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ORIGINAL PAPER

Performance of *E. conferta* and *G. atroviridis* fruit extracts as sensitizers in dye-sensitized solar cells (DSSCs)

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Abstract Natural dyes extracted from *Eleiodoxa conferta* and *Garcinia atroviridis* were used for the first time as photosensitizers in dye-sensitized solar cells (DSSCs). Anthocyanin was identified as the main pigments that sensitize the semiconductor of TiO_2 film. Anthocyanin pigment contains hydroxyl and carboxylic groups in the molecule that can attach effectively to the surface of TiO_2 film. The optical characteristics of the extracted dye and photovoltaic performance of the cells were studied. The extracts showed UV–vis absorptions in the range of 530–560 nm with broad maxima absorption at ~ 430 nm. FTIR spectra of extraction revealed the presence of anchoring groups. For *E. conferta*, the photovoltaic performance of the sample with 3.16-μm-thick TiO_2 produced the best results with open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), fill factor (FF), and energy conversion efficiency (η) values of 0.37 V, 6.56 mA/cm^2, 0.49, and 1.18%, respectively. The best photovoltaic performance for *G. atroviridis* was also obtained from the sample with 3.16-μm-thick TiO_2 with V_{OC}, J_{SC}, FF, and η values of 0.35 V, 3.74 mA/cm^2, 0.65, and 0.85%, respectively.

Keywords Natural dyes · *E. conferta* · *G. atroviridis* · Dye-sensitized solar cell

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Introduction

Research on dye-sensitized solar cells (DSSCs) have drawn much attention in recent years, mainly due to their low manufacturing cost, easy fabrication, and relatively high-energy conversion efficiency (η) [1, 2]. The DSSC consists of a metal oxide semiconductor as a photo anode, a dye sensitizer, an electrolyte, and a counter electrode [3]. In DSSC, the photo excitation of the dye sensitizer is followed by injection of electrons into the conduction band of the semiconductor. The dye molecule is self-regenerated by redox system at the counter electrode by electrons passing through the load [4]. The optimization of each component in DSSC is essential to achieve maximum efficiency.

In conventional DSSC, ruthenium (Ru) complex is the most efficient sensitizer for the sensitization of nanocrystalline TiO_2 semiconductor. However, the high cost and long-term unavailability of Ru complexes pushed many researchers to discover other cost-efficient sensitizers. The preparation of synthetic dyes also requires complicated procedures, organic solvent demands, and has low yield issues [5, 6]. Therefore, various investigations on easily available dyes extracted from natural sources that can be used as photosensitizers were conducted due to their large absorption coefficients, high light harvesting efficiency, low cost, easy preparation, and environmental friendliness [7–9]. The natural pigments are found in the shoot and root systems of plants such as flowers, leaves, fruits, stems, and roots. Several natural dye pigments, such as chlorophyll, betanins, carotenoids, anthocyanins, and tannins, are successfully used as sensitizers in DSSC application [10–12]. As reported by Wongcharee et al. [13], power conversion efficiency of DSSC using dyes extracted from blue pea, rosella, and mixture of both were 0.37, 0.05, and 0.15%, respectively. DSSC fabricated by dyes extracted from ivy gourd fruits and red

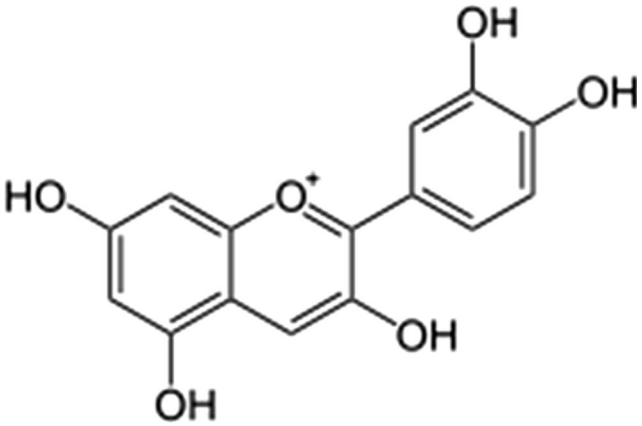

Fig. 1 Structure of anthocyanin (cyaniding derivatives)

frangipani flowers were reported to reach an efficiency of 0.08 and 0.30%, respectively [12]. DSSCs fabricated using extracts from *Nerium oleander* (red pink), buogainvillea (dark pink), and hibiscus (red) were found to give conversion efficiency of 0.06, 0.05, and 0.19%, respectively [14]. Anthocyanins are the most important vascular pigments, belonging to the class of compounds named flavonoids [15]. The anthocyanins are responsible for the bright orange, pink, red, purple, and blue colors in some plant flowers and fruit, depending on the pH [16]. The hydroxyl and carbonyl groups present in the anthocyanin molecules [17] can be bound to the surface of porous TiO_2 film, as shown in Fig. 1. This enhances the feasibility of electron transfer from the anthocyanin molecule to the conduction band of TiO_2 [18]. To achieve higher efficiency, the natural dyes must bind strongly to the TiO_2 surface by means of their anchoring group to ensure efficient electron injection into the conduction band of TiO_2 [19]. The performance of natural dyes that contain anthocyanin pigment as sensitizers were evaluated by short-circuit current (J_{SC}), open-circuit voltage (V_{OC}), and energy conversion efficiency (η) as is normally done by other researchers and is summarized as in Table 1.

The performance of two types of tropical fruits, i.e., *Eleiodoxa conferta* and *Garcinia atroviridis* that are also known as *asam kelubi* and *asam gelugur*, respectively, in Malaysia, as sensitizers have never been reported. *E. conferta* contains oxalic, ascorbic, and malic acids [35]. It is reported that the highest concentration of oxalic acid (1.33 g/ml^{-1}) can be obtained from young fruits compared to mature stage (1.26 g ml^{-1}) and ripe stage (1.23 g ml^{-1}). Meanwhile, *G. atroviridis* fruit is containing citric, tartaric, malic, and ascorbic acids. Therefore, the selection of both *E. conferta* and *G. atroviridis* fruit is due to their raw natural dye extract that should perform better with the presence of natural extracts like organic acids and alcohols which behave as co-absorbate [23]. These suppress recombination of dye with electrolyte, favoring charge injection and reducing dye aggregation [36].

In this present work, *E. conferta* and *G. atroviridis* were extracted and used as a sensitizer for DSSC without further purification. The extracted dyes were characterized by ultraviolet–visible (UV–vis) and Fourier transform infrared (FTIR) spectroscopy. The photovoltaic performance (V_{OC}, J_{SC}, FF,

Table 1 Previous works on photovoltaic performance of natural dyes that contain anthocyanin pigment used in DSSC as sensitizers (TiO_2 as photoanode)

Dye solution	Pigment used	J_{SC} (mA/cm^2)	V_{OC} (V)	η (%)	Ref
Rosa chinensis	Anthocyanin	0.80	0.540	0.29	[20]
Black turtle beans	Anthocyanin	5.00	0.35	1.42	[21]
Saraca asoca	Anthocyanin	0.29	0.510	0.09	[22]
Callindra haematocephata	Anthocyanin	0.25	0.370	0.06	[23]
Canarium odontophyllum	Anthocyanin	9.74	0.35	1.43	[24]
Begonia	Anthocyanin	0.63	0.537	0.24	[25]
Rhododendron	Anthocyanin	1.61	0.585	0.57	[25]
Bauhinia tree	Anthocyanin	0.96	0.572	0.36	[25]
Lithospermum	Anthocyanin	0.14	0.337	0.03	[25]
Yellow rose	Anthocyanin	0.74	0.61	0.26	[25]
Rosa xanthine	Anthocyanin	0.64	0.49	-	[26]
Hibiscus rosasinesis	Anthocyanin	2.46	0.40	0.59	[27]
Pomegranate	Anthocyanin	12.20	0.39	2.00	[28]
Pomegranate	Anthocyanin	0.62	0.46	1.57	[29]
Brassica olercea (Redcabbage)	Anthocyanin	0.50	0.37	0.13	[30]
Brassica olercea (Redcabbage)	Anthocyanin	3.47	0.59	1.40	[31]
Punica granatum (Pomegranate)	Anthocyanin	2.05	0.56	0.59	[32]
Lawsonia inermis (Henna)	Anthocyanin	1.87	0.61	0.66	[33]
Black carrot (*Daucus carota* L)	Anthocyanin	1.30	0.40	0.25	[34]

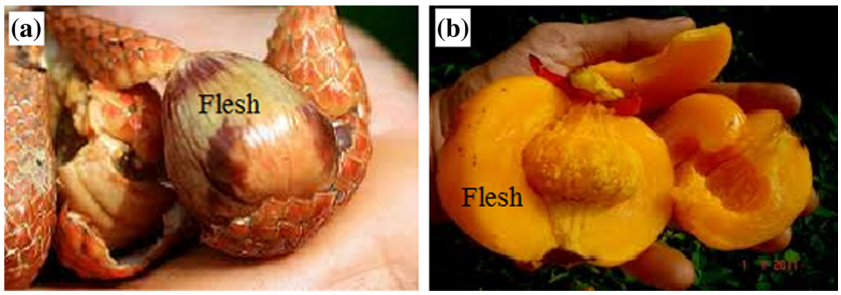

Fig. 2 **a** *E. conferta* and **b** *G. atroviridis* fruits

and η) of the fabricated DSSC was investigated using these extracts as sensitizers.

Materials and methods

Preparation of TiO_2 electrode

TiO_2 paste was prepared by blending 20 g of commercial TiO_2 nanocrystalline powder (Degussa P25) which was purchased from Sigma-Aldrich with 20 ml of ethanol and 3 ml of 0.1 M acetic acid until a thick paste was formed. Fluorine-doped tin oxide (FTO) conductive glass with a sheet resistance of ~ 7 Ω/cm^2 was cleaned in a detergent solution, rinsed using deionized water and ethanol, and then dried. The conductive site of the FTO conductive glass was identified using digital multimeter (All-Sun EM420B digital multimeter). TiO_2 films in thicknesses of 1.83, 3.16, and 7.60 μm (as measured by FESEM) were obtained by taping 1-, 2-, and 3-layer thick adhesive tape, respectively, onto the conductive site in order to control the thickness. The TiO_2 paste was coated onto the FTO substrate using the doctor blade technique and sintered at 450 °C for 30 min.

Preparation of natural dye sensitizers

The flesh of *E. conferta* and *G. atroviridis*, as shown in Fig. 2, were separated from the seeds and completely dried at room temperature. The flesh was crushed to powder form using a mortar. In total, 50 g of the powder was put into a beaker and added with 500 ml ethanol (1:10) and stirred. The mixture was left for 24 h in the dark at room temperature. The solid residues of the mixture were filtered out to obtain a pure and clear natural dye solution.

Preparation of counter electrode

Carbon black was mixed with TiO_2 using the solid-state method as the counter electrode with weight ratio of 5:1 for TiO_2/carbon black. The homogeneous carbon black paste was prepared by mixing the mixture (TiO_2/carbon black) with 0.1 ml of Triton X-100 for 3 h. The conducting side of FTO glass was coated with 10 mM H_2PtCl_6 solution in ethanol, and the mixed paste was applied onto FTO glass using the doctor blade technique and sintered at 500 °C for 1 h.

Assembly of DSSC

The TiO_2-coated glass was obtained by immersing the films into the natural dye (*E. conferta* and *G. atroviridis,* respectively) for 24 h at room temperature. The sensitized electrodes were rinsed using ethanol to remove any unanchored dye. A drop of redox electrolyte (Iodolyte HI-30 with a concentration of 30 mM (Solaronix) and acetonitrile as solvent) was cast on the surface of sensitized photoanodes. The counter electrode was then clipped onto the top of TiO_2 working electrode with a cell active area of 6.5 cm^2 and then sealed using slurry tape.

Cell characterization

UV–vis (HP 8453) was used to determine the absorption spectra of all samples. The FTIR spectra of dye extracts and dye-adsorbed TiO_2 films were measured using a Shimadzu FTIR spectrometer (IRAffinity-1) in the wave number range of 4000–500 cm^{-1} with a maximum resolution of 0.5 cm^{-1}. The thickness of the sample was observed using field emission scanning electron microscopes (FESEM) (Zeiss Supra 35VP). The photocurrent–voltage (I–V) curves of the DSSCs were recorded with a computer-controlled digital source meter (Keithley 2400) under an irradiation exposure of 100 $mWcm^{-2}$.

Results and discussion

XRD analysis

Figure 3 shows the XRD patterns of the pure TiO_2. The peaks indicate that the complete anatase structure (ICDD file no. 98-007-6028). The crystallite size was measured as per Scherer's equation, where the average crystallite size of pure TiO_2 is 8.51 nm [37].

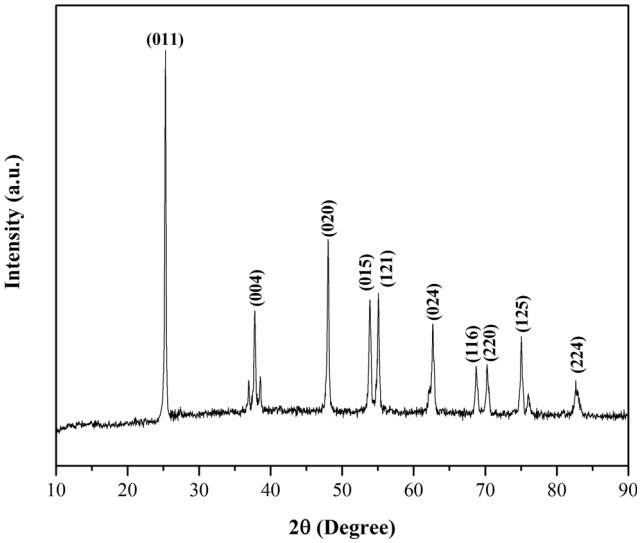

Fig. 3 XRD patterns of pure TiO_2

FTIR spectra

The FTIR spectroscopy of pure and natural dye-sensitized TiO_2 nanoparticles is shown in Fig. 4. Both spectra have the characteristic vibration of Ti–O bond at 659 cm^{-1} (in pure) and 801 cm^{-1} (in natural sensitizers) which normally occurs in between the standard range of 450–1000 cm^{-1} [38]. The FTIR spectrums obtained from *E. conferta* and *G. atroviridis* are shown in Fig. 4b which demonstrates the presence of anthocyanin as all the characteristic peaks are matched to other similar research works [20, 23, 39]. The anthocyanin pigments were observed based on strong peak absorption in the range of 3000–3600 cm^{-1} with wide and strong bands at 3336 and 3342 cm^{-1} for *E. conferta* and *G. atroviridis,* respectively. The peaks correspond to the –OH stretching vibration for the anthocyanin dye of *E. conferta* and *G. atroviridis*. Both samples show peaks at 2974 and 2884 cm^{-1} which corresponds to the –CH stretching modes that prove the presence of aromatic CH group. The broad absorption at 2078 cm^{-1} indicates further electron delocalization into adjacent rings [13]. The C=O group stretching vibrations occur at 1741 cm^{-1}. Since this group can also conjugate with ring double bonds, there is a strong stretching vibration at 1643 cm^{-1} due to C=C aromatic ring stretching vibrations. The peaks at 1380 and 1381 cm^{-1} for *E. conferta* and *G. atroviridis*, respectively, were assigned to the asymmetric –CH deformation modes of CH_3 group. The peaks at 1087 and 1046 cm^{-1} could be attributed to C–O vibrations. Based on FTIR results, it is confirmed that the presence of hydroxyl (−OH) and carbonyl (C=O) groups in the molecular structure of anthocyanin dye can possibly bind with the surface of porous TiO_2 film. These bonds can be either monodentate or bidentate bridging. When illuminated, anthocyanin will absorb the light and electrons that are present when the HOMO state gets excited into the LUMO state. Therefore, electron injection takes place through the functional C=O and –OH groups into the conduction bands of TiO_2.

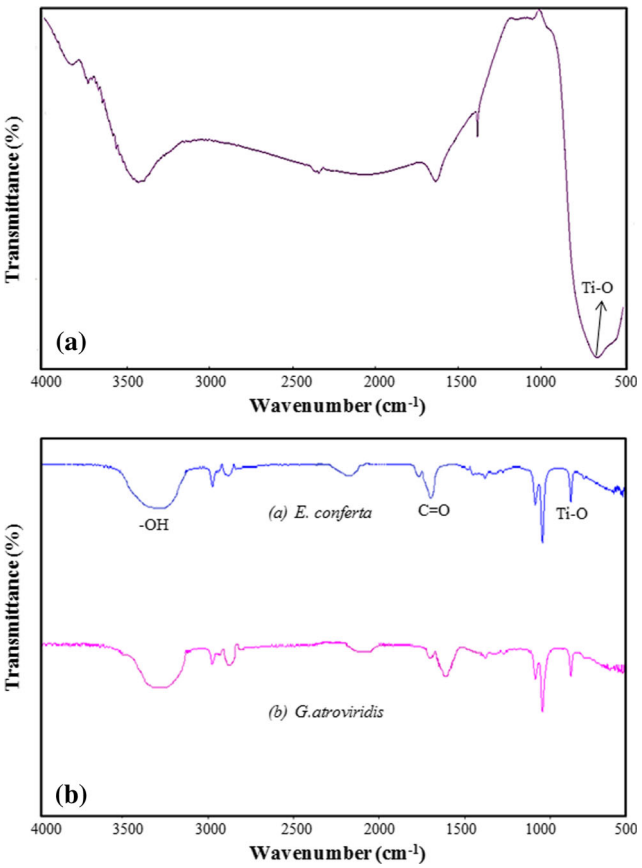

Fig. 4 **a** Absorption spectrum of pure TiO_2 and **b** FTIR spectra of natural dye sensitized TiO_2 to indicate the presence of –OH, C=O, and Ti–O bonds

UV–vis absorption

Figure 5 shows the absorption spectrum of pure TiO_2 and TiO_2 films adsorbed by (i) *E. conferta* and (ii) *G. atroviridis* dye solutions, respectively. The UV–vis absorption spectrum of pure TiO_2 nanoparticles shown in Fig. 5a indicated that the TiO_2 nanoparticles absorb light photons in UV and nearby regions only. Therefore, a separate dye sensitizer attached with TiO_2 is needed to ensure it is suitable for solar cell applications [40]. The absorption spectrum of natural dye-sensitized TiO_2 in Fig. 5b shows the enhancement of light photon absorption and extension of absorption region as compared to pure TiO_2. The visible absorption band shifts to higher energy levels, showing a broad maximum around 530–560 nm with maximum absorption at 540 nm for *E. conferta*. Meanwhile, the absorption peaks were observed to be between 540 and 550 nm with maximum absorption at 540 nm for *G. atroviridis*. The spectrum obtained between 530 and 560 nm confirms the extraction of anthocyanin (cyaniding derivatives) [41]. Anthocyanin is

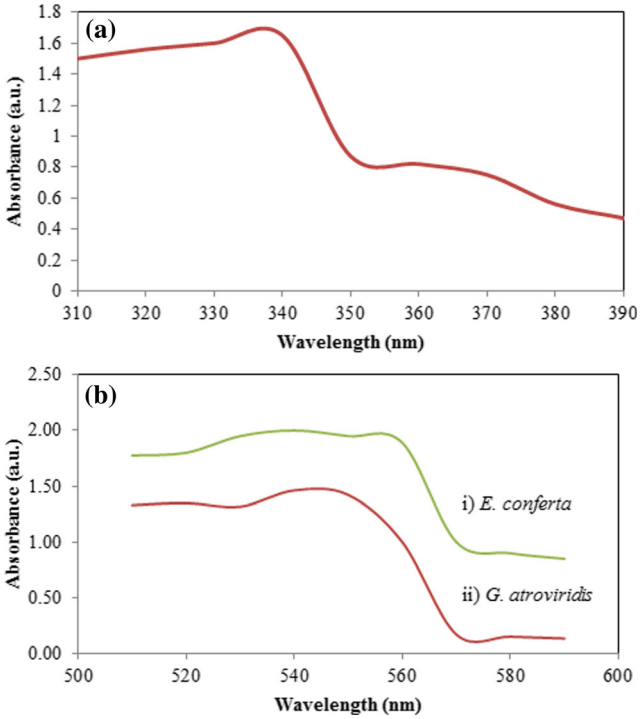

Fig. 5 **a** Absorption spectrum of pure TiO_2; **b** Absorption spectrum of natural dye sensitized TiO_2

an important composition of some natural dyes and is often found in fruits, flowers, and leaves of plants. Due to its color which ranges from red to blue, it is prospected to become an efficient sensitizer for wide band gap semiconductors [39]. The broad absorption of *E. conferta* may result in absorption in photon energy at broader wavelengths which results in the generation of more photoelectrons [20]. The presence of hydroxyl and carbonyl groups in anthocyanin molecules allows it to easily bind with the surface of TiO_2 porous film; this is why it is suited for the application as sensitizers [42].

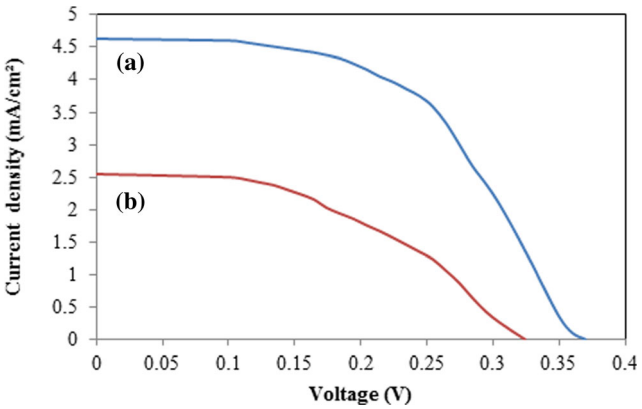

Fig. 6 Current–voltage (*J-V*) characteristics of dye extracted from **a** *E. conferta* and **b** *G. atroviridis*

Photovoltaic performance

Figure 6 shows the variation of the current–voltage (*J-V*) curve of *G. atroviridis* and *E. conferta*-based DSSCs, and Table 2 shows the performance of the natural dyes as sensitizers in DSSCs evaluated by J_{SC}, V_{OC}, FF, and η. *E. conferta* extracts produced promising photo electrochemical performance showing J_{SC} = 4.63 mA/cm^2, V_{OC} = 0.37 V, FF = 0.56, and η = 1.00%. This is due to the presence of anthocyanin in the extract. With the help of anthocyanin, the extract sticks onto the oxide surface and increases its light harvesting ability. *G. atroviridis* extract has less efficiency values compared to *E. conferta* because of the low interaction between the extract and TiO_2 film. Based on Table 2, cells fabricated with *E. conferta* extract achieved highest power conversion efficiencies with maximum photocurrent, 4.63 mA/cm^2. Natural extracts produced low V_{OC} due to possible efficient electron/dye cation recombination pathways and the acidic dye adsorption environment [43]. The H^+ ions are potential determining ions for TiO_2, and proton adsorption causes a positive shift of the Fermi level of the TiO_2, thus limiting the maximum photovoltage that could be delivered by the cells.

Photovoltaic performance with different thicknesses of TiO_2 layers

Figure 7 shows FESEM images of the different thicknesses of TiO_2 layered onto FTO glass. In Fig. 6, 1.83 μm represents one layer of adhesive tape, 3.16 μm represents two layers of adhesive tape, and 7.60 μm represents three layers of adhesive tape. *E. conferta* and *G. atroviridis* used with the different thicknesses of TiO_2 layers indicated different photovoltaic performances, as shown in Figs. 8 and 9.

Figure 8 indicates that 3.16-μm-thick TiO_2 gave the highest result of 6.56 mA/cm^2 followed by TiO_2 7.60 and 1.83 μm in thickness which gave results of 5.83 and 4.63 mA/cm^2, respectively. In Fig. 9, the TiO_2 3.16 μm in thickness also provides the highest result which is 3.74 mA/cm^2, followed by the TiO_2 1.83 μm and 7.60 μm in thickness which provided 2.55 and 1.82 mA/cm^2, respectively. The photovoltaic performances of DSSC prepared with different thickness layers of TiO_2 are given in Tables 3 and 4 for *E. conferta* and *G. atroviridis*, respectively. Table 3 shows that the DSSC

Table 2 Photovoltaic performances of DSSCs sensitized with *G. atroviridis* and *E. conferta*

Dye source	Jsc (mA/cm^2)	V_{OC}/V	FF	η (%)
G. atroviridis	2.55	0.32	0.63	0.51
E. conferta	4.63	0.37	0.56	1.00

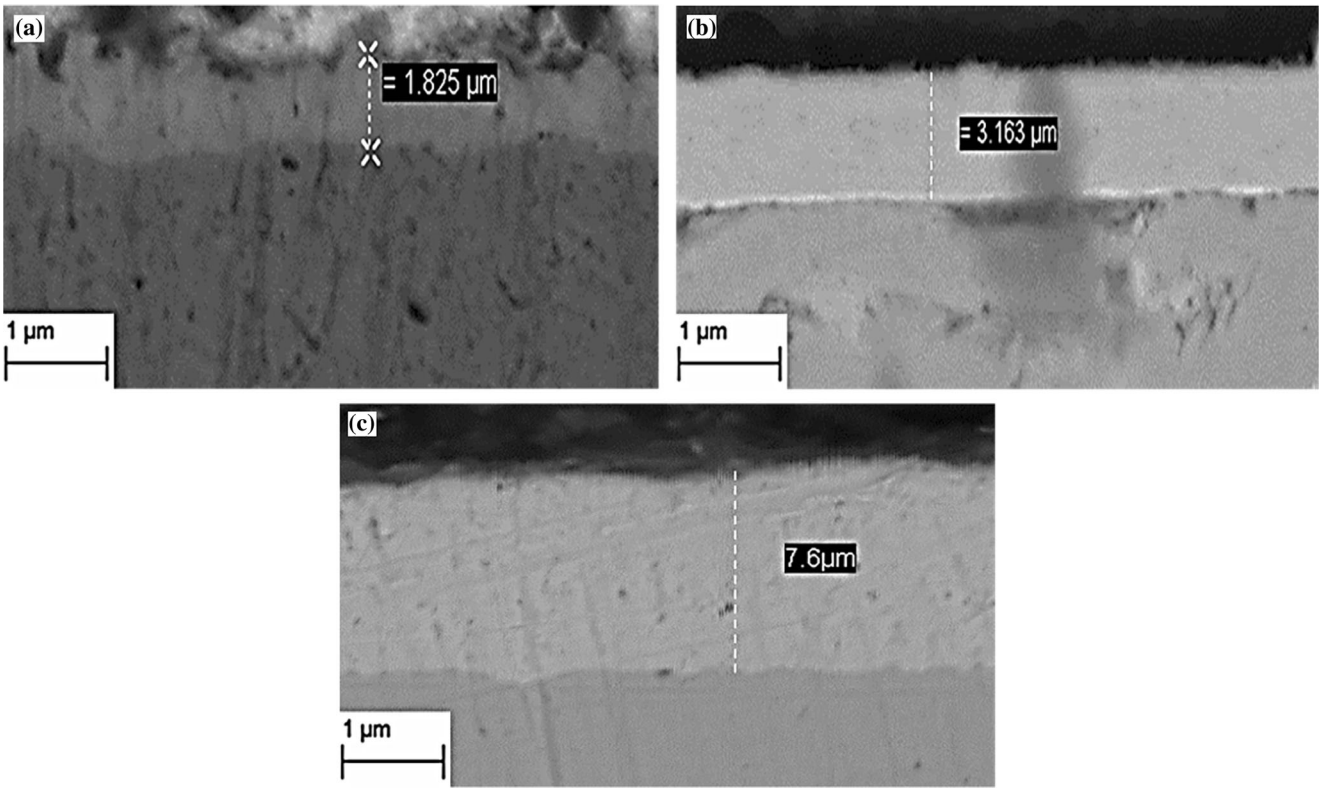

Fig. 7 FESEM images of TiO_2 in three different thicknesses on FTO glass **a** 1.83 μm (1 layer of adhesive tape), **b** 3.16 μm (2 layers of adhesive tape), and **c** 7.60 μm (3 layers of adhesive tape)

sensitized with 3.16-μm-thick TiO_2 achieved V_{OC} = 0.37 V, FF = 0.49, and η = 1.18% which is higher compared to TiO_2 1.83 and 7.60 μm in thickness. Meanwhile, for Table 4, the DSSC using 3.16-μm-thick TiO_2 achieved V_{OC} = 0.35 V, FF = 0.65, and η = 0.85%. These results indicate that the efficiency of DSSC also depends on the thickness of TiO_2 together with the types of sensitizers used. The enhancement in photocurrent with different thicknesses of TiO_2 is due to the inherent energy barrier that leads to decrease in recombination of the electron [44].

The thickness of TiO_2 affects the photovoltaic performance of DSSC because TiO_2 is necessary in DSSC as it acts as an electron carrier after the electron was excited by the dye sensitizer when photon was absorbed. The increase in carrier amount as the thickness increases or when it reaches optimum thickness will increase the efficiency of the excitation-recombination process of the electrons which in turn results in increased output [45]. Generally, the DSSC efficiency performance that is dependent on TiO_2 thickness is directly proportional to the increase in TiO_2 layer, thereby leading to an

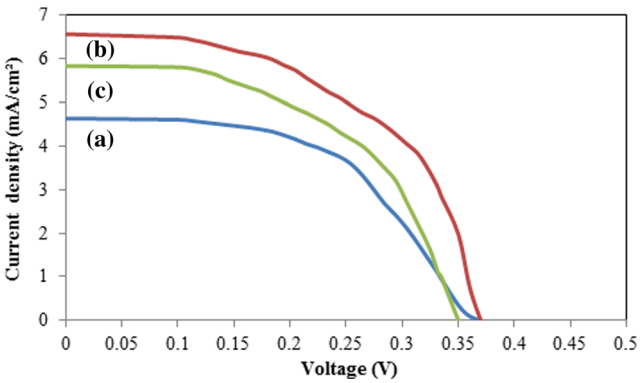

Fig. 8 Comparison of current voltage (*J–V*) characterizations of *E. conferta* coated on different thicknesses of TiO_2 layers: **a** 1.83 μm, **b** 3.16 μm, and **c** 7.60 μm

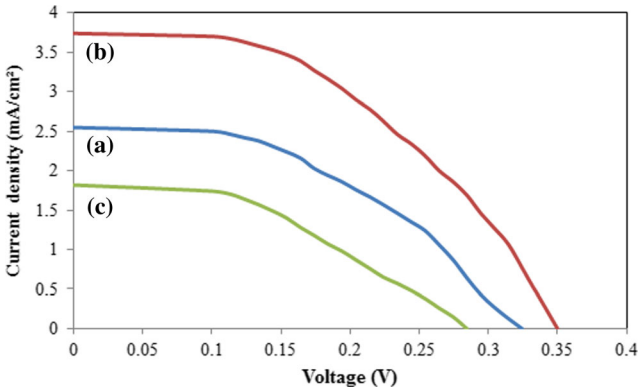

Fig. 9 Comparison of current voltage (*J–V*) characterizations of *G. atroviridis* coated on different thicknesses of TiO_2 layers: **a** 1.83 μm, **b** 3.16 μm, and **c** 7.60 μm

Table 3 Photovoltaic performances of *E. conferta* coated on different thicknesses of TiO_2 layers

Thickness of TiO_2	Jsc (mA/cm^2)	V_{OC}/V	FF	η (%)
1.83 μm	4.63	0.37	0.56	1.00
3.16 μm	6.56	0.37	0.49	1.18
7.60 μm	5.83	0.35	0.54	1.10

increase in absorbed photons which increases the amount of generated electrons [46]. Nevertheless, the increase in TiO_2 thickness increases the excitation-recombination process of electrons which may cause competition between rates of electron excitation and the recombination. Thus, this might help in determining the optimum thickness of TiO_2 for each extraction as the efficiency in DSSC performance begins to decrease.

Comparison of photovoltaic performances for 3.16-μm-thick TiO_2 layer

Table 5 presents photovoltaic DSSC parameters that were obtained from different dye extractions, *E. conferta* and *G. atroviridis*, and 3.16 μm thickness of TiO_2. Their η are 1.18 and 0.85%, respectively. Extraction using *E. conferta* produced higher results compared to *G. atroviridis*; this is related to the anthocyanin bound to TiO_2 surface due to the reduction in undesirable contamination components in the dye matrix [47].

The η from natural dye extraction produces lower efficiencies compared to synthetic dyes (N719). This is due to the molecular structure of natural dye, the anchoring group in the natural dye (interaction dye with TiO_2), and its stability. In natural dye, long chain structure with R groups such as xanthophylls hinders the bonding of the pigment with the oxide surface of TiO_2 [48]. Therefore, it prevents the dye molecules from becoming arrayed effectively on the TiO_2 film. Hence, there is a lack of electron transfer from the dye molecules to the conduction band of TiO_2 [49]. An improved efficiency using *E. conferta* is due to the presence of anthocyanin which helps to create a suitable bond on the surface of TiO_2. In order to improve η, modification of photoanode and counter electrode will help to improve the efficiency using natural dye extract.

Table 4 Photovoltaic performances of *G. atroviridis* coated on different thicknesses of TiO_2 layers

Thickness of TiO_2	Jsc (mA/cm^2)	V_{OC}/V	FF	η (%)
1.83 μm	2.55	0.32	0.63	0.51
3.16 μm	3.74	0.35	0.65	0.85
7.60 μm	1.82	0.28	0.53	0.27

Table 5 Photovoltaic performances of DSSCs of dye extracts at the optimum TiO_2 thickness

Dye extracts	TiO_2 thickness	Jsc (mA/cm^2)	V_{OC}/V	FF	η (%)
E. conferta	3.16 μm	6.56	0.37	0.49	1.18
G. atroviridis	3.16 μm	3.74	0.35	0.65	0.85

Conclusions

The extracts obtained from *E. conferta* and *G. atroviridis* were used as sensitizers in TiO_2 photoanode. The FTIR spectra of *E. conferta* and *G. atroviridis* confirmed the presence of –OH and C=O groups in the molecular structure of anthocyanin dye which means that it can be bound to the surface of porous TiO_2 film. The broad absorption of *E. conferta* may have resulted in absorption in photon energy at broader wavelengths, bringing about the generation of more photoelectrons, compared to *G. atroviridis,* affecting the photovoltaic performance. *E. conferta* indicated the highest photovoltaic performance compared to *G. atroviridis* using 3.16-μm-thick TiO_2 layer. *E. conferta* produced 1.18% of η with V_{OC}, J_{SC}, and FF values of 0.37 V, 6.56 mA/cm^2, and 0.49, respectively.

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Conflict of interest No conflict of interest.

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