.; Supervision, Hidayani Jaafar.; Project administration, Hidayani Jaafar.; All authors have read and agreed to the published version of the manuscript.

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