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Purity-performance relationship of anthocyanidins as sensitizer in dye-sensitized solar cells

Ibrahim Olasegun A.[1]*, Bello Isah A.[2], Semire Banjo[2], Bolarinwa Hakeem S.[3] and Boyo Adenike[4]

[1]Department of Chemical Sciences, Fountain University, Osogbo Nigeria.
[2]Department of Pure and Applied Chemistry, Ladoke Akintola University of Technology, Ogbomoso, Oyo State. Nigeria.
[3]Department of Physics, Electronics and Earth Sciences, Fountain University, Osogbo Nigeria.
[4]Department of Physics, Lagos State University, Ojo, Lagos Nigeria.

A comparative analysis between crude and purified extracts obtained from withered leaves of *Terminalia catappa* (*T. catappa*) and pure compounds of anthocyanidins as organic sensitizers in solar cells. The chemical and electronic properties of the extracts and the pure anthocyanidins were examined using spectroscopic studies: ultraviolet (UV), Fourier transform infrared (FT-IR) and gas chromatography coupled with flame ionization detector (GC-FID). Solar cells were fabricated using TiO_2 mesoporous film and the extracts and pure compounds as sensitizers. The prominent transitions in U-V spectra were $n \longrightarrow \pi^*$ and $\pi \longrightarrow \pi^*$ in nature. There were observed shifts in the wavelengths of the absorptions (around 350 to 380 nm) and a characteristic decrease in the absorption between the crude (TCE) and purified (TCP) extracts. The FT-IR spectra of the crude and purified sample have similar absorbances with bathochromic (red) shifts on the hydroxyl group and hypsochromic (blue) shifts on the benzene ring. The GC-FID chromatograms and spectra revealed the presence of six anthocyanidins and their amounts in mg per 100 g of the sample. The results showed that delphinidin was most abundant, and its quantity increases with purification of the extracts, while other anthocyanidins decreased with purification in both extracts. The photovoltaic performances also increase with purity. The best results were obtained with cyanidin-TiO_2 solar cells with efficiencies up to 2.27%.

Key words: *Terminalia catappa*, anthocyanins, solar cell, efficiency, purification, extracts.

INTRODUCTION

Anthocyanins are water-soluble glycosides of polyhydroxyl and polymethoxyl derivatives of 2-phenylbenzopyrylium or flavylium salts and an anthocyanin without sugar moiety is referred to as an anthocyanidin (Middleton, 2000). Anthocyanins and anthocyanidins have been widely applied in various fields

such as sensitizers in dye-sensitized solar cells (DSSCs). DSSC provides a technically and economically credible alternative concept to present day junction photovoltaic devices (Middleton, 2000; Simmonds, 2003). The redox and optical properties of natural pigments (like anthocyanins) make them well suited for a variety of applications (Taofeek et al., 2011; Fossen et al., 2004; Kim et al., 2003; Harborne and Williams, 2000). Anthocyanins from *Terminalia catappa* (*T. catappa)* have been shown to have high antioxidant activity (Jordheim et al., 2006; Boyo et al., 2013) indicating a relatively low oxidation potential (Adenike et al., 2013; Wang et al., 2010). Many research works have examined the qualitative analyses of anthocyanins in parts of plants: leaves, flowers, seeds, etc. (Bisquert et al., 2004; Bisquert, et al., 2006). This study explores the application of the extracts (crude and purified) as sensitizers in photovoltaic, DSSCs. The DSSCs light (from the sun) is absorbed by a sensitizer, which is anchored to the surface of a wide band gap oxide semiconductor, like TiO_2. Charge separation takes place at the interface via photo-induced electron injection from the dye into the conduction band of the solid (Grätzel, 2004; Andre and Neyde, 2006; Pooman and Mehra, 2007). Transition metal coordination compounds (ruthenium polypyridyl complexes) have been used as the effective sensitizers, due to their intense charge-transfer absorption in the whole visible range and highly efficient metal-to-ligand charge transfer (Bisquert et al., 2006; Kelly and Meyer, 2001). However, ruthenium polypyridyl complexes have a heavy metal, which is undesirable from point of view of the environment (Chen et al., 2011; Brouillard et al., 2003). Moreover, the process to synthesize the complexes is complicated and costly (Boyo et al., 2012; Hwan et al., 2011). The availability and low cost of the natural dyes made them better candidates to be used for the same purpose with an acceptable efficiency. The ability of these molecules to convert the light into electricity and to induce redox reactions can be very interesting with respect to their implementation in artificial systems (Duthie et al., 2000; Close and Beadle, 2003), but it has also been faced with challenges of low efficiency and stability. Hence, the examination of the relationship between purity and efficiency of the anthocyanidins in the extracts, of the withered leaves of *T. catappa*, being employed as sensitizers in the fabrication of DSSCs.

EXPERIMENTAL

Extraction and purification of anthocyanidins in *T. catappa*

Plant material and sample preparation

Withered leaves of *T. catappa* were obtained within the campus of Fountain University, Osogbo, Nigeria. The samples were air dried under shade for ten days at room temperature. They were pulverized with the aid of liquidizer.

Extraction and purification of the anthocyanidins

The extraction of the pulverized sample was done using a solvent system that comprised of distilled water, methanol and 1 M HNO_3 in ratio 10: 9: 1, respectively. Fifty gram of the pulverized sample was completely submerged in 175 ml of the solvent system and then covered in air tight glass bottle. Extraction was allowed to proceed for 24 h. The extract was decanted and the solvent reduced by evaporation in water bath at 50 ± 5°C to obtain concentrated extract. The concentrated extracts were stored in dark bottles at room temperature. Anthocyanin purification was done using the method of Taofeek et al. (2011). The filtered extract was transferred into a separatory funnel and "washed" three times with equal volumes of ethylacetate to remove flavones. The third volume of the ethylacetate added to the extract were mixed thoroughly in the separatory funnel and left overnight. The ethylacetate-free layer, containing the partially purified anthocyanin, was obtained. Then, equal volumes of the ethylacetate-free extract and that of 0.5% neutral lead acetate (Pb $(COO)_2$) solution were mixed and kept in the refrigerator at 4°C for 48 h to ensure complete precipitation of anthocyanin. After 48 h, blue supernatant was found and part of it was discarded. The precipitate was re-suspended in the remaining supernatant and transferred into test tubes and was centrifuged at 5,000 rpm for 5 min. Supernatant (blue in color) and dark precipitate (anthocyanin) were obtained, the remaining supernatant was discarded. About 5 ml of 0.5% solution of sulfuric acid was added to the precipitate to remove lead as lead sulfate ($PbSO_4$), and the precipitate was simultaneously re-solubilized to give a red solution. The mixture was filtered to remove the $PbSO_4$ and the filtrate. The filtrate was concentrated in a water bath at 50 ± 5°C to obtain the purified anthocyanin, which was stored in a dark plastic bottle in a refrigerator until use.

Structural elucidation of the samples using ultraviolet (UV), Fourier transform infrared (FT-IR) and gas chromatography coupled with flame ionization detector (GC-FID)

Absorption spectroscopy

UV-visible absorbance spectra of TCE and TCP were scanned between 350 and 1,000 nm with a PerkinElmer UV-visible spectrometer (Lambda EZ201; PerkinElmer, Waltham, Massachusetts, USA).

Fourier transform infrared (FT-IR)

The FT-IR was done under high vacuum (10 mbar) conditions using FT-IR over the 4000 to 350 cm^{-1} spectra range at 500 cm^{-1} resolution.

Gas chromatography coupled with flame ionization detector (GC-FID)

The type and amount of the anthocyanins in the extracts were determined using GC-FID HP6890 powered with HP chem. Station Rev. A.09.01 (1206) software.

Photovoltaic studies

Preparation and deposition of titanium dioxide (TiO2) film

TiO_2 film was prepared using the methods of Boyo et al. (2013). Glass plates coated with a conductive layer of fluorine doped SnO_2 (obtained from Hartford Glass Co. Inc., P.O. Box 613, Hartford City,
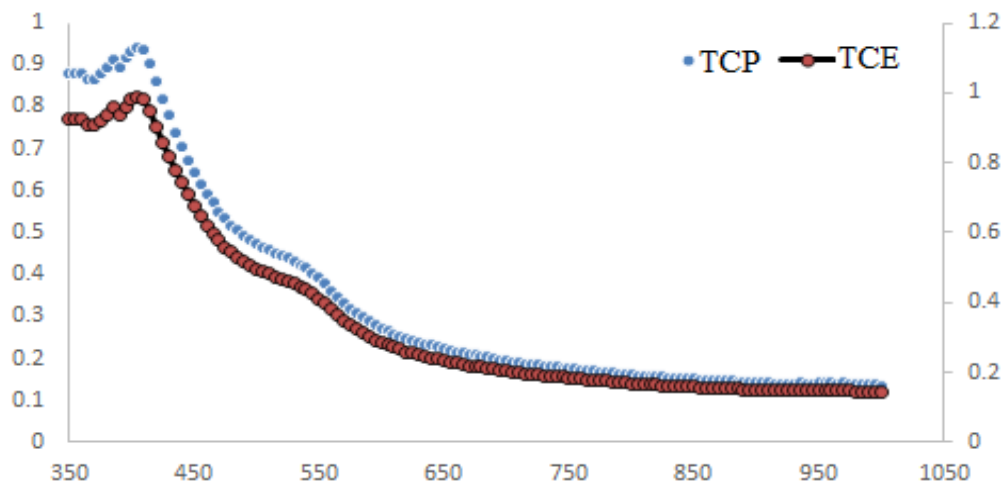
Figure 1. U-V spectra of the crude and purified (TCE and TCP) extracts of *T. catappa* respectively.

IN 47348, USA, Fax 765-348-5435) and the cells were prepared using the methods of Grätzel (2004).

Staining of the titanium dioxide with the dye

Concentrated samples (0.1 g each) were dissolved in 10 ml of distilled deionized water, filtered and used as dye solution (Takeda et al., 1994). TiO_2 coated glass plate was soaked (facing the dye solution) for 10 min in each of the various types of anthocyanin extracts, until the white TiO_2 paste could not be seen upon viewing the stained film from either side of the supporting glass plate.

Carbon coating the counter electrode

While the TiO_2 electrode was being stained in the anthocyanidin solution, the counter electrode was made from another piece of conductive SnO_2 coated glass using the method of Grätzel (2004). The carbon-coated counter electrode was annealed at 450°C for about 5 min (Kalaignan and Kang, 2006). The thin carbon layer served as a catalyst for the tri-iodide to iodide regeneration reaction (Kay and Grätzel, 2002).

Assembling the solar cell and measuring the photovoltaic characteristics

The solar cells were assembled using the methods of Grätzel (2004), Bisquert, et al. (2006) and Boyo et al. (2013). The completed solar cell/light detector was taken for indoor measurements, the cell was illuminated by a 50 W (GE 12V) Tungsten Halogen lamp equipped with integral parabolic reflector and UV and IR blocking filter. The full current-voltage (I-V) curves were measured using a 1000 Ω potentiometer as a variable load. The current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and the efficiency (η) were used to characterize the performance of the solar cells.

The maximum power density occurs somewhere between V = 0 (short circuit) and V = V_{oc} (open circuit) at a voltage V_m. The corresponding current density, Jm and the maximum power density $P_m = J_m V_m$. In these studies, P_s used was 50 W throughout.

RESULTS AND DISCUSSION

In Figure 1, the U-V spectra of the extracts of *T. catappa* are shown. The spectra of the extracts were relatively similar with purified extract having higher absorbance than the crude extract. The implication is that the extracts have similar chemical (or electronic) properties with the crude having compounds that inhibit its electronic properties. In Figure 2, the U-V spectra of the pure anthocyanidins are shown. The spectra of the pure compounds absorbed at close wavelengths in the order Cy> Pg> Dp> Mv. This implied that the compounds have similar functional group(s). In all the samples, the nature of electronic transitions were predominantly π – π* and n – π* transitions. The former implied the transitions as results conjugations and aromaticity while the latter are transitions as a result lone pair of electrons.

The FT-IR spectra of the crude and purified extracts have similar absorbances, even at the finger print regions. The spectra of the crude and purified extracts have similar absorbances, ditto for those of pure anthocyanidins, even at the finger print regions. This implied that the extracts have similar functional groups. However, the spectra of the purified samples have bathochromic (red) shifts on the hydroxyl group and hypsochromic (blue) shifts on the benzene ring. The GC-FID chromatograms revealed the presence of six anthocyanidins in the crude and purified extracts, as well as the quantity of the anthocyanidins (Table 1) in mg per 100 g of the sample. The results showed that delphinidin was 86% abundant in TCE and 92.97% in TCP. It was observed that the quantity of the delphinidin increased with purity of the extract, while the amount of others decreased with purity.

The results obtained for the four quantities; current density (J_{sc}), open circuit voltage (V_{oc}), fills factor (FF) and the efficiency (η), are presented as Table 2. In Figure 3,
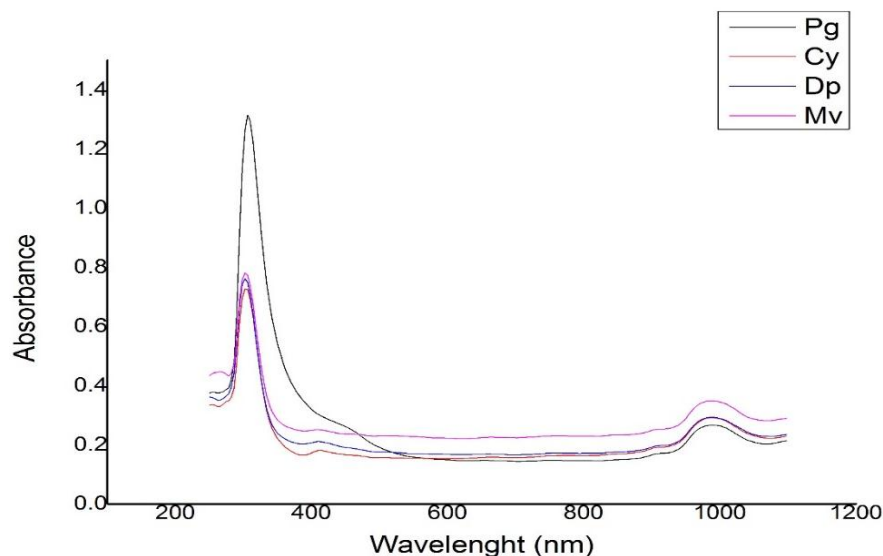
Figure 2. U-V spectra of the pure anthocyanidins.

Table 1. U-V absorbance and peaks of the extracts and pure anthocyanidins.

Sample	Absorbance	Wavelength (nm)	Nature of transition
TCE	3.000	320	$\pi \to \pi^*$
	1.820	410	$n \to \pi^*$
TCP	3.000	320	$\pi \to \pi^*$
Pg	0.417	320	$\pi \to \pi^*$
Cy	0.108	330	$\pi \to \pi^*$
Dp	0.109	330	$\pi \to \pi^*$
Mv	0.115	305	$\pi \to \pi^*$

Table 2. Amount of anthocyanidins in the samples.

S/N	Anthocyanidin	TCE (mg/100 g)	TCP (mg/100 g)
1	Pelargonidin (Pg)	4.148	2.250
2	Delphinidin (Dp)	535.313	563.365
3	Cyanidin (Cy)	72.700	43.817
4	Petunidin (Pt)	1.826	0.837
5	Peonidin (Pn)	1.223	0.121
6	Malvidin (Mv)	1.217	0.034
7	Total	616.426	610.423

current-voltage curves for the extracts of *T. catappa* are shown. The curves have the shapes of a typical I-V (shown as Figure 7) characteristic curve for DSSC. The TCP-TiO$_2$ sensitized cell has better photovoltaic properties than the TCE-TiO$_2$ sensitized cell.

In Figures 4 to 6, the photovoltaic curves of solar cells fabricated using pelargonidin, cyanidin and delphinidin as sensitizers are shown, respectively. From these curves, when compared with a typical current-voltage curve for dye sensitized solar cell (Figure 7); the fill factors increased with purity of the compounds. However, delphinidin with highest percentages in the extracts has the least values in terms of photovoltaic performances.

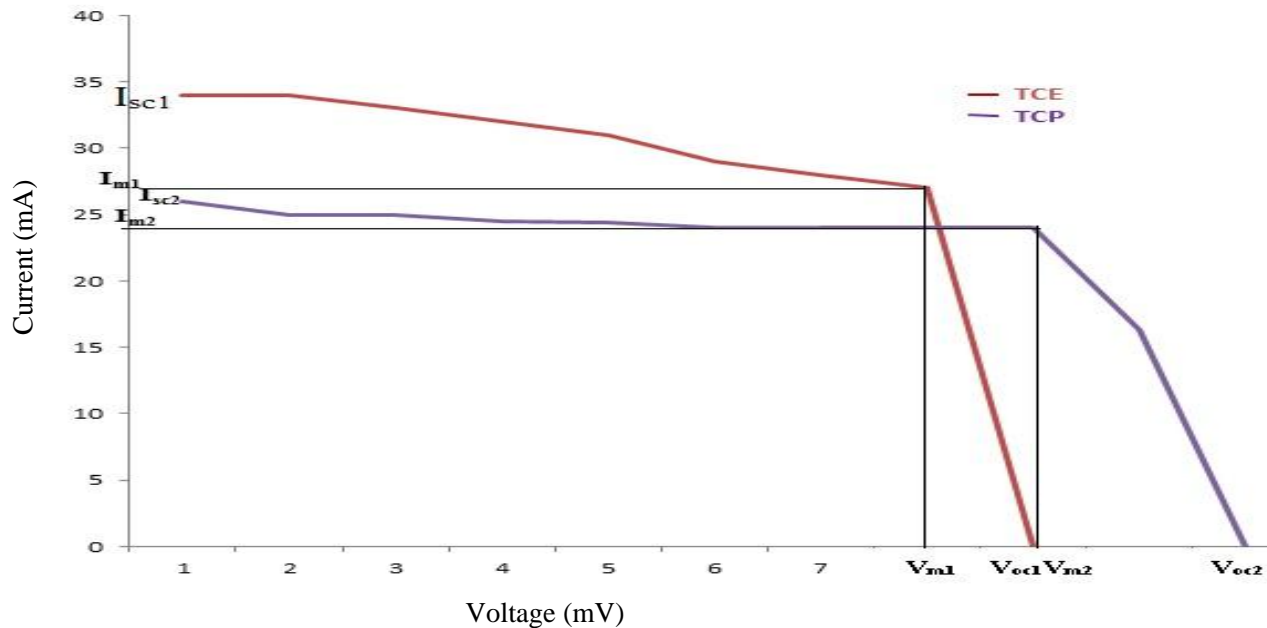In Table 3, the photovoltaic performances are shown

Figure 3. Current-voltage curve of solar cells fabricated using crude and purified extracts of *T. catappa* as sensitizers. I_{sc1} = Short circuit current for TCP; I_{sc2} = Short circuit current for TCP; I_{m1} = Maximum short circuit current for TCE; I_{m2} = Maximum short circuit current for TCP; V_{oc1} = Open circuit voltage for TCE; V_{oc2} = Open circuit voltage for TCP; V_{m1} = Maximum open circuit voltage for TCE; V_{m2} = Maximum open circuit voltage for TCP.
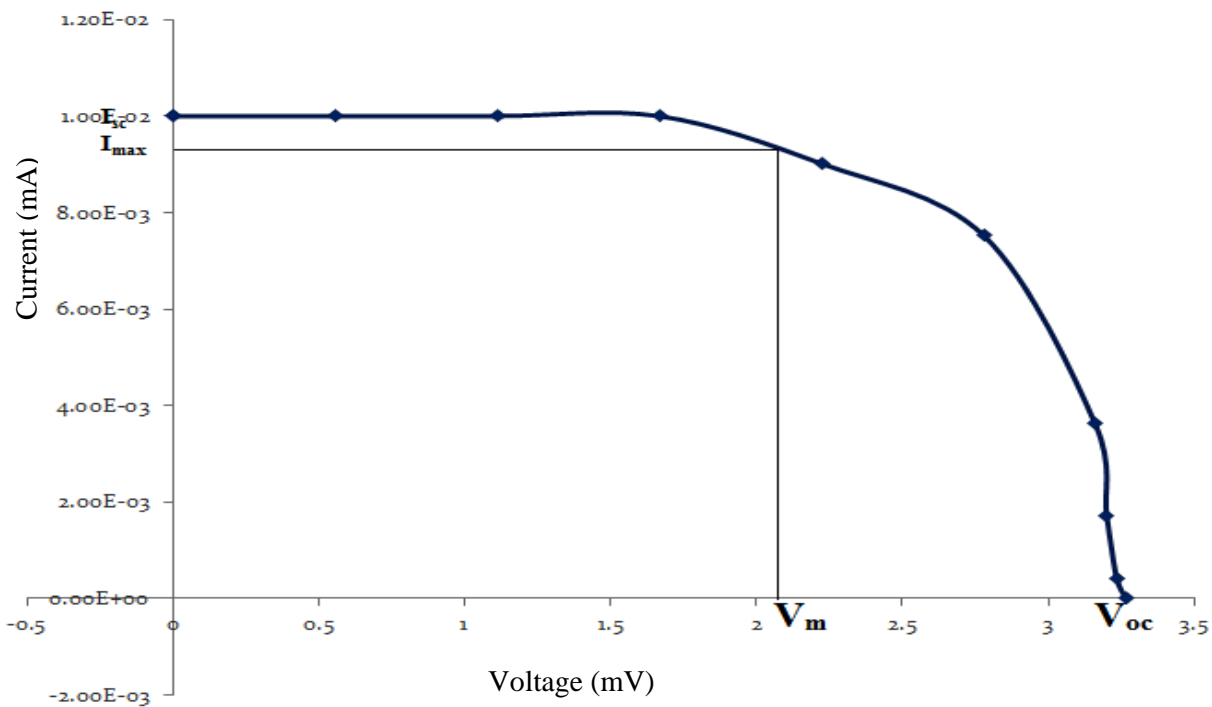

Figure 4. Pg: Current-voltage curve for solar cell using Pelargonidin as sensitizer.

for the crude (TCE), purified (TCP), extracts and three of the pure compounds (pelargonidin (Pg), cyanidin (Cy) and delphinidin (Dp)). The photovoltaic graph for the Mv-TiO_2 was linear, rather than a curve. It showed deviation
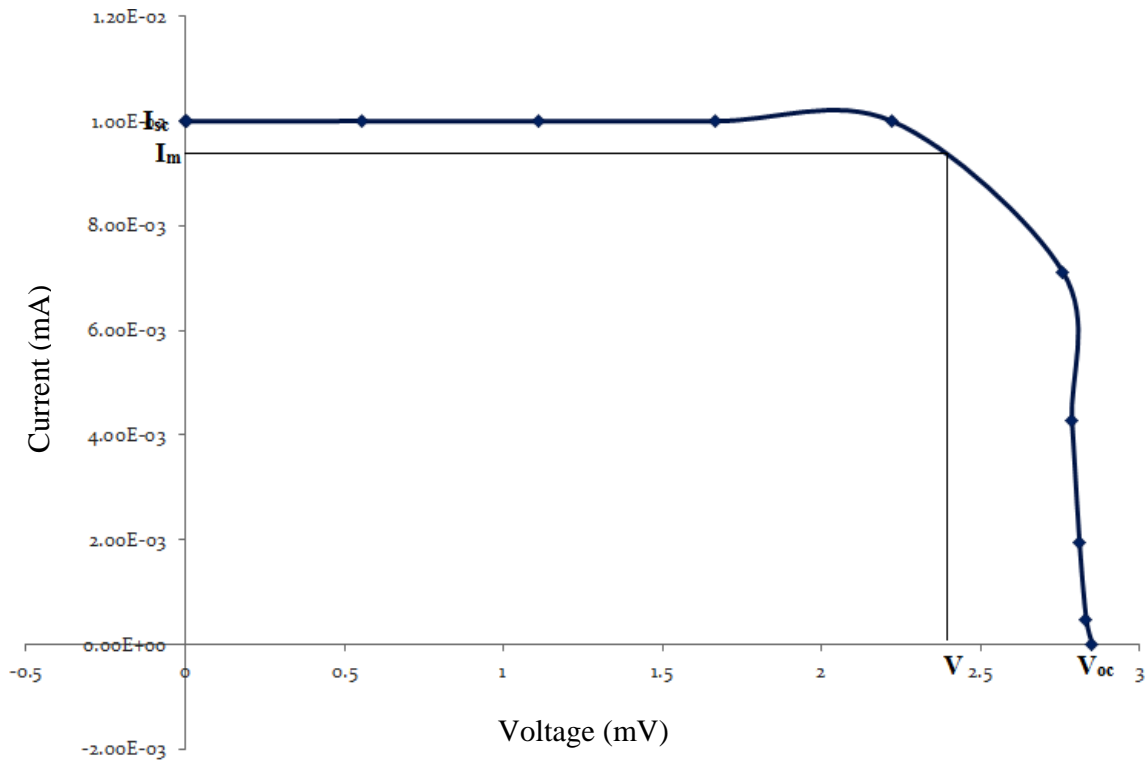
Figure 5. Current-voltage curve for solar cell using Cyanidin as sensitizer.
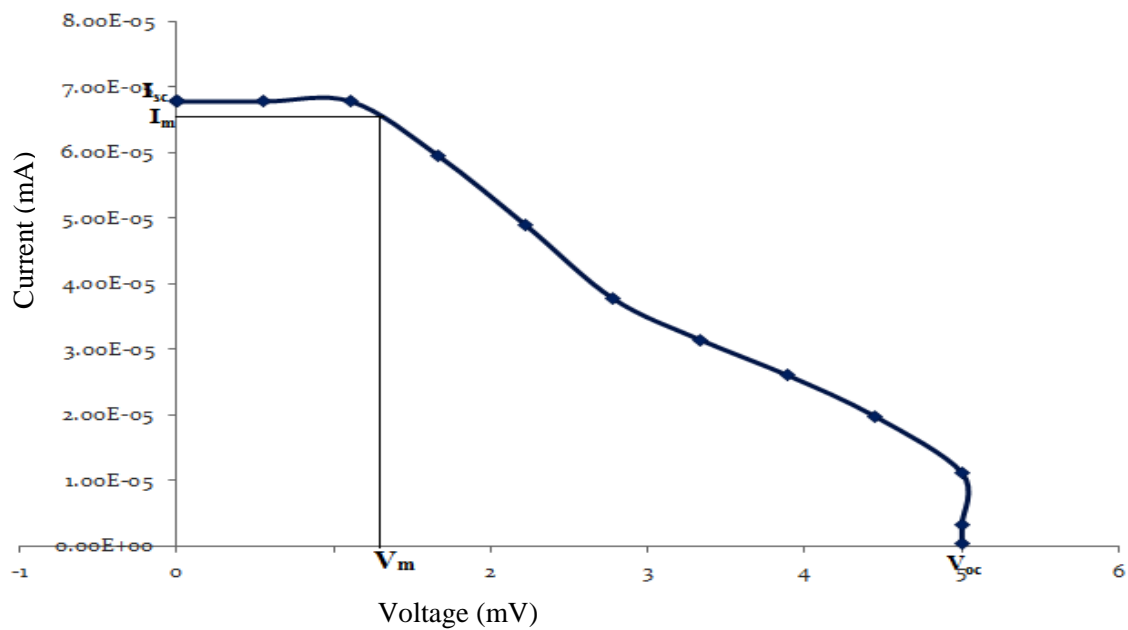

Figure 6. Current-voltage curve for solar cell using Delphinidin as sensitizer.

from the others.

The photovoltaic performance of the extracts and purified extracts of the samples applied as sensitizers in DSCCs, it is evident from these data that the purified sample has higher fill factor and efficiency than the extracts.
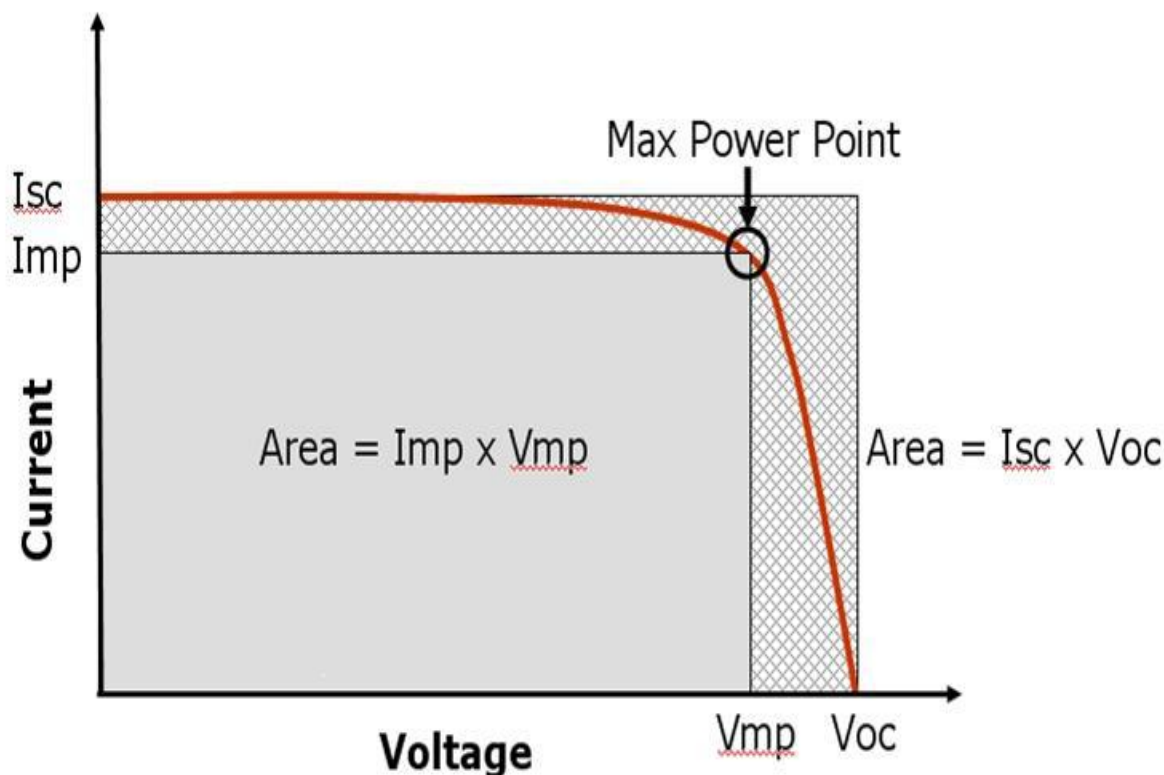
Figure 7. Typical current-voltage curve for dye sensitized solar cell; the Fill Factor is defined as the ratio of the two areas (Area₁/Area₂) (Boyo et al., 2012).

Table 3. Photovoltaic performance of the samples.

Sample	I_{sc} (mA)	J_{sc} (mA/cm^2)	V_{oc} (mV)	I_m (mA)	J_m (mA/cm^2)	V_m (mV)	FF	η (%)
TCE	0.037	0.009	25.000	0.016	0.004	10.500	0.280	0.336
TCP	0.027	0.007	27.000	0.025	0.006	14.920	0.493	0.746
Pg	1.100	0.278	31.200	1.010	0.250	28.600	0.826	1.43
Cy	1.130	0.283	48.200	1.020	0.255	44.500	0.835	2.27
Dp	0.068	0.017	26.89	0.068	0.017	11.12	0.415	0.004

Conclusion

The analysis of six common anthocyanins in the extract obtained from the calyxes of *T. catappa* was reported with delphinidin being the most abundant and its content increased with purification of the extract. DSSCs were constructed using the extracts of the withered leaves of *T. catappa*. The cell efficiencies increased with purity, with the best efficiencies of 2.27% for the Cy-sensitized TiO$_2$ cell.

The low efficiencies of the cells fabricated with TCE and TCP as sensitizers. These may be connected to the inhibitory effects of the composite anthocyanin (and other) molecules in the extracts. They reduce the sensitizing capability of the dyes to have low injection efficiencies. Thereby, making the overlap of the dye excited states and the metal oxide conduction band, the dye regeneration kinetics and the dye excited state lifetime were not optimal. In order to enhance cell performance isolated compounds should by employed instead of the direct applications of the extracts.

Conflict of Interests

The authors have not declared any conflict of interests.

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