Enhancement of Sensitization Capacity of Dye from Melastoma Malabathricum L. in DSSC by Organic Acid Treatment

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Abstract - Melastoma malabathricum L. dye was investigated as a sensitizer in DSSC after treatment with five different organic acids: citric, deoxycholic, lactic, ascorbic and acetic acids. These treated dyes were evaluated as sensitizers of dye sensitized solar cell and the performances were investigated. The treated dyes were shown to enhance the short circuit photocurrent density (J_{sc}) and hence contributing to the increase in power conversion efficiency. The overall efficiency enhancement of the acidified treated dyes were due to the combined effect of increased light absorption at visible range, efficient adsorption of dye molecules onto TiO_2 film and low electron transport resistance for efficient electron diffusion at TiO_2/dye/electrolyte interface. Dye treated with 1000 mM citric acid showed the best performance with overall conversion efficiency of 0.79±0.01%, which is an increment of 41% of the overall cell performance efficiency from the original, untreated dye (η = 0.56±0.01%).

Keywords- Natural dye, Anthocyanin, Organic acid, Dye sensitized solar cell

1. Introduction

A dye-sensitized solar cell (DSSC) is primarily comprised of nanocrystalline semiconductor, photosensitizer, redox electrolyte and transparent conductive oxide (TCO). The breakthrough was achieved with TiO_2 based DSSC using a ruthenium polypyridyl complexes as the dye sensitizer [1] owing to their intense charge transfer absorption in the visible range, long excited lifetime of the electron and good transfer of charge from the dye to TiO_2 film [2]. Nevertheless, the main drawbacks of ruthenium based sensitizers are the long-term unavailability, high cost, complexity in the synthesis process and a threat to the environment due to the presence of heavy metal. Alternatively, plant-derived natural dyes that are easily extracted have been extensively investigated for the use as dye sensitizers in DSSCs. Dye sensitizer is one of the crucial components in DSSCs that significantly determining the power conversion efficiency [3]. Although the highest overall conversion efficiency demonstrated by natural dye based DSSCs is around 2% [4] which is still far lower in terms of cell performance compared to the conventional Ru – dye DSSC, they provide cheaper, non-toxic, biodegradable and environmental-friendly solution [5, 6]. Thus, making researches in natural dye based DSSC profoundly worthwhile.

The sensitization of wide bandgap semiconductors integrating natural pigments is often ascribed to anthocyanins dye [2]. Anthocyanins constitute of a major flavonoid group that are responsible for the color expression in the range of visible from red to blue found in fruits, leaves and flowers. The presence of hydroxyl and carbonyl moiety in the anthocyanin facilitate in the binding of the molecule to the surface of semiconductor TiO_2, thus enable electron injection into the TiO_2 conduction band upon excitations [7]. Anthocyanins from various plants source have demonstrated different sensitizing performances [8]. This is due to limited and poor interaction between the dye and the surface of semiconductor which may arise from the steric hindrance by glycoside groups in the anthocyanin limiting efficient electron transfer towards the conduction band of TiO_2 film [2]. Removal of glycoside group in the anthocyanin structure would improve the efficiency in comparison to the presence of longer glycoside groups [9]. Moreover, electron injection can also be influenced by the possible aggregation of planar anthocyanin molecules on the metal oxide surface [10]. Some undesirable reactions such as electron recombination at the TiO_2 surface can also lead to losses in cell efficiency [11]. It has been reported that often raw natural dye mixtures performed better than commercial or purified analogues [12]. This can be related to the organic acids naturally presence in the extracts which may act as co-adsorbents, suppressing recombination of electrons with the electrolyte, reducing dye aggregation and favoring charge injection [13]. Successful attempts have been achieved by Chiang-Yu Chien [14] and Hee-Je Kim [15] in improving the cell conversion efficiency by utilizing organic acids into the natural dye based DSSC. In addition, organic acids as co-adsorbents such as deoxycholic acid (DCA) [16, 17] and citric acid [18, 19] have been extensively studied in DSSC sensitized with synthetic dyes that they can inhibit aggregation of dye molecules making electron injection more efficient thus, improving the cell efficiency. These have stimulated the current study of the usage of organic acids in natural dye based DSSC for optimization of the cell overall conversion efficiency.

In this study, the dye sensitized solar cells were fabricated using natural dye extracted from the fruit of *Melastoma malabathricum L.* The dominant type of anthocyanin present in the fruit of *Melastoma malabathricum L* extract is cyanidin-3-glucoside [20, 21]. Organic acids such as citric acid, deoxycholic acid, lactic acid, ascorbic acid and acetic acid were used to treat anthocyanins in order to increase its color intensity and hence the effect of these organic acids on the performance of DSSCs was evaluated.

2. Experimental

2.1. Preparation and characterization of dye sensitizer solutions.

The pulps of *Melastoma malabathricum L.* labeled as "KK" (20 g of fresh weight) were ground in 70% ethanol to extract the anthocyanin pigment and left overnight at 3 °C, to make 100 mL of dye extract. The extract was then stirred for two hours and filtered to remove solid residue which was then purified using petroleum ether. The resultant extract was centrifuged at 4500 rpm for 15 minutes to remove any remaining small solid residues. Decanted extract (100 mL) was refrigerated in a glass bottle covered with aluminium foil to avoid degradation of dye on exposure to light.

The absorption spectra of the extracted KK dye solutions and KK dyes adsorbed onto TiO_2 surface were investigated in the range 350 nm to 800 nm using UV-vis spectrophotometer (1601 PC Shimadzu). The total monomeric concentration of anthocyanin pigments in the dye extract was then determined by pH differential method [20] measured at wavelength of 520 nm and 700 nm:

Anthocyanin pigment content (mg/L):

$$= \frac{A \times MW \times DF \times 10^3}{\varepsilon \times L}$$

where $A = (A_{520nm} - A_{700nm})$ pH 1.0 – $(A_{520nm} - A_{700nm})$ pH 4.5, MW (molecular weight) = 449.2 g/mol for cyanidin-3-glucoside (cyd-3-glu), *DF* = dilution factor = 1/10, ε (molar extinction coefficient) = 26900 L mol^{-1}cm^{-1}, 10^3 is the factor for converting g to mg, and *L* is the path length in cm.

2.2. Fabrication of photo-electrode.

Photoelectrodes were fabricated using a TiO_2 paste Solaronix (nanoxide-T, colloidal anatase particles size: ~13 nm, ~120 m^2 g^{-1} (BET, Switzerland). The TiO_2 was coated on pre-cleaned fluorine-doped conducting tin oxide (FTO) glasses (Nippon sheet glass ~7 Ω sq^{-1}) by Doctor Blade method. Electrodes were pre-heated (~50 ^{o}C) using a hot air blower and sintered at 450 ^{o}C for 30 min. The thickness of the TiO_2 electrodes used for this investigation was ~9 µm (Scanning Electron Microscope, SEM). Photographs of the active, exposed cell area were taken and enlarged in a computer to accurately measure the cell area [22].

2.3. Dye synthesized solar cell preparation and current-voltage measurement.

Extracted KK dye was treated with 3 different ranges of concentration of the selected organic acids (Table 1). The three selected concentrations of organic acids sufficiently produced significant changes on the UV-Vis spectra and hence selected as treatments to KK dye. Prepared photoelectrode was then dipped into the dye extracts (0.1 mM as a standard) for overnight allowing adsorption of dye molecules onto TiO_2 surface. Similarly, another photoelectrodes were subsequently dipped in 0.1 mM of the dye extract containing three different concentrations of selected organic acids at equal v/v ratio. Overnight dipping is necessary to allow enough time for dye molecules to attach onto TiO_2 surface. The dyed electrode was then rinsed, which was then assembled after introducing electrolyte containing tetrabutyl ammonium iodide (TBAI, 0.5 M)/I_2 (0.05 M), in a mixture of acetonitrile and ethylene carbonate (6:4, v/v) in between the dyed electrode and the platinum counter electrode. The assembled cell was then exposed to irradiation of 100 mW cm^{-2} (1 sun illumination) for 4 hours prior to the current-voltage measurement, allowing optimum incorporation of electrolyte into the TiO_2 layer. The photoelectric current-voltage (I-V) measurement was carried out by placing the assembled cell under solar simulator (model: DYESOL LP-156B) [22]. Progressive error analysis were carried out to estimate experimental errors and hence included the error estimated when reporting the cell performances.

2.4. Electrochemical impedance measurement.

The electron kinetics of the cell was investigated using electrochemical impedance spectroscopy. This measurement was carried out using computer controlled electrochemical interface (SI 1287, Solatron) and impedance/gain-phase analyzer (SI 1260, Solatron). The frequency range and the amplitude of alternative voltage used were from 0.01 Hz to 10^6 Hz and 10 mV, respectively, with applied potential set at open circuit voltage. The impedance measurements were performed at open circuit condition under irradiation of 100 mW cm^{-2}. Impedance parameters and equivalent circuits were then obtained by fitting the spectra with ZView software (v3.3, Scribner Associate Inc.).

3. Results and discussion

3.1. UV-Vis absorption spectra

Only treated *Melastoma malabathricum* L. (KK) dye extracts that showed the best power conversion efficiencies (Table 1) were collated for the ease of comparison in determining the effect of organic acid treatments on the performance of DSSCs.

Table 1. Performances of the dye sensitized solar cell fabricated using the *Melastoma malabathricum* L. (KK) at different concentration of organic acid treatments, in comparison to the untreated extract.

Sample	*Jsc* (mA cm^{-2})	*Voc* (V)	Fill Factor ff	Efficiency, η (%)
0.1mM KK	3.68	0.340	0.45	0.56 ±0.01
Citric acid				
KK + 1.0mM	4.54	0.331	0.44	0.66 ±0.02
KK + 100mM	4.85	0.327	0.49	0.78 ±0.02
KK + 1000mM	5.31	0.291	0.50	0.79 ±0.01
Deoxycholic acid (DCA)				

KK + 1.0mM	2.90	0.337	0.47	0.51 ±0.01
KK + 5.0mM	4.17	0.335	0.44	0.68 ±0.02
KK + 10mM	3.30	0.339	0.46	0.57 ±0.01
Lactic acid				
KK + 1.0mM	3.83	0.330	0.48	0.67 ±0.02
KK + 5.0mM	3.43	0.328	0.49	0.62 ±0.02
KK + 10mM	3.48	0.311	0.50	0.54 ±0.02
Ascorbic acid				
KK + 1.0mM	3.66	0.341	0.51	0.64 ±0.02
KK + 50mM	3.89	0.335	0.47	0.62 ±0.02
KK + 100mM	2.06	0.282	0.47	0.27 ±0.01
Acetic acid				
KK + 1.0mM	4.42	0.343	0.39	0.58 ±0.02
KK + 500mM	4.05	0.321	0.47	0.61 ±0.01
KK + 1000mM	3.66	0.331	0.50	0.60 ±0.02

It was observed that the addition of citric, acetic and lactic acids increased the color intensity of the dye to brighter red coloration which ascribed to the presence of anthocyanin in KK dye [8, 23]. This changes in color was due to the interaction of dye with the acid, whereby the glycon (glucose) bound to flavylium ion of the anthocyanin was detached and aglycon (anthocyanidin) was released [9, 22] as shown in Fig. 1a.

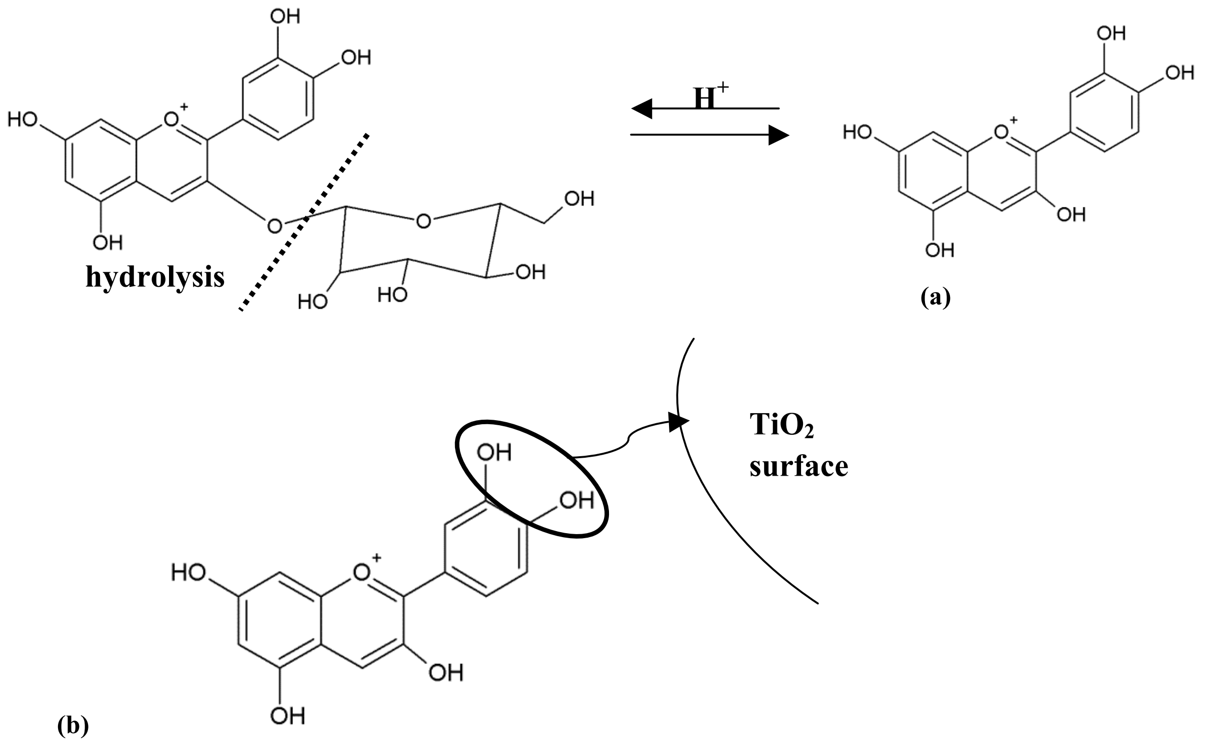


Fig. 1. (a) Chemical structures showing the transition of anthocyanin to anthocyanidin, (b) Chelation of anthocyanidin onto TiO_2.

Fig. 2 shows the absorption spectra of KK dye before and after treatments with selected organic acids at various concentrations. It was found that dye treated with these organic acids displayed stronger light absorption at ~531nm region compared to the original, untreated extract that further verified the presence of anthocyanins in KK dye. These absorption behaviour originates from electron transfer transitions (π-π* transition) of HOMO to LUMO [4]. The intensity of light absorption by the dye is greatly affected by its pigment structure. The reason is presumably related to more delocalization of π-electrons in the anthocyanidin structure which require lower energy for excitation of loosely bound electrons to a higher energy level [8]. The light absorption was the highest with the citric acid-treated followed by acetic acid-treated, lactic acid-treated, DCA-treated and finally ascorbic acid-treated dye.

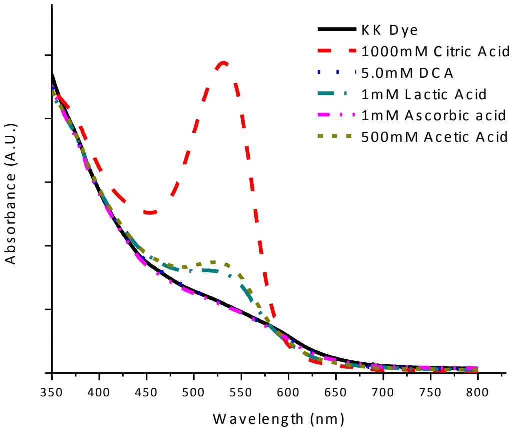


Fig. 2. UV- Vis absorption spectra of natural dye extracted from *Melastoma malabathricum* L. (KK) at different treatment with the selected acid concentrations.

The TiO_2-coated electrodes dipped in 0.1 mM solution of KK dye extracts containing 1000 mM citric acid, 5 mM DCA, 1 mM lactic acid, 1 mM ascorbic acid and 500 mM acetic acid, were observed to turn purple color for all the treated dyes. This suggests that these treated dye were able to rapidly adsorbed onto the surface of TiO_2, forming a strong complex [7]. The surface adsorbed complex ascribed to quinonoidal form of anthocyanin (Fig. 1b) in equilibrium with small amount of flavylium form was responsible for the purple coloration of both treated and untreated KK dye adsorbed onto TiO_2 film.

Fig. 3 shows UV-Vis absorption spectra of sensitized TiO_2 film with the original untreated KK dye as well as the treated KK dyes. The broadening of absorption of light in the visible range or bathochromic shift [24] in all samples implied that the dye adsorbed well onto the TiO_2 film, that lead to better charge transfer upon sensitization [15, 25-27].

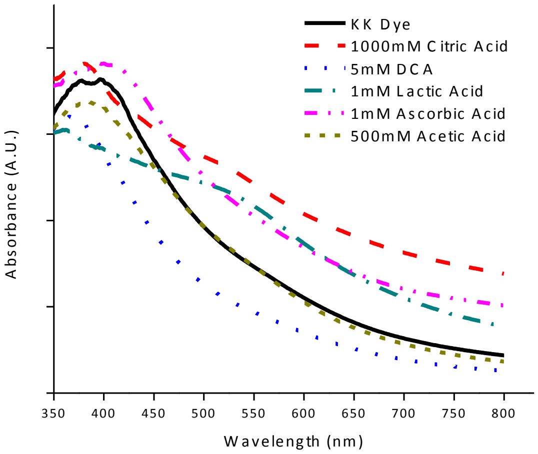


Fig. 3. UV-Vis absorption spectra of treated *Melastoma malabathricum* L. (KK) dyes adsorbed onto TiO_2.

Various intensities were also observed which suggests the amount of dyes adsorbed onto the TiO_2 film. The lowered absorption peak as shown by dye treated with 5mM DCA, 1 mM lactic and 500 mM acetic acid (Fig. 3), as compared to the untreated KK dye may be related to the reduction in the amount of KK dye adsorbed onto the TiO_2 semiconductor when the co-adsorbent was added into the dye solution [14, 16-19, 28-31]. It was reported that DCA, acetic and lactic acids are able to anchor onto the semiconductor surface along with the dye by way of its carboxyl groups [14, 31, 32]. Thus, the reduction in dye adsorption might indicate the presence of co-adsorption of acids while reducing dye aggregation.

3.2. Current-voltage measurement for DSSC

Fig. 4 represents photocurrent-voltage characteristics of DSSCs fabricated using treated and untreated KK dye extracts. The corresponding photovoltaic parameters including short–circuit photocurrent density (J_{sc}), open–circuit voltage (V_{oc}), fill factor (FF) and energy conversion efficiency were tabulated in Table 1. The efficiency of the citric acid-treated dye was 0.79±0.01%, which is the highest compared to the untreated KK dye (0.56±0.01%), DCA (0.68±0.02%), lactic acid (0.67±0.02%), ascorbic acid (0.64±0.02%), acetic acid (0.61±0.01%) treated dyes respectively. These findings are in agreement with what has been reported that acidic environment could enhance adsorption properties of the pigment to TiO_2 and resulted in increased overall performance of DSSCs [15].

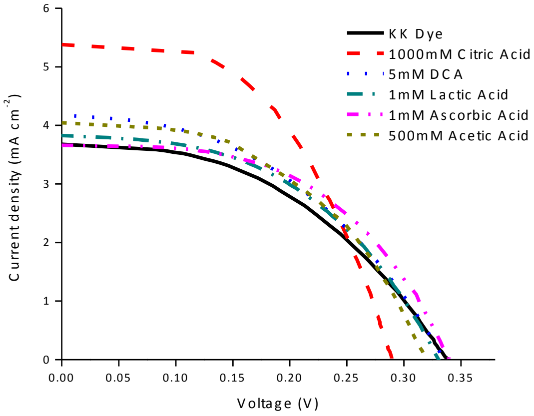


Fig. 4. Current – voltage behaviour of the DSSCs fabricated using *Melastoma malabathricum* L. (KK) dye treated with different acids.

The increase in photocurrent density may arise from proton H^+ adsorption which positively shift the conduction band edge of TiO_2 generating larger driving force for electron ejection from excited dye molecules [14, 16]. The more positive TiO_2 conduction band edge on the contrary is offset by minor loss in V_{oc} [17, 30]. In the case of DCA, acetic acid and lactic acid, a decrease in the amount of dye loading might indicate co-adsorption of acids is taking place on TiO_2 surface. Addition of co-adsorbent, though significantly decreased dye loading via co-adsorption, usually led to an improve photovoltage and photocurrent [14, 16-19, 28-31]. This is because non aggregated dye molecules or strongly bound dyes are more favorable to inject electrons into TiO_2 than aggregated dyes [14, 17]. In addition, improved photovoltaic could be also due to a difference in dye adsorption mode where chemical bonding prevails in acids treatment that may promote bonding between the hydroxyl groups and the surface of the TiO_2 film [33]. 5mM DCA, 1mM lactic and 500mM acetic acid in KK solution seems to play more important role in preventing dye aggregation rather than co-adsorption. The tendency of lactic acid, DCA and acetic acid towards breaking up aggregation is due to the binding ability of its anchoring group [34]. DCA has two hydroxyls and a single carboxyl group to ensure stronger anchorage onto TiO_2 film compared to a single carboxyl group presence in acetic, while a single hydroxyl and carboxyl group in the case of lactic acid. This might be the reason that makes DCA relatively more effective in inhibiting dye aggregation contributing to the relatively higher photocurrent. Highest conversion efficiency acquired was 0.79±0.01% with 1000 mM citric acid which is mainly due to the improved photocurrent density. Higher amount of adsorbed anthocyanidin molecules with citric acid increases the light harvesting capability of the photoelectrode, thus contributed to the higher short–circuit photocurrent density [19]. In addition, a stronger binding of citric acid treated dye on TiO_2 indicated by the intense and broad absorbance peak (Fig. 3) might also contribute to the photocurrent enhancement [25-27]. From the above results, organic acids adopted in the present study have been demonstrated to be useful in optimizing the DSSCs power conversion efficiency.

3.3. Electrochemical Impedance Spectroscopy (EIS)

The DSSC performances of the organic acids treated dye was further evaluated using electrochemical impedance spectroscopy (EIS), which investigate the kinetics of electron in DSSCs under the irradiation of 100 mW cm^{-2} at open–circuit condition. The Nyquist plot of DSSCs typically features three semicircles. The large semicircle in the Nyquist plot located in the middle is attributed to electron kinetics at TiO_2/dye/electrolyte interface [35-40]. The fitted results using an equivalent circuit (as inset) from the EIS measurement are shown in Fig. 5. Parameters summarized in Table 2 include recombination resistance (R_{rec}), charge/electron transport resistance (R_{ct}), effective electron lifetime (τ_{eff}), electron density (η_s) and diffusion coefficient (D_{eff}).

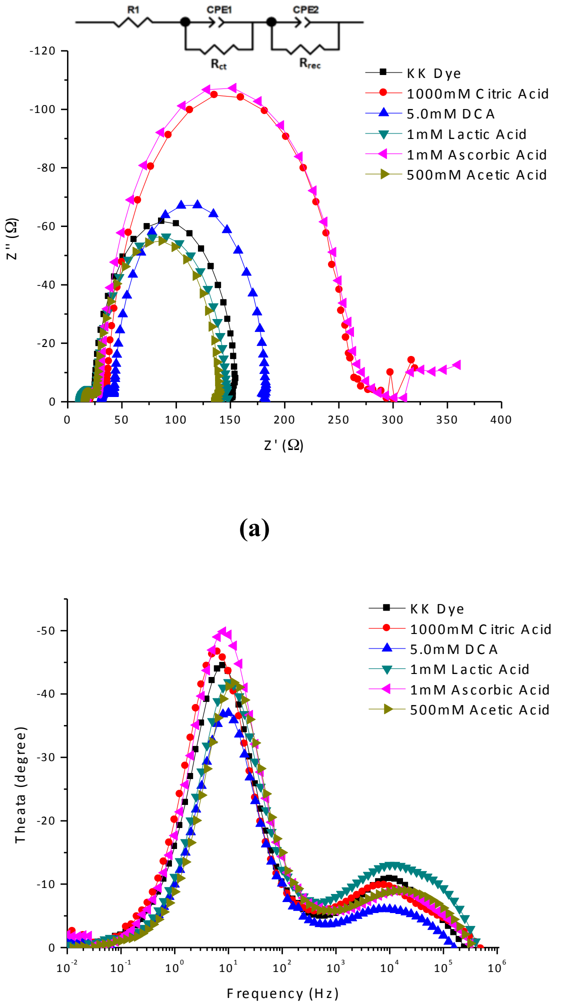
Table 2. Parameters determined from EIS and *J-V* measurements of DSSCs based on selected *Melastoma malabathricum* L. (KK) dyes.

Sample	J_{sc} (mA cm^{-2})	V_{oc} (V)	R_{rec} (Ω)	R_{ct} (Ω)	τ_{eff} (s^{-1})	η_s (cm^{-3})	D_{eff} (cm^2 s^{-1})	*η*%

0.1 mM KK dye	3.68	0.340	131	13.1	0.126	8.28E+24	6.43E-09	0.56±0.01
KK + 1000mM Citric	5.31	0.291	62	3.9	0.063	9.18E+24	2.05E-08	0.79±0.01
KK + 5.0mM DCA	4.17	0.335	140	9.3	0.079	5.35E+24	1.53E-08	0.68±0.02
KK + 1.0mM Lactic	3.83	0.330	120	8.0	0.063	6.51E+24	1.93E-08	0.67±0.02
KK + 1.0mM Ascorbic	3.66	0.341	543	33.9	0.063	1.10E+24	2.05E-08	0.64±0.02
KK + 500mM Acetic	4.05	0.321	114	7.6	0.079	6.57E+24	1.53E-08	0.61±0.01

A higher recombination resistance (R_{rec}) value indicates lesser charge recombination is taking place [36, 41]. Low recombination resistance as observed for DSSC based on acidified KK dye indicate acceleration in electron recombination with the tri-iodide ions probably caused by proton adsorption and thus, decay in the experimental V_{oc}. Lower electron transport resistance (R_{ct}) in TiO_2 corresponds to more efficient electron transfer along the TiO_2 interface [39, 42]. Reduction in R_{ct} values were observed in most of the organic acids treated dyes which implied more efficient electron injection into the conduction band of TiO_2 was taking place and thus further verifying the increment in photocurrent density, J_{sc}. These results indicate that upon addition of the lactic, DCA and acetic acid in the dye solution, the aggregation of anthocyanin molecules were retarded, and hence resulting in the enhancement of photocurrent density. The addition of organic acids increased the electron density (η_s) which is proportional to J_{sc} [17] possibly involving the positive shift of the TiO_2 conduction band edge and stronger binding of dye on to TiO_2 film which leads to decrease in charge transfer resistant and thus, contributing to an increase in J_{sc} of the DSSCs [35, 39].

Among all the organic acid treated dyes, the dye treated with citric acid recorded the best performance in DSSCs opted to the increase in J_{sc} explained by the increase in electron density η_s which leads to the decrease in R_{tr} and high electron diffusion coefficient D_{eff}.



(a)

(b)

Fig. 5. Electrochemical impedance spectra of DSSCs sensitized with acid treated dyes, (a) Nyquist plot with an inset showing the equivalent circuit diagram, and (b) Bode plot, as obtained from EIS analysis measured

under the illumination (100 mW cm^{-2}) and open circuit conditions.

4. Conclusion

Natural dyes extracted from *Melastoma malabathricum* L. (KK) were fabricated as sensitizers in DSSC. The effect of organic acids; acetic, deoxycholic, citric, ascorbic and lactic acid in the natural dye treatment was investigated and their performances as sensitizers in DSSCs were evaluated. Different organic acids showed different influence on the dye sensitizing performances due to their distinction in terms of molecular structure. Treatment using this selected organic acids have indicated acid-TiO_2 interaction as well as interaction with the dye. The use of citric, acetic and lactic acid at sufficient concentration (1000 mM citric acid, 5 mM deoxycholic acid, 1 mM lactic acid, 1 mM ascorbic acid and 500 mM acetic acid) changes the absorption spectra of the dye that indicates anthocyanin's transition to anthocyanidin which the latter posed stronger binding capability to semiconductor surface thus making significant contribution to the enhancement in photocurrent density J_{sc}. Although the amount of dye adsorbed onto TiO_2 film from the lactic, DCA and acetic acid treated dyes was reduced, it was compensated by the removal of dye aggregation hence increase in the overall cell performances. Among the treated dye sensitizers with the selected five organic acids, citric acid treatment recorded the best overal cell performance of DSSC with power conversion efficiency of 0.79±0.01%. Overall, the results have shown that organic acid employment in improving DSSCs performance has a good perspective with exciting concept.

5. Acknowledgement

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6. Conflict of interest

The manuscript is approved by all of the authors, host authorities and no conflict of interest expressed regarding the publication of this paper.

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