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Potential natural sensitizers extracted from the skin of *Canarium odontophyllum* fruits for dye-sensitized solar cells

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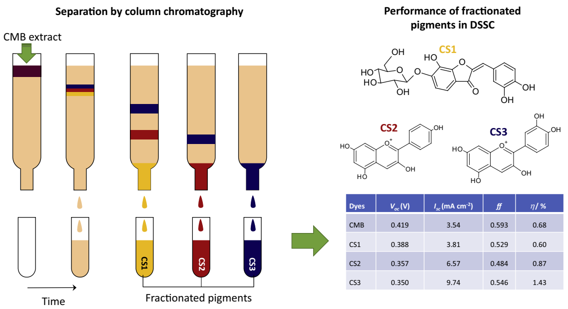
HIGHLIGHTS

- Natural dye was extracted from *Canarium odontophyllum.*
- Dye constituents were separated by column chromatography.
- DSSCs were sensitized with the constituents.
- Improved performances of DSSCs using constituents.

GRAPHICAL ABSTRACT



Dyes	V_{oc} (V)	I_{sc} (mA cm^{-2})	*ff*	η / %
CMB	0.419	3.54	0.593	0.68
CS1	0.388	3.81	0.529	0.60
CS2	0.357	6.57	0.484	0.87
CS3	0.350	9.74	0.546	1.43

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ABSTRACT

Possibility of use of dye extract from skin samples of a seasonal, indigenous fruit from Borneo, namely *Canarium odontophyllum*, in dye sensitized solar cells (DSSCs) are explored. Three main groups of flavonoid pigments are detected and these pigments exhibit different UV–vis absorption properties, and hence showing different light harvesting capabilities. When applied in DSSCs. The detected pigment constituents of the extract consist of aurone (maritimein), anthocyanidin (pelargonidin) and anthocyanidin (cyanidin derivatives). When tested in DSSC, the highest conversion efficiency of 1.43% is exhibited by cyanidin derivatives, and this is followed by conversion efficiencies of 0.51% and 0.79% for aurone and pelargonidin, respectively. It is shown that individual pigments, like cyanidin derivatives and pelargonidin, exhibit higher power conversion efficiency when compared to that of *C. odontophyllum* skin pigment mixture (with a conversion efficiency of only 0.68%). The results indicate a possibility of masking effects of the pigments when used as a mixture. The acidification of *C. odontophyllum* skin pigments with concentrated hydrochloric acid improves the conversion efficiency of the mixture from 0.68% to 0.99%. The discussion in this paper will draw data and observations from the variation in absorption and adsorption properties, the HOMO–LUMO levels, the energy band gaps and the functional group compositions of the detected flavonoids.

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Introduction

Increasing concern about the market demand, rise on fossil fuel prices, sustainability of the uninterrupted energy and climate change have made renewable energy to play a vital role in producing local, clean and inexhaustible amount of energy source. This alternative energy source can be found in Brunei Darussalam where the Sultanate receives maximum exposure to sunlight throughout the year which resulted into a vast rainforest cover [1] with high species richness and diversity. This represents a significant potential in solar-energy resource, making solar energy technologies as one of Brunei's most promising technological development in the production of alternative energies.

Solar energy technology is directed to conversion of solar energy such as radiant light and heat, into useful energy carriers which include heat, electricity and transport fuel [2]. The study of natural photosynthesis process has highlighted the functionality of natural pigments in harnessing solar energy [3]. This knowledge has further improved understandings on properties of pigments and has shown the pathways to the use of dyes or pigments for capturing solar radiation, and converting it to more manageable forms of energy. This was first successfully demonstrated by Gratzel and co-workers in 1991 [4].

This nature-mimicking device is a photoelectrochemical device that works by converting visible light from solar energy into electricity based on the photosensitization of semiconductors, TiO_2 called dye sensitized solar cell (DSSC). DSSC relies on photosensitization to function. Photosensitization is a process whereby energy of absorbed light is transferred from a photosensitizer (light-absorbing molecules such as dyes) to an acceptor (such as semi-conductors) [5,6].

The performance of DSSC is highly dependent on the dye sensitizer and the acceptor materials and the new generation of DSSC using cobalt-based redox mediators has achieved 12.3% under full sun illumination [7,8]. Till now there is a vast interest in utilizing new families of dyes, new designs of the metal complexes and effective redox mediators to improve the performance of sensitizers. The power conversion efficiencies record of DSSC stands at 13%, which uses a combination of reengineered light harvesting donor-π-acceptor (D-π-A) porphyrin dyes with cobalt-based redox mediators [8].

At the fundamental level, the interest is on the charge distribution. Generally, the dye used in DSSCs consists of an electron-donating group, the π-spacer and the electron acceptor. It has been shown that small variations within any of these components can cause significant differences in photovoltaic performance of the DSSC [9].

The procedures in the preparation and development of synthetic dyes as sensitizer of DSSC normally involve variety of solvents, chemical reactions and time consuming purification processes, making synthetic dye production prohibitively expensive for the industry [10]. Due to the high cost of heavy-metal complexes and inconsistent supply of these noble metals, there is a need to search for alternative photosensitizers for the use in TiO_2-based photovoltaic devices.

Several researchers have reported the possibility of using natural dyes as DSSC sensitizer [11–13]. Although the stability of DSSCs equipped with natural dyes as sensitizers is still a challenge [11], they offer many advantages over the rare transition metal complexes and other synthetic dyes. The availability of natural dyes in large quantities, the convenience in extraction process, the ability for DSSC application without fine purification, environmentally-friendly by-products, and low production cost are some of the motivations for the study of these dyes [11,14].

Studies on potential DSSC based on natural dyes as sensitizers has marked 4.6% efficiency using isolated chlorophyll as reported by Wang et al. [15] and 2.3% was obtained using *Monascus Yellow* dye as sensitiser [16]. This paper reports on the study of the characteristics and performance of natural pigments of *Canarium odontophyllum*, an indigenous fruit from Borneo Island located at the South East Asia region, as a dye sensitizer in DSSC. The extract from the skin of the fruit has three main groups of flavonoid pigments, and they each exhibit different UV–vis absorption properties, and hence each having different light harvesting capabilities. The pigment constituents of the extract were found to consist of aurone (maritimein), anthocyanidin (pelargonidin) and anthocyanidin (cyanidin derivatives). Anthocyanins from various natural sources have been reported to produce various sensitizing performances [13].

The investigated skin of *C. odontophyllum* fruit is normally discarded prior to consuming the flesh. It is regrettable, that it has not being utilized in any dye-sensitized solar cell application. However, this paper shows the use of the extracted natural pigments from the skin of the *C. odontophyllum* for generating electricity from solar radiation. Based on the findings of current work, isolated flavonoids from the skin have been found useful as sensitizers of DSSCs and have shown the potential, value added benefits in the fabrication of the low cost dye-sensitized solar cells.

Materials and methods

Samples

C. odontophyllum or locally known as Kembayau is a fruit indigenous to Borneo. Once the outer dark purplish colored skin is removed, the quality and matured fruits of *C. odontophyllum* have an oily-yellowish appearance. *C. odontophyllum* is a tropical and seasonal fruit with high nutritional values in minerals, proteins, carbohydrates and fats [17].

In this study, matured and freshly harvested fruits of *C. odontophyllum* were obtained from an orchard. The skin was peeled and labeled as "CMB" (abbreviated from "Kembayau"). This skin sample was then used for dye extraction, analysis of chemical components, and potential usage of the dye as sensitizer in the dye-sensitized solar cell device.

Experimental methods

Dye extraction and pigment separation

The dye was extracted by grinding 20 g of fruit skin sample on fresh weight basis in 70% ethanol. The ethanol was diluted from Scharlau 99.9% with distilled water. The contents were then heated at 60 °C in a constant temperature water bath to further concentrate the extract. The residual solids were filtered off, and the extract was then centrifuged at 4500 rpm to separate any remaining solid content to obtain a clear extract.

The CMB pigments separation was done by column chromatography, whereby the glass column was filled with 40 g of silica gel (type 60) using slurry method, and chloroform was used as the developing solvent. The separated dye components were collected, recovered and concentrated *in vacuo* in a rotary evaporator below 60 °C.

Further analyses were carried out using thin layer chromatography (TLC), Fourier transform infrared spectroscopic measurement (Shimadzu IR Prestige-21, FTIR), and UV–vis absorption spectroscopy (Shimadzu UV-1800), detecting the presence of flavonoids mainly, anthocyanins and aurone [18].

Fabrication of photo-electrode and preparation of dye-sensitized solar cell

The photoelectrodes were fabricated using a TiO_2 paste Solaronix (nano-oxide-T, colloidal anatase particles size: ~13 nm, ~120 $m^2 g^{-1}$ (BET)) and were coated on pre-cleaned fluorine-doped conducting tin oxide (FTO) glasses (Nippon sheet glass 10–12 Ωsq^{-1}) by Doctor Blade method. The films were sintered for 30 min at 450 °C. After sintering the thickness of TiO_2 was ~9 µm (Dektak profilometer; Veeco, Dektak 3). The sintered TiO_2 electrodes were dipped in the respective dye solutions for overnight at room temperature and then dried under a flow of nitrogen. The active solar cell area was measured using photo graphs of each cells (~0.25 cm^2). The cells were assembled using Dyesol's Test Cell Assembly Machine. The sealant was Surlyn (50 µm, Dyesol) and the electrolyte was tetrabutylammonium iodide (TBAI; 0.5 M)/I_2 (0.05 M) in a mixture of acetonitrile and ethylene carbonate (6:4, v/v) [19–21]. These DSSCs were then placed under Solar Simulator LP-156B (Dyesol) and *I*–*V* data were obtained under one sun condition.

Power conversion efficiencies, HOMO–LUMO and band gap calculations

The power conversion efficiency (η) was calculated using the following, described relation:

$$\eta = ff \times I_{SC} \times V_{OC}/P$$

where I_{sc} is the short-circuit photocurrent density (A cm^{-2}), V_{oc} is the open-circuit voltage (*V*), *P* is the intensity of the incident light (W cm^{-2}) and *ff* is the fill factor defined as $ff = I_m V_m / I_{sc} V_{oc}$, in which I_m and V_m are the optimum photocurrent and voltage that can be extracted from the maximum power calculated from the *I*–*V* data [19–23].

Studies of the electrochemical behavior of the dyes were carried out using cyclic voltammetry with the following specifications: eDAQ Potentiostat equipped with e-corder 401; software: EChem Application Ver. 2.1.5; scan rate: 100 mV per second; range of −1000 mV to +1000 mV; initial direction is positive and number of cycles is 2. The electrolyte used was 1 M KNO_3 solution. Both absorption spectra and reduction onset were used to calculate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the investigated pigments [19–21]. The energy band gaps of the CMB extract and its recovered pigments were estimated using UV–vis absorbance spectra, cyclic voltammetry data and the Tauc relation [20–23]. For comparison, HOMO level of a selected dye was estimated by photoelectron spectroscopy (Riken Keiki AC3). The dye adsorbed on a porous TiO_2 layer was used for this measurement.

Electrochemical impedance spectroscopic measurement

The electrochemical impedance spectroscopic measurements of the DSSCs were carried out using computer controlled electrochemical interface (SI 1287, Solatron) and impedance/gain-phase analyzer (SI 1260, Solatron). The frequency range was from 0.01 Hz to 65 MHz, and the amplitude of alternative voltage was 10 mV [24]. The impedance measurements were performed at open circuit condition under the illumination of 100 mW/cm^2. Impedance parameters and equivalent circuits were obtained by fitting the spectra with ZView software (v3.3, Scribner Associate Inc.).

Results and discussion

The column chromatographic separation showed three different colored bands; yellow (CS1), followed by reddish-blue (CS2), and lastly dark blue band (CS3).

When assayed using UV–vis spectrophotometry, FTIR and TLC techniques three possible groups of flavonoids were detected, namely aurone (maritimein), anthocyanin (pelargonidin) and anthocyanidin (cyanidin derivatives). Identification of the flavonoids was carried out by comparing UV–vis spectral data, see Table 1, to specific dye standards from the literature [18,25,26].

It is evident from Table 1, that an aurone, being one of the flavonoids detected in the extract, showed different absorption characteristics to that of anthocyanins with numerous peaks below 500 nm wavelength. See also Fig. 1. A minor peak at 651 nm is also observed. A broad peak at around 510–550 nm signifies the presence of anthocyanins, as shown by CMB, CS2, and CS3 absorption curves, respectively. However, the minor but considerable differences of peak positions of CS2 and CS3 curves, at 530–533 nm and 536–538 nm, indicate the presence of two detected anthocyanins, possibly pelargonidin, and cyanidin derivatives [25,26].

The anthocyanins are sensitive to pH changes due to a reversible structural change that occurs in the C ring of the molecules [27]. The addition of concentrated hydrochloric acid (HCl) to the CMB extract resulted in an equilibrium shift of anthocyanin towards their flavylium cation (AH^+) which accounted for the bright red coloration of the acidified extract [28]. Fig. 2 compares the absorption spectra of non-acidified and acidified anthocyanin extract of the CMB dye which shows an intense peak at 540 nm wavelength in the latter case.

The broad and intense absorption peak around 540 nm which emerges after CMB dye acidification (by adding concentrated HCl) facilitates DSSC to absorb visible light spectrum effectively at low energy solar radiation, thus resulting in an improved overall photovoltaic performance. This indicates that light absorption properties of the pigment influences the performance of DSSC.

The analysis of the functional groups of the three recovered flavonoid groups is carried out using Fourier Transform Infrared (FTIR) spectroscopy, with KBr as the background reference. Both

Table 1
UV–vis absorption peaks of fruit skin of *Canarium odontophyllum* (CMB) crude extract, and its components separated by silica gel column chromatography.

Dyes	Absorbance peaks (nm)	Types of flavonoids (dye)
CMB	280, 348, 541	Mixture of flavonoids
CS1	273, 336, 420, 651	Aurone
CS2	273, 320, 530	Anthocyanidin (Pelargonidin)
CS3	280, 333, 536	Anthocyanidin (Cyanidin derivatives)

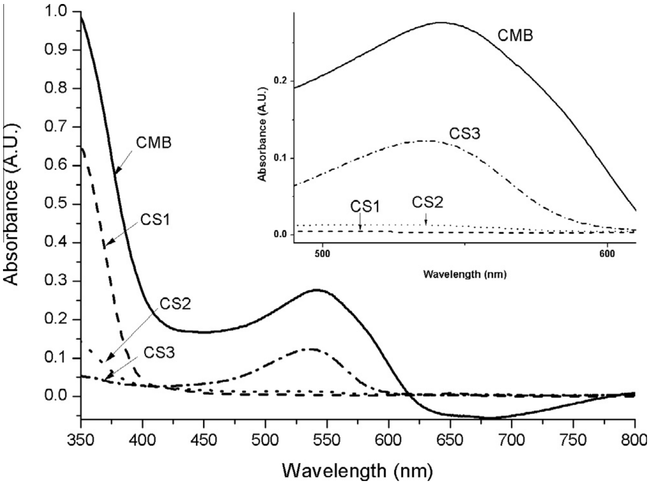


Fig. 1. UV–vis absorption spectra of CMB dye and the three recovered flavonoids as exemplified by CS1, CS2 and CS3.

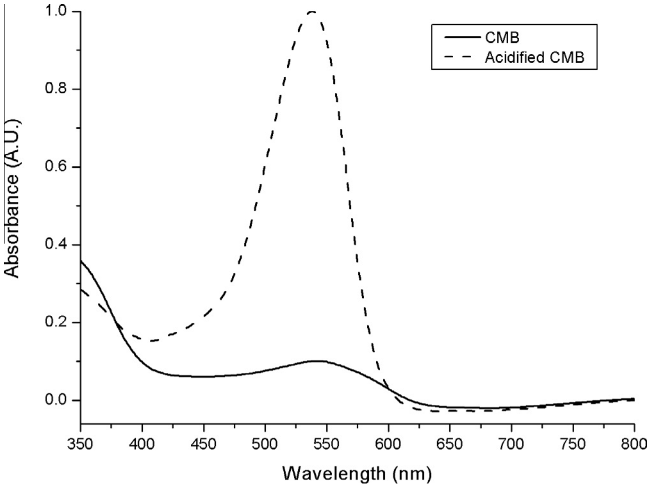


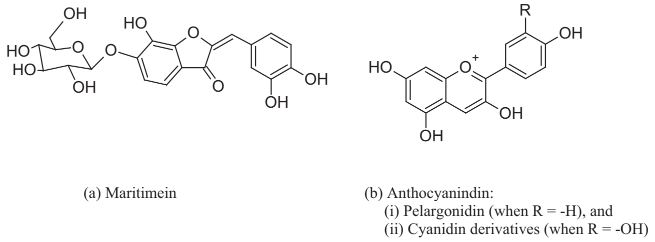
Fig. 2. UV–vis absorption spectra of CMB dye (with and without acidification).

aurone and anthocyanin exhibit the presence of hydroxyl groups. Aurone shows the presence of carbonyl (ketone) functional group but not for the anthocyanin groups. Peaks appeared at (2892 and 2927) cm^{-1}, (2897 and 2975) cm^{-1}, as well as (2832 and 2944) cm^{-1} as shown in Fig. 3, correspond to the –CH stretching modes. The broad and intense peak at wavenumber 3372, 3363 and 3361 cm^{-1}, shown in A, B, and C correspond to the –OH stretching vibration for the aurone and anthocyanins [29].

The presence of carbonyl and hydroxyl groups in aurone, and hydroxyl groups in anthocyanin molecules respectively (Fig. 4), help in the binding of the dye molecules to TiO_2, thus contributing to the photoelectric conversion efficiency [30].

The UV–vis absorption spectra of CMB, acidified CMB, and the three recovered flavonoids adsorbed onto TiO_2 film are as depicted in Fig. 5.

It is shown that acidification of the original CMB by HCl enhanced the absorption at 500–550 nm on the TiO_2 film, which has positive effect on the performance of the DSSC. Furthermore, HCl has been shown to enhance the performance of TiO_2 electrode as the result of HCl treatment procedures [31]. The UV–vis absorption of the three flavonoids on TiO_2 is CS3 > CS1 > CS2. In addition, we have reported the details study on the absorption behavior of CMB onto TiO_2 nanoparticles [19].



(a) Maritimein

(b) Anthocyanindin:
(i) Pelargonidin (when R = -H), and
(ii) Cyanidin derivatives (when R = -OH)

Fig. 4. Chemical structures of maritimein, pelargonidin and cyanidin derivatives.

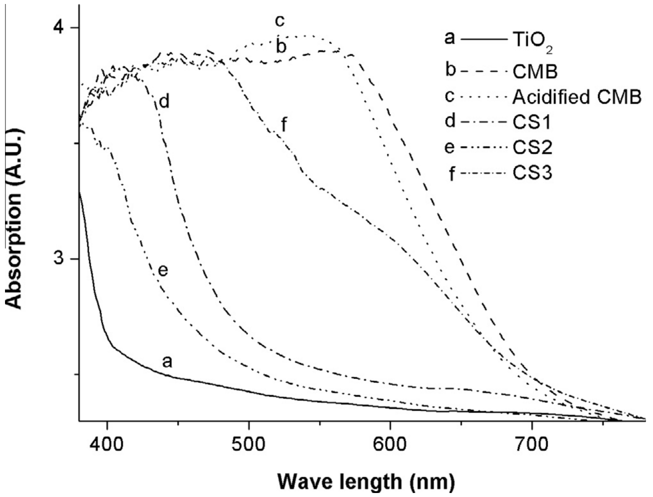


Fig. 5. UV–vis absorption spectra of CMB, acidified CMB and the three recovered flavonoids on TiO_2 film.

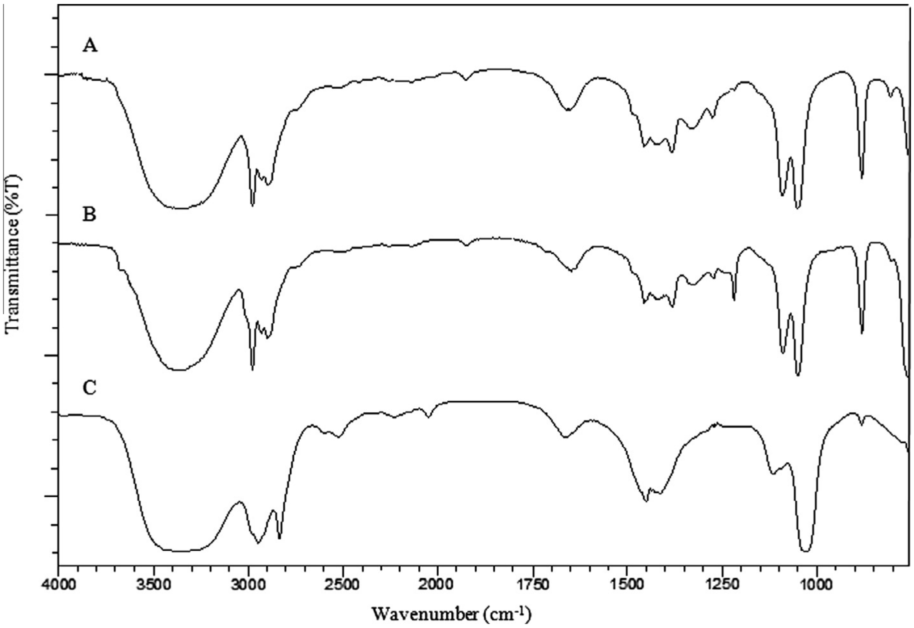


Fig. 3. FTIR spectra of (A) aurone from CS1, (B) pelargonidin from CS2 and (C) cyanidin derivatives from CS3.

Table 2 summarizes the *I–V* (current density–voltage) characteristics and power conversion efficiencies (η) of the DSSCs sensitized with CMB extract, acidified CMB extract, CS1, CS2 and CS3. The results are compared to the standard N719 dye.

Table 2 shows that DSSC sensitized with CMB has achieved the conversion efficiency (η) of 0.68%, with open circuit voltage (V_{OC}) of 419 mV, short circuit current density (I_{SC}) of 3.54 mA cm^{-2} and fill factor (*ff*) of 0.59, under irradiance of one sun. On the other hand, acidification of CMB dye extract has shown improvement in the photocurrent conversion efficiency of DSSC (Fig. 6), with enhanced power conversion efficiency (η) of 0.99%, with open circuit voltage (V_{OC}) of 331 mV, short circuit current density (I_{SC}) of 10.33 mA cm^{-2}, and fill factor (*ff*) of 0.38, under irradiance of one sun.

The photocurrent conversion efficiency of DSSC sensitized with CMB dye is lower when compared to that of the two recovered portions of anthocyanins. This may indicate a possible masking effect when all components are present as a mixture. Anthocyanin in nature, plays a protective role in senescing leaves as "sunscreens" where it acts by masking the light (protection from excess irradiance) to prevent heat buildup in the leaves, and limiting oxidative damage to the leaf's cells [32]. DSSC sensitized by aurone (CS1), however, did not perform well in this investigation. This could suggest that aurone extract did not adsorb efficiently onto TiO_2, or the excited electrons were not efficiently transferred to the electrode from the aurone pigment.

The best performance among the natural extracts is observed from the DSSC sensitized with CS3, which shows a conversion efficiency (η) of 1.43%, with open circuit voltage (V_{OC}) of 350 mV, short circuit current density (I_{SC}) of 9.74 mA cm^{-2} and fill factor (*ff*) of 0.55 under irradiation of one sun. This performance is comparably better than many anthocyanin extracts reported from other sources [11], which suggests that isolated anthocyanin dyes from CMB performed better than when they are in their naturally occurring dye mixture. Such promising performance would further the research line in assessing the stability of DSSCs based on natural dyes, which still remains debatable, however that could be another scope of study altogether.

Table 2
Current–voltage (*I–V*) characteristics and power conversion efficiencies (η) of DSSCs sensitized with different constituents of extracted and recovered dyes. Results of N719 (ruthenium-based dye) are shown for comparison.

Dyes	V_{oc} (V)	I_{sc} (mA cm^{-2})	*ff*	η/%
CMB	0.419	3.54	0.593	0.68
Acidified CMB	0.331	10.33	0.376	0.99
CS1	0.388	3.81	0.529	0.60
CS2	0.357	6.57	0.484	0.87
CS3	0.350	9.74	0.546	1.43
N719	0.564	22.91	0.603	5.98

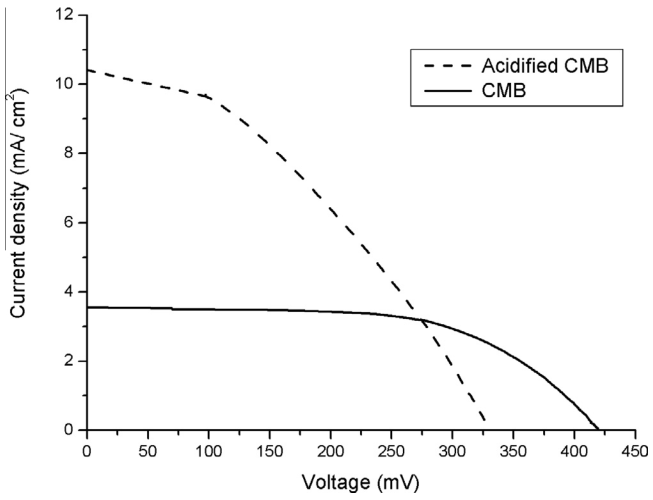


Fig. 6. Comparison of current voltage (*I–V*) characterisations of DSSCs sensitized with CMB dye (with and without acidification).

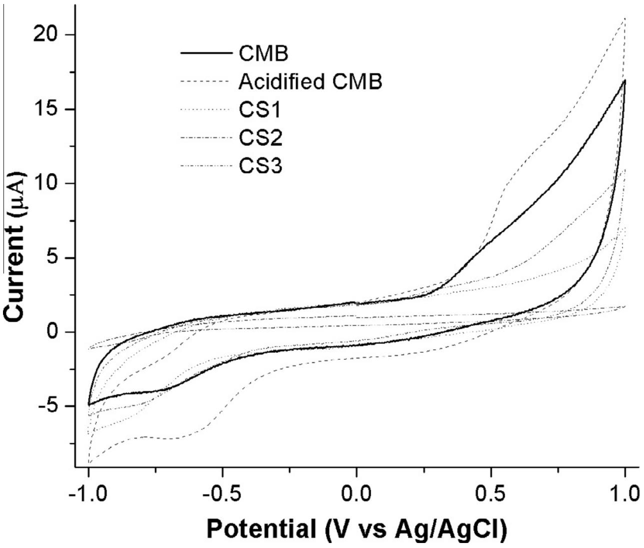


Fig. 7. Cyclic voltammograms of the dye pigments.

Table 3
Calculated HOMO–LUMO energy levels and band gap energies of *Canarium odontophyllum* (CMB), acidified CMB and three groups of recovered flavonoids. The values (HOMO and Band gap) correspond to the new energy level formed in acidified CMB are also given (in italic).

Dyes	Reduction potential (eV)	Band Gap (eV)	HOMO (eV)	LUMO (eV)
CMB	−0.41	3.79	−7.78	−3.99
Acidified CMB	−0.32	*2.10*	*−6.18*	−4.08
CS1	−0.60	3.15	−6.95	−3.80
CS2	−0.70	3.28	−6.98	−3.70
CS3	−0.39	2.11	−6.12	−4.01

The electrochemical properties of dye pigments were investigated by using cyclic voltammetry to determine the energy levels of HOMO and LUMO. A long life time of oxidized dye at LUMO causes inefficient dye regeneration that leads to a decay of V_{OC}. For efficient regeneration of dye to take place, the HOMO level of the dye has to be at least 100–200 mV more positive than the redox potential of the mediator [24]. Our results reveal that the HOMO of the acidified CMB is closer (1.38 eV) to the redox potential compared to that of CMB (2.98 eV) which explains the reduction of the V_{OC} of the DSSC sensitized with acidified CMB.

Fig. 7 shows the cyclic voltammograms of the dye pigments. The calculated positions of HOMO and LUMO levels of the investigated dye pigments are shown in Table 3, with their respective reduction potential onset.

An illustration of the changes taking place in the HOMO and LUMO levels for CMB, acidified CMB and recovered flavonoid components are shown in Fig. 8. The edges of the conduction and valence bands of TiO_2 are also shown in the illustration.

Fig. 2 shows an absorption peak emerging at around 540 nm upon the addition of concentrated hydrochloric acid to the CMB. This gives rise to an energy level (HOMO at −6.18 eV) formed near the middle of the TiO_2 band gap. This HOMO level facilitates efficient electrons transfer to the conduction band. This HOMO level

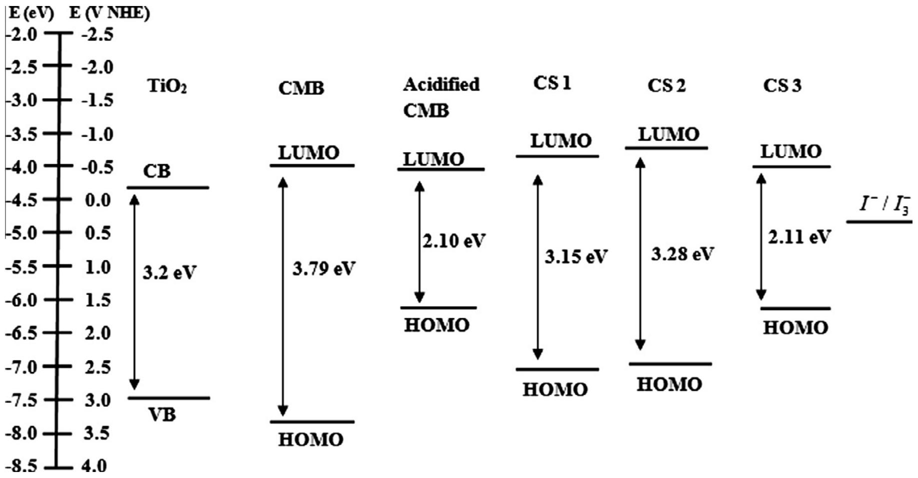


Fig. 8. Schematic diagram showing the calculated positions of HOMO and LUMO levels of the investigated dye pigments with respect to the vacuum level and NHE.

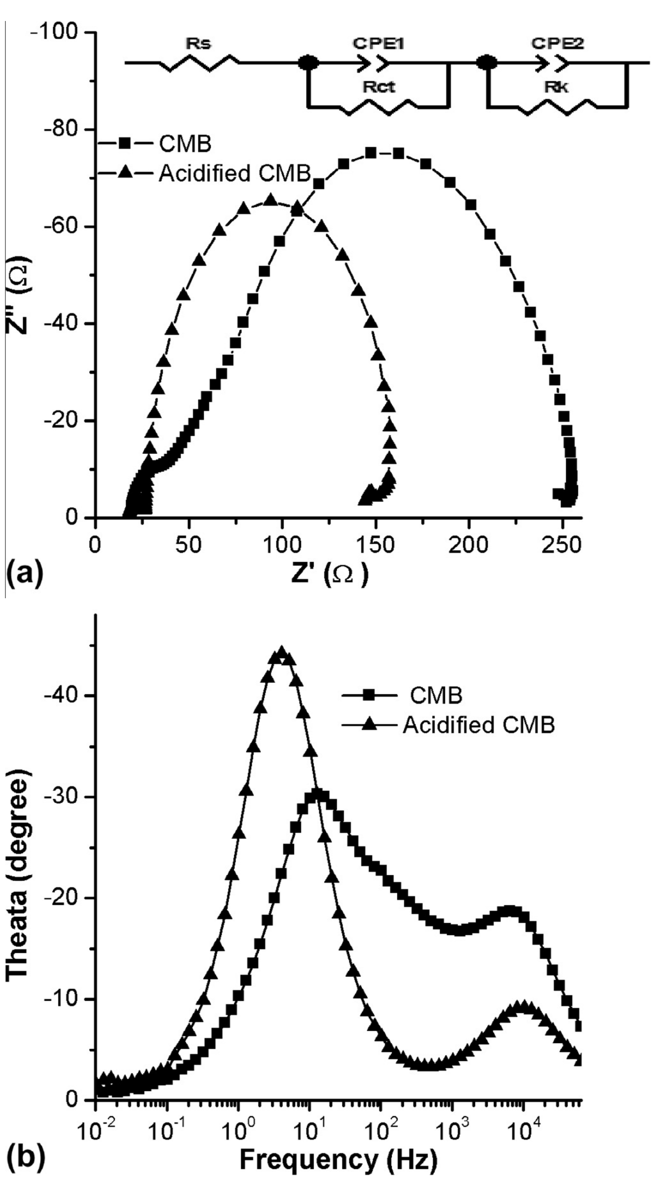


Fig. 9. Electrochemical impedance spectra measured under the illumination (100 mW cm^{-2}) and open circuit conditions for DSSCs sensitized with CMB and acidified CMB. (a) Nyquist plots. (b) Bode phase plot. Inset of (a) shows the equivalent circuit diagram for EIS.

was also estimated by using photoelectron spectroscopy (Riken Keiki AC3), and the estimated value is −6.23 eV, which shows the accuracy of the energy values calculated using experimental data.

Electrochemical impedance spectroscopy (EIS) is a useful method to analyze the kinetics of electrochemical and photoelectrochemical processes in DSSC [24,33–36]. Fig. 9(a) shows the Nyquist plots of DSSCs sensitized with CMB, and acidified CMB, both under the same illumination. Two arcs are clearly obtained in the frequency regimes of 10^3–10^5 and 0.1–10^2 Hz. These arcs correspond to the impedances at Pt electrode/electrolyte and TiO_2/dye/electrolyte interfaces, respectively. The impedance in each interface is determined after fitting the EIS data with ZView software in terms of an appropriate equivalent circuit (see inset of Fig. 9(a)). The charge transfer resistances related to the recombination of electrons (R_k) in TiO_2/dye/electrolyte interface are determined by using the large arc of Nyquist plot. The R_k values are 216 and 136 Ω for DSSCs sensitized with CMB and acidified CMB, respectively [33]. A higher R_k value corresponds to a lower probability in the recombination of electrons. The low recombination resistance (R_k) in TiO_2/dye/electrolyte interface directly affects on decay of V_{oc} in DSSCs due to high recombination process [24]. This is consistent with experimentally obtained V_{oc} values from DSSCs sensitized with CMB and acidified CMB.

Fig. 9(b) illustrates the Bode plot of CMB and acidified CMB sensitized DSSCs. The peaks at the low frequency and the high frequency are associated with effective life times of electrons on the surface of TiO_2 nanoparticles, and on the platinum electrodes, respectively. The peak frequencies are inversely proportional to the respective effective life-times of electrons [33]. The peak frequency at the low frequency regime, that is in the range of 0.1–10^2 Hz for acidified CMB sensitized DSSC, is at 4.1 Hz. This is of much smaller value than that of CMB sensitized DSSC which is at 13.4 Hz. This indicates a higher effective life-time of electrons in acidified CMB. To obtain an efficient DSSC, higher effective life-time of electrons in TiO_2 film is required. The acidified CMB sensitized DSSC has more than three times higher effective life-time of electrons in the TiO_2 film when compared to CMB sensitized DSSC. This is in the agreement with the experimental *I–V* results.

Conclusions

DSSC fabrication using natural dye extract and recovered flavonoid groups from the skin of *C. odontophyllum* as photosensitizer and the performance of the dye and its constituents in solar energy conversion are reported. The results of this investigation show that one group of aurone and two groups of anthocyanins are present in the recovered flavonoid groups in CMB. The best overall energy conversion efficiency of 1.43% was observed from the recovered cyanidin derivatives group, CS3. The acidification of skin pigment using concentrated hydrochloric acid has demonstrated an improved overall conversion efficiency as likely caused by improvement of both absorption and adsorption properties of the pigments.

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