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Potential Dye Suji Leaves (*Pleomele angustifolia*) Chlorophyll and Red Dragon Fruit Peel (*Hylocereus polyrhizus*) Anthocyanins as Natural Dyes for Dye-Sensitized Solar Cells

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In this study, the quality analysis of chlorophyll and anthocyanin extraction dyes from suji (*Pleomele angustifolia*) leaves and red dragon fruit (*Hylocereus polyrhizus*) peel was extracted using ethanol as a natural dye for dye-sensitized solar cells (DSSCs). Dye characterization was carried out using UV-visible spectrophotometry to determine the wavelength absorption and bandgap using the Tauc plot method, electrochemical characterization of dye was carried out using cyclic voltammetry. The efficiency of DSSC was measured using a digital multimeter. In this study, chlorophyll was produced with absorption wavelengths at 663 nm and 439 nm while anthocyanin dye was at a wavelength of 532 nm. The bandgap of chlorophyll was calculated to be 2.51 eV and that of anthocyanins to be 2.1 eV using the Tauc plot method.. The electrochemical results shows that chlorophyll dye of suji leaves has HOMO energy (highest occupied molecular orbital) at -5.68 eV and a LUMO energy (lowest unoccupied molecular orbital) at -3.17 eV while anthocyanin has HOMO energy of -5.16 eV and a LUMO energy of -3.06 eV. The efficiency produced by DSSC with chlorophyll dye was 3.4163×10^{-3} % and anthocyanins were 6.3994×10^{-3} %. These results show that chlorophyll and anthocyanin dyes from suji leaves and red dragon fruit peel are promising reagents to be used as DSSC dyes.

Keywords: DSSC, Suji leaves, Red dragon fruit peel, *Pleomele angustifolia*, *Hylocereus polyrhizus*, Efficiency.

INTRODUCTION

Nowadays, the increasing need for energy is accompanied by the depletion of energy availability from fossil fuels. Subsequently, alternative and renewable energy need to be created. One of the renewable energy possibilities are solar energy, this energy source is exceptionally promising since of its large amount and supportability [1]. Indonesia as a tropical nation has significant potential. The conversion of sunlight to power by photovoltaic cells is of specific concern to analysts since it has preferences such as low production costs, environmental friendliness, great energy transformation even in cloudy or dark conditions [2,3].

Dye-sensitized solar cells (DSSCs) components, which are third-generation photovoltaic cells, consist of electrolytes as transport medium, conductive glass or substrates as working electrodes and counter electrodes, dye molecules as photosensitizers [4]. A dye is an important portion of DSSC is capable of the absorption of light and transmit electrons to the conduction band of the semiconductor. Dye significantly influences the effectiveness of the DSSC. Each sensitizer must have a few extraordinary characteristics: (i) appear the spectral absorption in the visible light range and the near-infrared, (ii) contains a carboxyl (C=O) or hydroxyl groups (O-H) which can tie strongly to the surface semiconductor oxide to encourage the productive electronic infusion to slit the conduction band of semiconductor, (iii) has good stability in absorbing photons, (iv) HOMO energy level must be lower than the redox potential of the electrolyte, and (v) LUMO energy level must be high enough out of the semiconductor band conduction [5,6].

Ruthenium has great effectiveness as a metal-complex in DSSC, but ruthenium complex has numerous disadvantages such as being difficult to get, not naturally friendly, uncommon, costly, difficult to synthesize [7]. The improvement of natural dye proceeds to overcome this issue indeed even though of the fact that natural dyes have lower effectiveness than complex metal colours [8]. Natural dye has many advantages including easy to obtain, easy to extract, non-toxic, environmentally cheap, friendly, renewable and low production costs [7-10]. In common, natural dyes are extricated from plants, the plant parts utilized are blossoms, leaves, roots, fruit. Each part of the plant features a natural colour and diverse pigmen [9]. Types of dyes commonly utilized in DSSC of which is chlorophyll and anthocyanins [11].

Suji leaves are commonly found in Asia which are abundant in Indonesia and Malaysia, but their use is still not optimal, usually used as food colouring or non-food [12]. Meanwhile, in the utilization and processing of red dragon fruit, red dragon fruit peel is still a waste whose utilization needs to be developed. In this study, the authors analyzed the performance of natural chlorophyll and anthocyanin dyes. Suji (*Pleomele angustifoli*a) leaves as a chlorophyll producer and red dragon fruit (*Hylocereus polyrhizus*) peel as an anthocyanin producer. The UV-Vis spectrophotometry analysis was performed to identify absorption wavelength and band gap dyes, characterization using cyclic voltammetry to determine HOMO and LUMO energy levels of dyes and characterization with a digital multimeter to determine efficiency.

EXPERIMENTAL

Extraction of dye: The suji leaves (50 g) were cleaned and weighed. After that, the suji leaves were blanched by soaking the suji leaves in distilled water at 100 ºC for 1 min, then the blanching process were made in order to reduce chlorophyllase activity. Then the suji leaves were dried, chopped and blended at medium speed for 1 min [13]. Extraction of dragon fruit peel was done by weighing (50 g) the dragon fruit peel then blended for 1 min. The extraction of chlorophyll and anthocyanin were performed using 96% ethanol as solvent with a ratio w/v between suji leaves and solvent 1:5, dragon fruit and solvent 1:5. The extraction was carried out in dark for 24 h.

Absorption wavelenght of dyes: The dye absorption was analyzed using a UV-Vis spectrophotometer (Shimadzu) in the range of 400-800 nm [14]. Using Tauc's plot, the bandgap of the dye was calculated.

Electrochemical studies: The electrochemical measurements were made with voltammetry type 797 VA Computrace by cyclic voltammetry (CV) method. Copper was used as a working electrode, Ag/AgCl as a reference electrode and the electrolyte used was 1 M KCl, with potential range -1.6 V. Parameters such as deposition time, sweep rate and pH were selected after the initial test [15,16]. In this investigation, the pH was within the variation of 3, 4, 5 for red dragon fruit peel dye and 6, 7, 8 for suji leaves dye. At that point, the estimations were taken with a variation of the deposition time of 5 s, 10 s and 20 s. Then the optimization was done with a variation sweep rate of 0.1 V/s, 0.3 V/s, 0.5 V/s.

Fabrication of DSSC: TiO_2 paste was made by stirring TiO_2 powder 0.2 g, 0.1 M nitric acid solution 0.4 mL and 0.08 g polyvinyl ethylene glycol (PEG) stirred using a magnetic stirrer until a homogeneous paste was formed. A non-ionic Tween-80 surfactant (0.05 mL) was added to the colloid suspension, stirred using a magnetic stirrer for 30 min. After that tape the conductive glass ITO controlling the thickness and area of the TiO_2 film. TiO_2 paste was applied to the conductive glass measuring 1.5 cm × 1.5 cm with a doctor blade technique using a clean glass rod. TiO_2 was allowed to stand for a few minutes and then heated at 450 ºC for 1 h with a hot plate that solidifies TiO_2 [17]. Take a few moments until the glass cools, the glass films immersed in a dye solution, which has been prepared for 24 h at room temperature in the dark for dye adsorption is right on top of TiO_2. Excessive dye, which was not adsorbed on the TiO_2, the conductive glass was cleaned using ethanol [18]. The electrolyte gel was prepared from 0.8 g of 0.5 M KI mixed with 10 mL of PEG 400 solution and stirred. Furthermore, 0.127 g I_2 was added to the solution until the three ingredients dissolve completely. The electrolyte solution was stored first in a closed and dark vial [19]. The electrode counter was prepared by coating the conductive parts of the ITO glass using a Faber-Castell 2 B graphite pencil. Then the DSSC is made by arranging it like a sandwich with the order of glass substrate/ conductive part ITO/TiO_2/Dye/electrolyte/catalyst (graphite)/ ITO conductive part/glass substrate and then clamped using clips [20]. The DSSC performance was measured using a multimeter digital. DSSC performance estimations I-V were carried out utilizing daylight as an energy source. The maximum power of solar cells was measured using the following approach [21]:

$$P_{max} = \frac{V_{max} \times I_{max}}{A} \quad (1)$$

The efficiency of DSSC calculations were carried out using the following equation:

$$\eta = \frac{P_{max}}{i} \quad (2)$$

RESULTS AND DISCUSSION

UV-Visible studies: In this study, the characterization was carried out using UV-Vis spectrophotometry to investigate the light absorption of red dragon fruit peel extract and suji leaves extract at visible light wavelength. The anthocyanin absorption spectrum exhibits the wavelength at 532 nm, while the chlorophyll a has absorbance at 663 nm, while chlorophyll b absorbs light most strongly between 439 nm (Fig. 1) [5,22]. The energy gap of the dyes found in the red dragon fruit peel and suji leaves, respectively, was 2.1 eV and 2.51 eV, as determined by a tauc plot study of the bandgap dyes. This shows that the dye gap energy of the red dragon fruit skin dye and suji leaves is less than the 3.2 eV gap energy of the anatase phase TiO_2 semiconductor. Dye-sensitized solar cells (DSSCs) work by using visible-light photon absorption to activate electrons in the dye from the HOMO state to the LUMO region, from there they diffuse to the ITO layer through TiO_2 semiconductor. The energy of the gap dye shows the amount of energy required for excited electrons from the HOMO state to LUMO.

Electrochemical studies: The redox potential of the electrolyte, at -4.94 eV, must be less than the HOMO of dye in order to regenerate it and the LUMO must be higher than the semiconductor conduction band of TiO_2, at -3.2 eV, for the DSSC to use the dye as photosensitizer [6,15,23]. The HOMO state (E_{HOMO}) was calculated by reducing the E_{HOMO} with E_g from the UV-Vis spectra results [24].

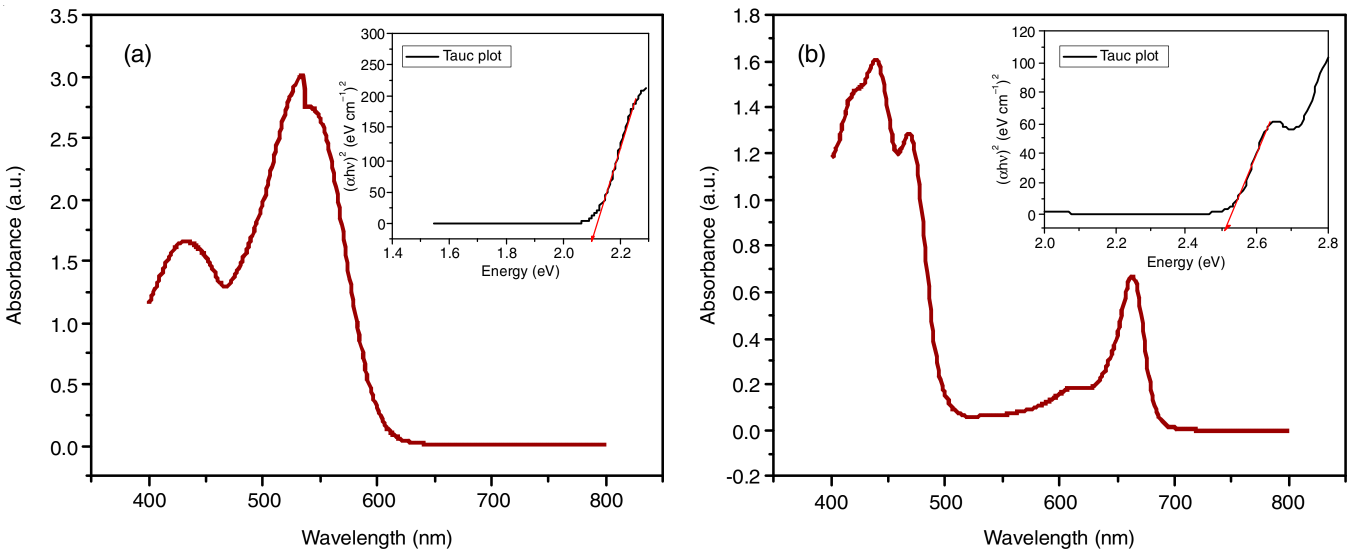

Fig. 1. Absorption wavelength extract (a) red dragon fruit peel and (b) suji leaves

pH measurement: Table-1 shows that the HOMO level is lowest at pH 3, making it the optimal pH for determining the pigmentation of red dragon fruit skins. Meanwhile, the pH determination of suji leaf extract obtained a pH of 7, which was the most effective because it had a lower HOMO level than the other variation and a much lower HOMO level than the TiO_2 conduction band (Fig. 2).

TABLE-1
HOMO-LUMO pH MEASUREMENT FOR THE BEST DYE WITH VARIOUS VARIATIONS

Dye	pH	HOMO CV	LUMO CV
Red dragon fruit peel	3	-5.06	-2.96
	4	-5.01	-2.91
	5	-5.04	-2.94
Suji leaves	6	-5.40	-2.89
	7	-5.53	-3.02
	8	-5.50	-2.99

Deposition time measurement: The time of deposition was determined by using a time variation of 5 s, 10 s, 20 s at optimum pH from each dye for characterization with CV. Based on its lower HOMO level compared to the redox potential of electrolytes, CV 10 s was found to be the most effective deposition time for electrochemical measurement of red dragon fruit peel dye (Table-2), while CV 20 s was found to be the most effective deposition time for electrochemical determination of suji leaf dye (Fig. 3).

TABLE-2
HOMO-LUMO VARIATION OF DYE DEPOSITION TIME

Deposition time (s)	Dye red dragon fruit peel		Dye suji leaves	
	$HOMO^{CV}$	$LUMO^{CV}$	$HOMO^{CV}$	$LUMO^{CV}$
5	-5.11	-3.01	-5.46	-2.95
10	-5.14	-3.04	-5.52	-3.01
20	-5.12	-3.02	-5.53	-3.02

Sweep rate measurement: In determining the sweep rate in the dye, the optimum deposition time and the optimum pH were used in CV measurements. An optimum sweep rate of 5 for both dyes was generated, since it has the lowest HOMO

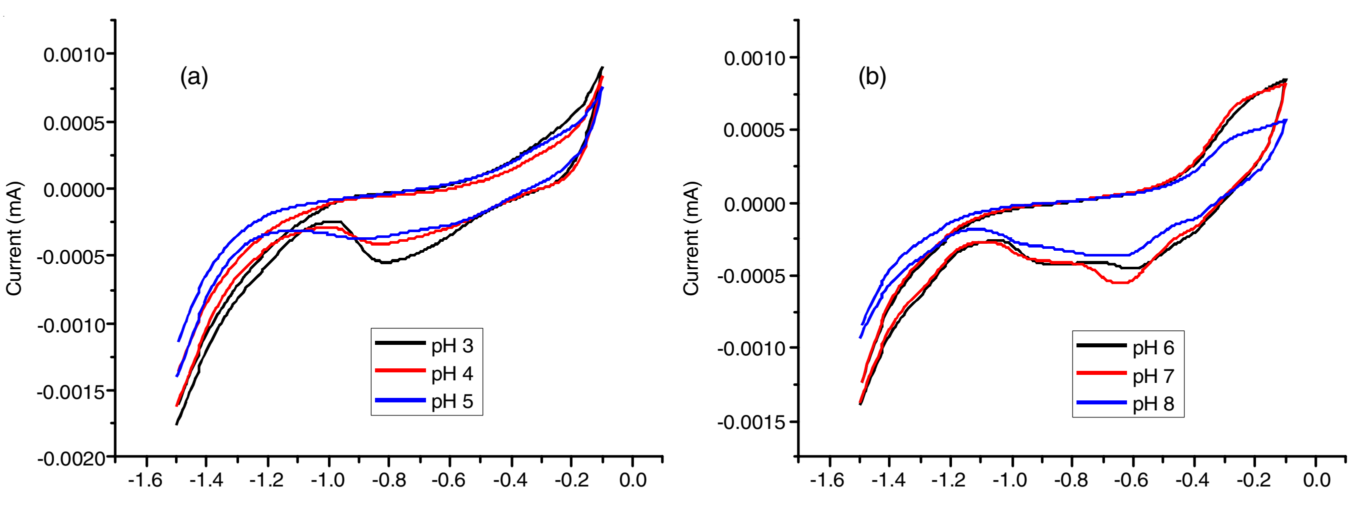

Fig. 2. Voltammogram of (a) red dragon fruit peel dye and (b) suji leaves. Best pH determination with various pH variations

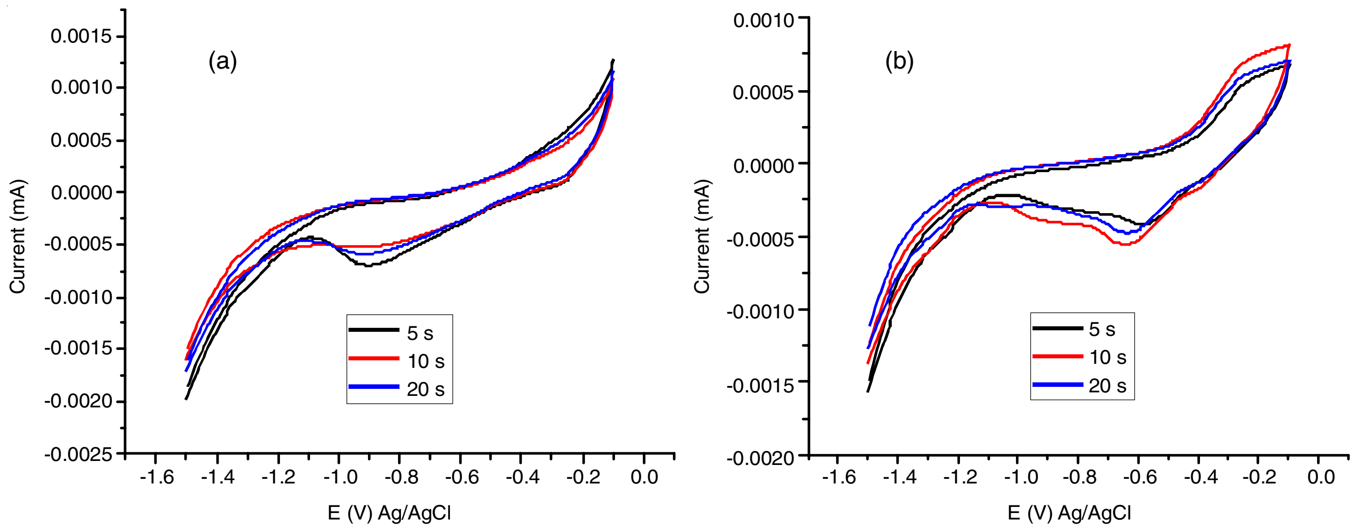

Fig. 3. Voltammogram results of time variation deposition of (a) red dragon fruit peel dye and (b) suji leaves dye

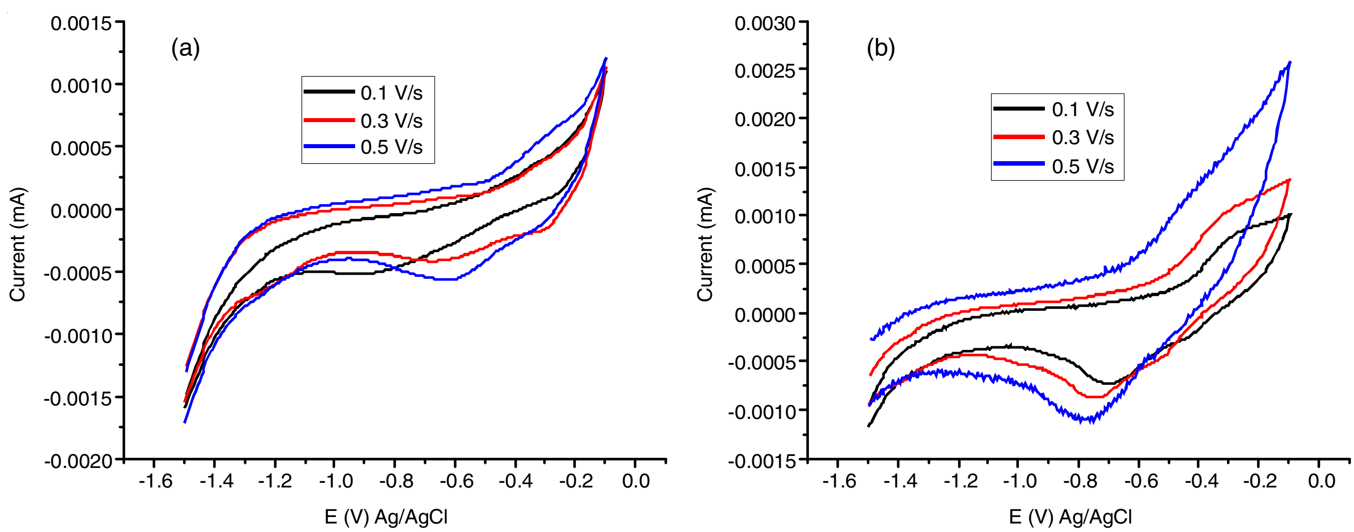

Fig. 4. Voltammogram result of sweep rate variation of (a) red dragon fruit peel dye and suji leaves dye

level than the other sweep rate variations (Fig. 4). Due to the requirement of the LUMO energy level for introducing electrons into the TiO_2 semiconductor, this energy level is immensely essential; the closer the LUMO energy of the dye is to the LUMO energy of the TiO_2 semiconductor, the more efficiently electrons will be injected. From Table-3, it can be seen that the LUMO energy at a sweep rate of 0.5 V/s has an energy that is very close to the TiO_2 conduction bandgap so that it is more optimal in injecting electrons (Fig. 5).

TABLE-3
HOMO-LUMO DYES WITH VARIOUS SWEEP RATES

Sweep rate (V/s)	Dye red dragon fruit peel		Dye suji leaves	
	$HOMO^{CV}$	$LUMO^{CV}$	$HOMO^{CV}$	$LUMO^{CV}$
0.1	-5.14	-3.04	-5.63	-3.12
0.3	-5.15	-3.05	-5.66	-3.15
0.5	-5.16	-3.06	-5.68	-3.17

DSSC performance: The daytime measurements were performed outside the chamber. where typical measurement circumstances for solar cells assume a solar radiation intensity

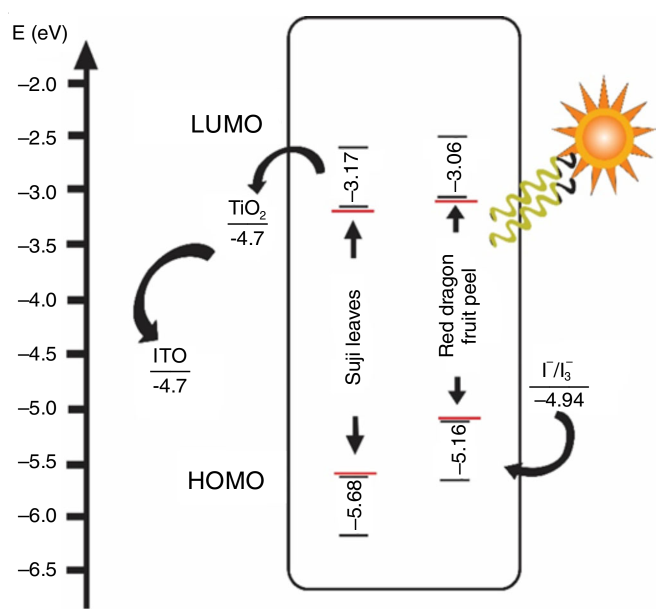

Fig. 7. Energy level diagram in DSSC based on suji leaves dye and red dragon fruit peel dye

of 100 mW/cm^2, as in eqns. 1 and 2. Red dragon fruit skin anthocyanin dye has a DSSC efficiency of 6.3994 × 10^{-3}%, which is significantly higher than the DSSC efficiency of 3.4163 × 10^{-3} % for suji leaves dye. This is possible because the red dragon fruit skin anthocyanin dye has a smaller optical bandgap than the suji leaf chlorophyll dye and thus is more efficient. Low optical bandgap plays a role in the dye regeneration process rapidly in the presence of redox electrolyte I^-/I^{3-} thereby increasing efficiency in DSSC [6].

Conclusion

This study demonstrates that the red dragon fruit skin and suji leaves contain a dye with the potential to be used as a sensitizer in DSSC. The bandgap energy of the two dyes is smaller than the semiconducting band TiO_2, allowing them to be used as a DSSC sensitizer, as shown by the UV-Vis absorption spectra of the dye. The dye from the red dragon fruit peel contains anthocyanins, which absorb photons at visible light wavelengths, while the chlorophyll in suji leaves absorbs photons at longer wavelengths. Cyclic voltammetry was used to characterize the two dyes, and it was found that their HOMO levels were below the TiO_2 conduction band and the redox electrolyte, while their LUMO levels were above the TIO conduction band. Dye performance measurements revealed that DSSC employing red dragon fruit skin dye achieves 6.3994 × 10^{-3}% higher efficiency than DSSC employing Suji leaf dye achieves 3.4163 × 10^{-3}%. The energy gap of the red dragon fruit peel dye is only 2.1 eV, whereas the energy gap of the suji leaf dye is 2.51 eV, making dye regeneration simpler and reducing the quantity of energy needed for electron transfer.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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