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Effect of Natural Dye Co-Sensitization on the Performance of Dye-Sensitized Solar Cells (DSSCS) Based on Anthocyanin and Betalain Pigments Sensitisation

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Abstract: Dye-sensitized solar cells (DSSCs) were prepared using natural pigments containing anthocyanin and betalain extracted from Flame tree and Bougainvillea glabra flowers respectively as sensitizers. The dyes were used as lone sensitizers exploring anthocyanin and betalain separately and as co-sensitizers exploring the combined anthocyanin and betalain (water extract) and combined anthocyanin and betalain (ethanol extract) separately. The effects of the sensitizers on the performance of the DSSCs were investigated, the study reveals that all the cells possess comparable values of V_{oc} of about 0.55◊0.1 V. However, of the two lone sensitisers, betalain based device gave a better efficiency of 0.21% while anthocynin based device achieved 0.17 %, this is attributed to their different anchoring functional groups. The, combined anthocyanin and betalain dyes (water extract) had the highest conversion efficiency of 0.26 % suggesting dye synergic absorption effect as a result of co-sensitisation, the lower efficiency of 0.24 %) achieved by combined anthocyanin and betalain (ethanol extract) is attributed to the contributory effect of the extraction solvents.

Key words: DSSCs · Anthocyanin · Betalain · Co-sensitization · Natural dyes

INTRODUCTION

The high global demand for alternative renewable and sustainable energy, dye-sensitized solar cells (DSSCs) are considered as one of the most promising candidates for energy conversion due to their environmental friendliness, low cost and simple fabrication process [1]. The technology was first reported by O'Regan and Gratzel (1991) featuring a low-cost dye-sensitized crystalline solar cell using organic dyes adsorbed on a nanocrystalline titanium (IV) oxide (TiO_2) film as the photoanode to absorb light and produce electric current that later became known as the Grätzel cell or dye-sensitised solar cell (DSSC) [2].

The diversity of DSSC components makes it attractive because novel materials are easily incorporated into a variety of photo-collection systems to conform and optimise their effect [3]. The compatibility between photosensitizers and the wide bandgap semiconductors (usually TiO_2) to produce high efficient DSSCs plays a crucial role in the photocurrent generation [4]. Synthetic dyes are most commonly used photosensitizers, which are highly efficient and possess a brilliant light harvesting capacity, nevertheless, the high cost; toxicity and scarcity have necessitated the shift of attention to natural dyes as an alternative option. On the other hand, natural sensitizers (dyes) have drawn a considerable attention due to their abundance in nature, low cost, easy extraction, non-toxicity and the environmentally benign nature [5]. Yet their efficiency is far lower than efficiencies of DSSCs based on synthetic dyes, which is attributed to the ratio of the rates of injection and recombination electron transfer and the rate at which the oxidized dye reacts with the reduced form of the redox mediator [6].

Among natural pigments, three main families of compounds: chlorophylls, anthocyanins and betalains have been investigated extensively as sensitizers in DSSCs [7].

Both anthocyanin and betalain pigments exhibit a more favourable overlap with the solar spectrum, which is associated with various co-pigments that modify their light absorption properties [6, 7].

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This work employed natural dyes based on anthocyanin and beta lain pigments extracted from flame tree and Bougainvillea glabra flowers as photosensitizers using water and ethanol as extraction solvents. The effects of the Flame tree anthocyanin and bougainvillea glabra betalain pigments sensitization and their co-sensitization on the performance of DSSCs were investigated through I-V characteristics measurement of the cells respectively.

MATERIALS AND METHODS

Preparation of Photosensitizer: The photosensitizers were natural dyes from anthocyanin and betalain pigments extracted from Flame tree and Bougainvillea glabra flowers respectively. 12 g of the Flame tree flower was crushed in a porcelain mortar and mixed with 20 ml of distilled water. The mixture was kept overnight at ambient temperature for adequate extraction, then filtered and the filtrate used as the sensitizing dye solution without further purification. Betalain pigments were extracted in a similarly manner.

The preparation of co-sensitizer involved the combination of anthocyanin and betalain. This was prepared with Flame tree and Bougainvillea glabra flowers of 6 g each crushed together and mixed with 20 ml of distilled water (water extract) or 20 ml of ethanol (ethanol extract).

Preparation of Photoanode: Fluorine doped tin oxide (FTO: TCO30-8 glass, 8 Ω/sq, 3 mm thick, Solaronix) glass sheets was cleaned with detergent solution, rinsed with distilled water, ethanol and dried under compressed hot air for 7 min at 70°C in a clean container. Mesoporous TiO_2 (m-TiO_2) paste (Ti-Nanoxide T300/SP, Solaronix) was screen-printed onto the prepared FTO glass substrates using a polyester mesh of 90 and dried on heating stage in an open air at 125°C for 6 min and allowed to cool down to the room temperature. Another layer of the m-TiO_2 was repeated using screen-printing method to obtain about 9μm thickness. The photoanode was sintered at the ramping rate of 50°C at the dwelling time of 2 min from 150°C to 500 °C. At 500°C, the films were sintered for 30 min in order to ensure proper electrical contact and mechanical adhesion on the glass.

The photoanodes were each soaked in four different petri dishes containing the sensitizing dyes: anthocyanin, betalain, combined anthocyanin/betalain (water extract) and combined anthocyanin/betalain (ethanol extract) for about 18 hours to complete the sensitiser uptake. After which the dye impregnated photoanodes were rinsed with ethanol (99%, Sigma Aldirch), to remove excess dye that were not properly adsorbed.

Assembly of DSSCs: The counter electrodes was first prepared by screen-printing a 0.5 x 0.6 cm^2 thin film of platinum (Pt) paste (Platisol T/SP, Solaronix) on a bare 2.5 x 2.5 cm^2 FTO glass substrate, then sintered at 100°C for 10 min prior firing at 400°C for 30 min and allowed to slowly cool to room temperature. A sandwich-type DSSCs were fabricated by assembling the dye impregnated photoelectrodes and counter-electrodes in an overlapping manner so as to establish electrical connection between the cells and the photovoltaic measurement equipment. The assemblage was then sealed using hot-melt sealing gasket of surlyn based polymer sheet (SX1170-25PF, Solaronix) leaving a pinhole for the electrolyte injection. The iodine based liquid electrolyte (iodolyte) was injected through the pinhole using micropipette before sealing with the hot-melt sealing gasket.

Characterization and Measurement: The UV-visible absorption spectra of dye solutions and dyes adsorbed onto m-TiO_2 surface were measured with UV-Vis (AVASPEC 2048) spectrophotometer in the near UV and visible region covering 380 – 700 nm. The FTIR spectra were recorded with a Nicolet Impact 410, FTIR-01-0542 in the range of 300 – 4000 cm^{-1} to identify the chemical bonds and the functional groups. The photovoltaic parameters of the cells were determined through a solar simulator Model 4200-SCS Semiconductor Characterization System coupled to Keithley 4200-SCS source meter under simulated AM 1.5 sunlight standard at an irradiance of 100mW/cm^2. The fill factor (FF) and power conversion efficiencies (??) of the cells were determined according to the relationship in equation (1) and (2) [8]:

$$Fill\ factor\ (FF) = \frac{P_{\max}}{V_{oc}J_{sc}} = \frac{V_{\max}J_{\max}}{V_{oc}J_{sc}} \tag{1}$$

where J_{max} and V_{max} indicate the maximum output values of current and voltage respectively and J_{sc} and V_{oc} indicate the short-circuit current and open-circuit voltage respectively. The total energy conversion ef?ciency is given as follows

$$Efficiency\ (\eta) = \frac{FF \times V_{oc} \times J_{sc}}{P_{in}} \times 100 \tag{2}$$

RESULTS AND DISCUSSION

UV-Vis Spectroscopy: The absorption spectra of anthocyanin, betalain, before and after adsorption onto TiO_2 surface are presented in Figure 1. Both Flame tree anthocyanin and Bougainvillea glabra betalain in aqueous solutions showed higher absorbance intensity in the visible region of the as shown in figure 1 indicating good candidates for the sensitisation of the wide band gap semiconductor [9]. The flame tree flower anthocyanin water extract solution shows distinct peak at 400 nm, highest absorbance at 440 nm and a broad absorbance band between 460 and and 600 nm wavelength which is ascribed to charge transfer to charge transfer transitions [10]. When adsorbed on TiO_2, it showed diminished absorbance with distinct peaks at 410 and 520 nm wavelengths as shown Fig. 1 (a). The absorption peak at 520 nm is due to the strong chelation on TiO_2 photo anode films [11]. Standard anthocyanin visible maximum lies between 515 and 545 nm [12].

In Fig. 1 (b) the betalain extract had high distinct absorbance peaks at 430 and 500 nm. The highest absorbance peak at 460 nm is due to yellow-orange betaxanthins [11] with a blue shift from 480 nm. The broad plateau between 520 and 560 nm is a result of presence of eleven violet-red pigments in Bougainvillea glabra [13]. The Betalain absorbed on TiO_2 two peaks at 390 and the highest at 410 nm and subsequently exhibited a diminishing absorbance in the long wavelengths.

Figure 2 shows the absorption spectra of combined anthocyanin and betalain extracts before and after adsorption on TiO_2. Figure 2 (a) showed a single strong absorption peak at 400 nm near a UV region and broad absorbance between 430 and 570 nm for combined dye water extracts. It exhibits reduced absorbance, with a drop between 380 and 480 nm wavelength and subsequently show a slight increase in absorbance drop in absorbance after adsorption onto TiO_2. In Fig. 2 (b), the absorbance show a progressive drop in between 380 and 680 nm for the combine ethanol dye extract. Similar drop in absorbance is observed with the combined dye adsorbed on TiO_2 in the wavelength range 380 – 490 nm.

Fourier Transform Infrared (FT-IR) Analysis: Figures 3 (a) and (b) shows the general chemical structures of anthocyanin and betalain indicating their requisite functional anchoring groups (-OH in anthocyanin and –COOH in betalain) which bind them onto TiO_2 surface respectively.

FTIR spectra in the range of 300 to 4500 cm^{-1}shown in Figure 4 (a) shows distinct peaks at 2939.61, 1638.58, 1300.66, 1068.99 and 1000.84 cm^{-1}. The observed transmission peaks shows characteristics of all the vibration of the functional groups present in Anthocyanin spectrum. The strong peak observed at 3438.23 cm^{-1} is associated with O-H stretching vibration rising for the dye extract, which shift a little away from 3429 cm^{-1} standard value. The strong peak observed at 2943.47 cm^{-1} may be due to C-H stretching of aliphatic groups. The vibrational stretch at 1724.51 cm^{-1} is due to carbonyl group and the band at 1640.51 cm^{-1} correspond to C=C stretching of Benzene ring [15].

In Figure 4 (b) the peak at 2939.6 cm^{-1} shifted a little from standard value of 2926.14 cm^{-1} is attributed to asymmetrical and symmetrical vibration of O-H of carboxyl group, also the wave number at 1638.58 cm^{-1} is due vibrational frequency of C=O of carboxyl group. The signal characteristics bands of C=O carbonyl stretching vibration at 1638.58 cm^{-1} and C – O vibrational stretch at 1300.66 cm^{-1} are due to presence of some aromatic esters [15].

Photoelectric Conversion Efficiency of the DSSCs: The J-V characteristics for both single and co-sensitising dye based DSSCs are shown in Figures 5 and 6 respectively. The open circuit voltages (V_{oc}) show no significant difference while there is considerable differences in the photogenerated current with the anthocyanin and betalain dye based DSSCs.

The photoelectric conversion efficiency of 0.21 % of the betalain extract based DSSC is higher than and efficiency of 0.17 % of the photoelectric conversion efficiency of Anthocyanin extract based DSSC. This is because the betalain sensitising dye employs a carboxylic anchoring moiety which adheres better to TiO_2 surface compared to the hydroxyl anchoring group of Anthocyanin based DSSC, thus enabling stronger electronic coupling and rapid forward and reverse electron transfer reactions [7].

The Antho_Bet (water) DSSC had the highest J_{sc} of 0.79 mA cm^{-2}, followed by a J_{sc} of 0.66 $mAcm^{-2}$ for Antho_Bet (ethanol), resulting in highest power conversion efficiency of 0.26 % and 0.24 % for Antho_Bet (water) DSSC and Antho_Bet (ethanol) DSSC respectively. The comparative photovoltaic parameters, short circuit current (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency (??) of the cells are summarised in the Table 1.

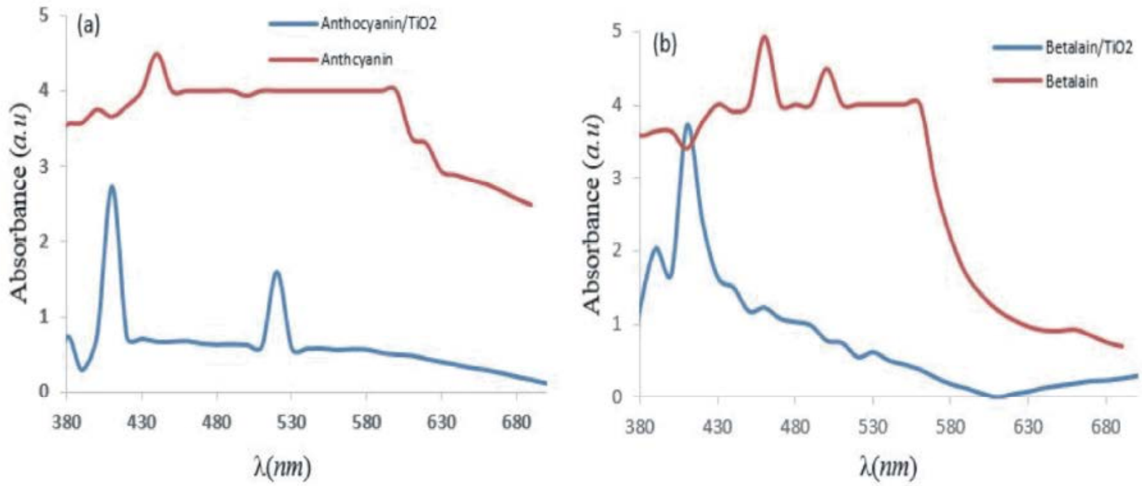

Fig. 1: Absorption spectra of Flame tree anthocyanin and Bougainvillea glabra betalain water extracts (a) before and (b) after adsorption onto m-TiO_2 surface

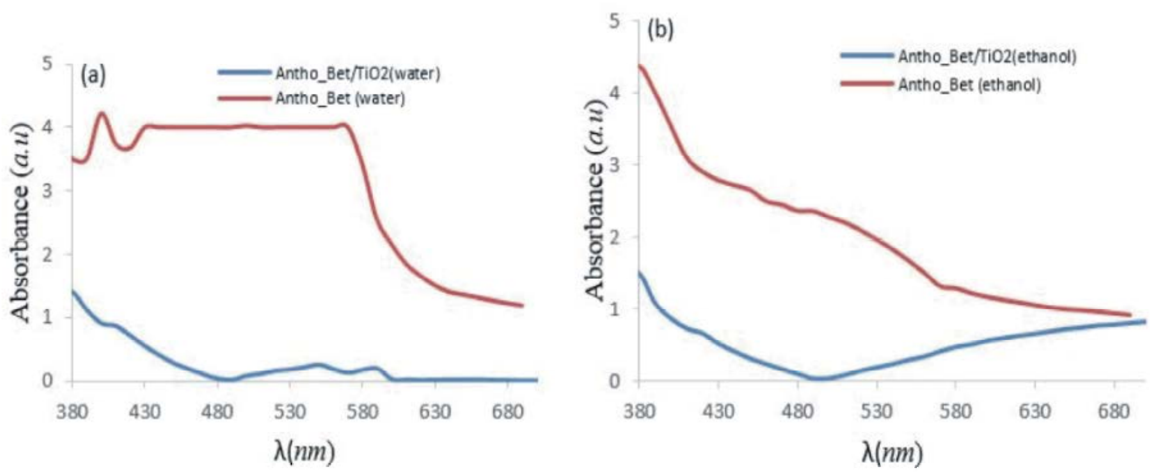

Fig. 2: Absorption spectra of (a) anthocyanin/betalain water extract dye solution and (b) combined anthocyanin/betalain ethanol extract dye solution before and after adsorption onto TiO_2 surface

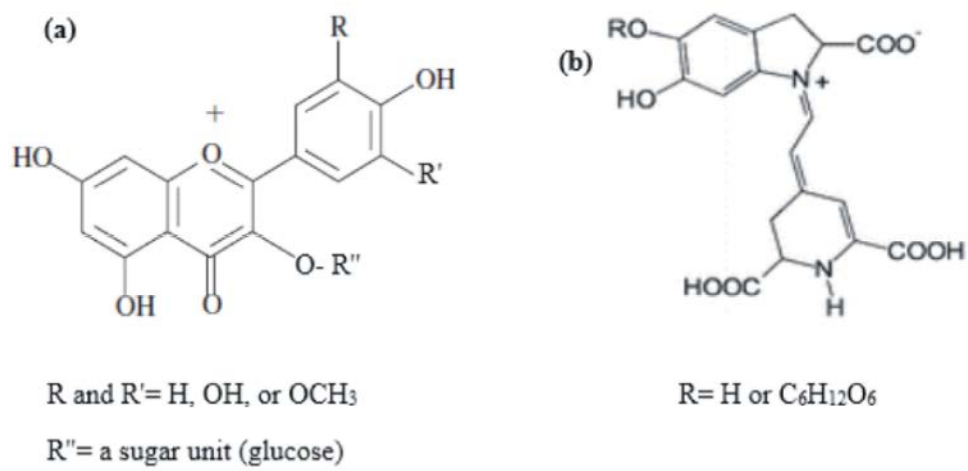

Fig. 3: General chemical structure of (a) anthocyanin and (b) betalain [14, 7]

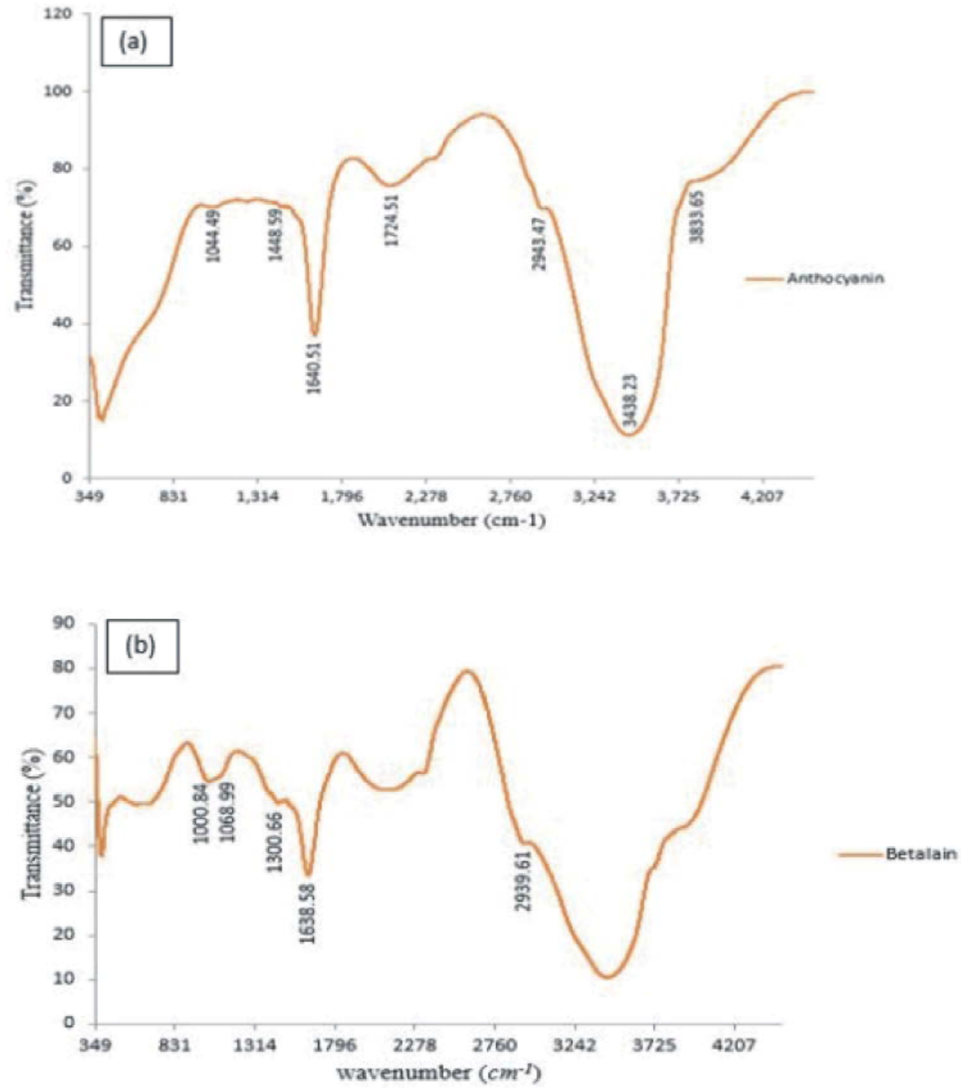

Fig. 4: FTIR Spectra of (a) Flame tree anthocyanin and (b) Bougainvillea glabra betalain water extracts.

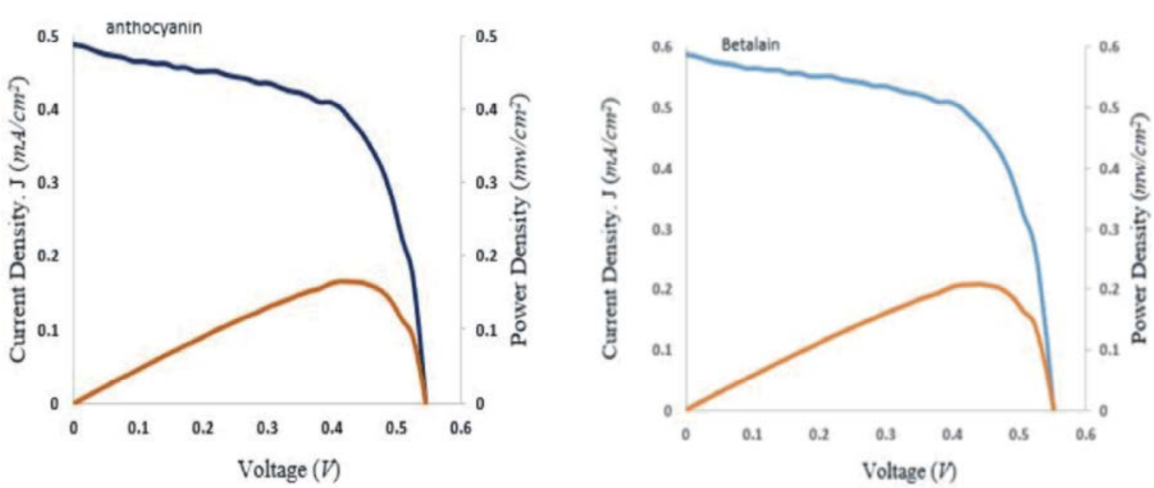

Fig. 5: J-V characteristics curves of Anthocyanin and Betalain

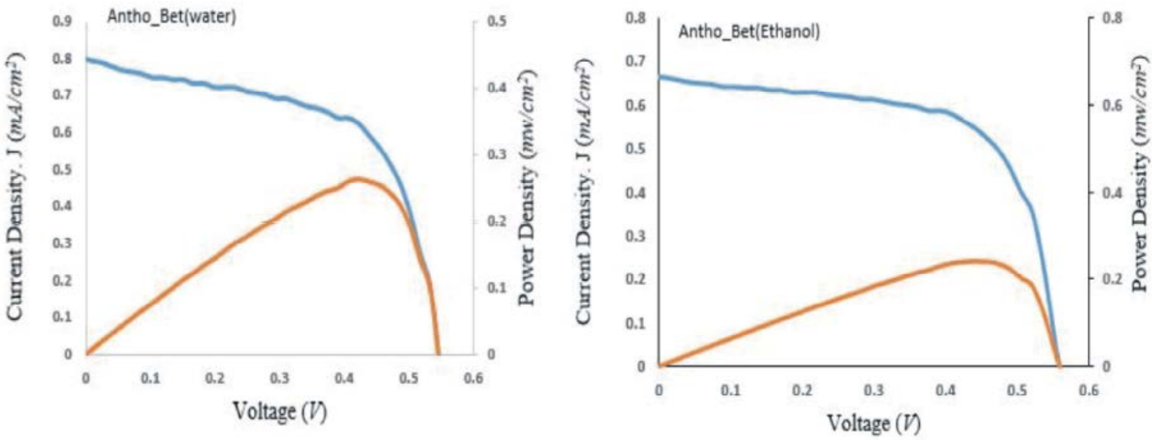

Fig. 6: J-V characteristics curves of Antho_Bet (water) and Antho_Bet (ethanol) DSSC

Table 1: Photoelectric Parameters Summary of the Cells

Device	J_{sc} (mA cm^{-2})	V_{oc} (mV)	Fill factor (FF)	(η (%))
$Antho\_{DSSC}$	0.49	0.56	0.61	0.17
Bet_{DSSC}	0.59	0.55	0.64	0.21
$Antho\_Bet_{Water\ DSSC}$	0.79	0.55	0.60	0.26
$Antho\_Bet_{ethanolDSSC}$	0.66	0.55	0.65	0.24

DSSC comprised of cocktail anthocyanin and betalain dyes (both water and ethanol extracts) shows beneficial effect to obtain higher photocurrent and thus enhancement in the photoelectric performance of the cells compared to DSSC based on just one dye sensitizer pigment. This indicate a synergistic mixed co-sensitization, which effectively transfer energy synergistically to the TiO_2 semiconductor resulting in enhanced photoconversion efficiency of the DSSCs. The Antho_Bet (ethanol) DSSC shows a lower efficiency of 0.24 % compared with Antho_Bet (water) DSSC despite the presence of same pigments (anthocyanin and betalain), this observation is attributed to the different solvents used for the extraction of the dyes as earlier reported [16].

CONCLUSSION

Natural dyes based on anthocyanin and betalain pigments extracted from Flame tree and Bougainvillea glabra flowers using water and ethanol as extraction solvents were used as photosensitizers for DSSCs application. The dyes were used as lone sensitizers exploring anthocyanin and betalain separately and as co-sensitizers exploring the combined anthocyanin and betalain (water extract) and combined anthocyanin and betalain (ethanol extract) separately. The effects of the sensitizers on the performance of the DSSCs was investigated, the study reveals that all the cells possess comparable values of V_{oc} as it does not depends on the sensitizers but rather on the difference between the Fermi level of electrons in the semiconductor and the redox potential of the electrolyte. The betalain sensitisers based device gives better efficiency of 0.21% than anthocynin based device cells with PCE of 0.17 %. This is attributed to the carbonxylic (-COOH) functional groups present in betalain that anchor better to the surface of TiO_2 to yield a strong electronic coupling and rapid forward and reverse electron transfer reactions than the functional groups (-OH) present in anthocyanin. Among the explored dyes, combined anthocyanin and betalain (water extract) gives the highest conversion efficiency of 0.26 % which is ascribed to the dye synergic absorption effect as a result of co-sensitisation, the lower efficiency achieved by combined anthocyanin and betalain (ethanol extract) is attributed to the contributory effect of the extraction solvents.

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