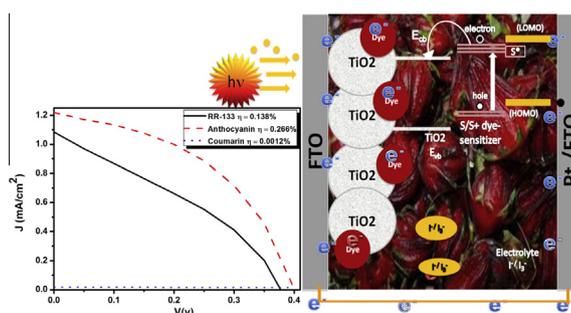# Photostability of low cost dye-sensitized solar cells based on natural and synthetic dyes

E.M. Abdou [a], H.S. Hafez [a,b,*], E. Bakir [a], M.S.A. Abdel-Mottaleb [a]

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HIGHLIGHTS

- Application of natural pigments and synthetic dye sensitizers in dye-sensitized solar cells (DSSCs).
- Photostability of the dyes over the TiO₂ film electrodes.
- The stability results favor selecting anthocyanin as a promising sensitizer candidate for DSSCs applications.

GRAPHICAL ABSTRACT

Anthocyanin dye showed the maximum current efficiency $\eta = 0.27\%$

ARTICLE INFO

ABSTRACT

This paper deals with the use of some natural pigments as well as synthetic dyes to act as sensitizers in dye-sensitized solar cells (DSSCs). Anthocyanin dye extracted from rosella (*Hibiscus sabdariffa* L.) flowers, the commercially available textile dye Remazole Red RB-133 (RR) and merocyanin-like dye based on 7-methyl coumarin are tested. The photostability of the three dyes is investigated under UV–Vis light exposure. The results show a relatively high stability of the three dyes. Moreover, the photostability of the solid dyes is studied over the TiO₂ film electrodes. A very low decolorization rates are recorded as; rate constants $k = 1.6$, 2.1 and 1.9×10^{-3} min^{-1} for anthocyanin, RR and coumarin dyes, respectively. The stability results favor selecting anthocyanin as a promising sensitizer candidate in DSSCs based on natural products.

Dyes-sensitized solar cells are fabricated and their conversion efficiency (η) is 0.27%, 0.14% and 0.001% for the anthocyanin, RR and coumarin dyes, respectively. Moreover, stability tests of the sealed cells based on anthocyanin and RR dyes are done under continuous light exposure of 100 mW cm^{-2}, reveals highly stable DSSCs.

Introduction

The dye-sensitized solar cell (DSSC) is a device for the conversion of visible light into electricity based on the sensitization of wide band gap semi-conductors [1,2]. The performance of the cell mainly depends on the dye used as sensitizer. The absorption spectrum of the dye and the anchorage of the dye to the surface of TiO₂ are important parameters determining the efficiency of the cell [3]. Generally, transition metal coordination compounds (ruthenium polypyridyl complexes) are 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 [4]. How-

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ever, ruthenium polypyridyl complexes contain a precious heavy metal, which is undesirable from the viewpoints of both cost and of the environment [5]. Moreover, the process to synthesize the complexes is complicated and costly. Alternatively, other including natural and commercial synthetic dyes can be used for the same purpose with an acceptable efficiency [1,3–9]. The advantages of natural dyes include their availability and low cost.

However, other natural and/or synthetic organic dyes, such as phthalocyanine, cyanine dyes, xanthene dyes, coumarin dyes and other, usually perform poorly in DSSCs because of weak binding energy with TiO_2 film and low charge-transfer absorption in the whole visible range, but these dyes are very cheap and easily prepared [10].

An important key factor in the application of these dyes in DSSCs is its stability. For this reason, the main objective of this work of research is to study the stability of the DSSCs that based on some natural pigments as well as synthetic dyes, which has been used as dye sensitizers in DSSCs such as; anthocyanin dye extracted from rosella (*Hibiscus sabdariffa* L.) flowers, Remazole Red RB-133 (RR) and merocyanin-like dye based on coumarin.

Experimental

Dyes

Anthocyanin dye extracted from rosella (*Hibiscus sabdariffa* L.) flowers, Remazole Red RB-133 (RR), from Dye Star Company and was used as received, and the merocyanin-like dye based on 7-methyl-coumarin previously reported [11]. The molecular structures of the three dyes are shown in Fig. 1

Materials

Conductive glass plates (FTO glass, fluorine-doped SnO_2 overlayer, sheet resistance 8 Ω per cm^2, made by Beijing Building Material Factory) were used as the substrate for precipitated porous TiO_2 porous film, and were cut into 1.5 cm^2 sheets. All chemicals and solvents were of analytical grades and were used as received without further purification.

Preparation of the TiO₂ electrode

Nanoporous TiO_2 film was prepared according to our previous work [12]. In a typical method, tetrabutyl titanate (20 ml) was rapidly added to distilled water (200 ml) and a white precipitate was formed immediately. The precipitate was filtered using a glass frit and washed three times with 100 ml distilled water. The filter cake was added to nitric acid aqueous solution (0.1 M, 200 ml) under vigorous stirring at 80 °C until the slurry became a translucent blue–white liquid. The resultant colloidal suspension was autoclaved at 200 °C for 12 h to form milky white slurry. The resultant slurry was concentrated to 1/4 of its volume, then 20,000 polyethylene glycol (PEG, 10 wt.% slurry) and a few drops of the emulsifying agent Triton X-100 was added to form a TiO_2 paste.

Fabrication of dye-sensitized solar cells

The TiO_2 colloid was dropped on the FTO glass plate using a doctor blade technique. The process was done for three times to form a thick TiO_2 film about 3–5 μm. Finally, the TiO_2 porous film was sintered by firing the conducting glass sheet at 450 °C in air for 30 min. After cooling to 80 °C, the TiO_2 film was immersed in concentrated dye solutions (4×10^{-5} M RR, 0.5 g l^{-1} aqueous anthocyanin and 1×10^{-4} M ethanolic coumarin derivative) in for 24 h to absorb the dye adequately, then the dye-sensitized TiO_2 film was washed with anhydrous ethanol and dried in moisture-free air. The active area of the DSSCs was approximately 0.25 cm^2. Sputtered Pt over FTO was the counter electrode. The two electrodes were clipped together, and a cyanoacrylate adhesive was used as sealant to prevent the electrolyte solution from leaking.

Characterization and measurements

The TiO_2 film electrode was investigated by X'pert Philips X-ray diffraction (XRD) with Cu Kα radiation (λ = 1.54056) with accelerating voltage of 40 kV and 30 mA and scan rate 5°/min, Scanning electron microscope (SEM) Quanta 250 FEG (Field Emission Gun), with accelerating voltage 30 kV, magnification 14× up to 1,000,000 and resolution for Gun.1n, and Transmission electron microscope, JEM-2000 EX (JEOL, Tokyo, Japan).

The absorption spectra of the dye solutions and the dyes adsorbed on TiO_2 film electrodes were recorded using a fiber optics UV–Vis spectrophotometer (Ocean optics USB 4000 UV–Vis spectrophotometer).

Solar energy conversion efficiency (η) measurements were done using a solar simulator (Xe-500W; Shanghai photoelectricity Device Company, Shanghai, china) which is served as light source; the light intensity being adjusted via a reference standard Si-solar
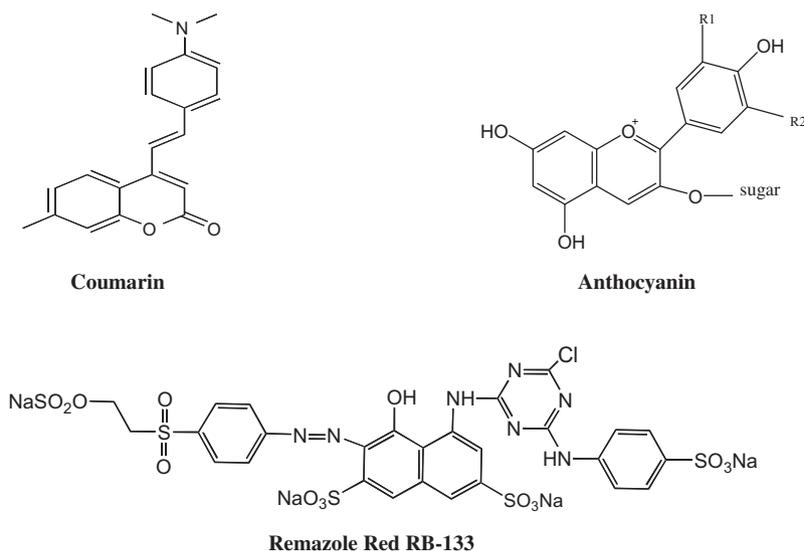

Coumarin

Anthocyanin

Remazole Red RB-133
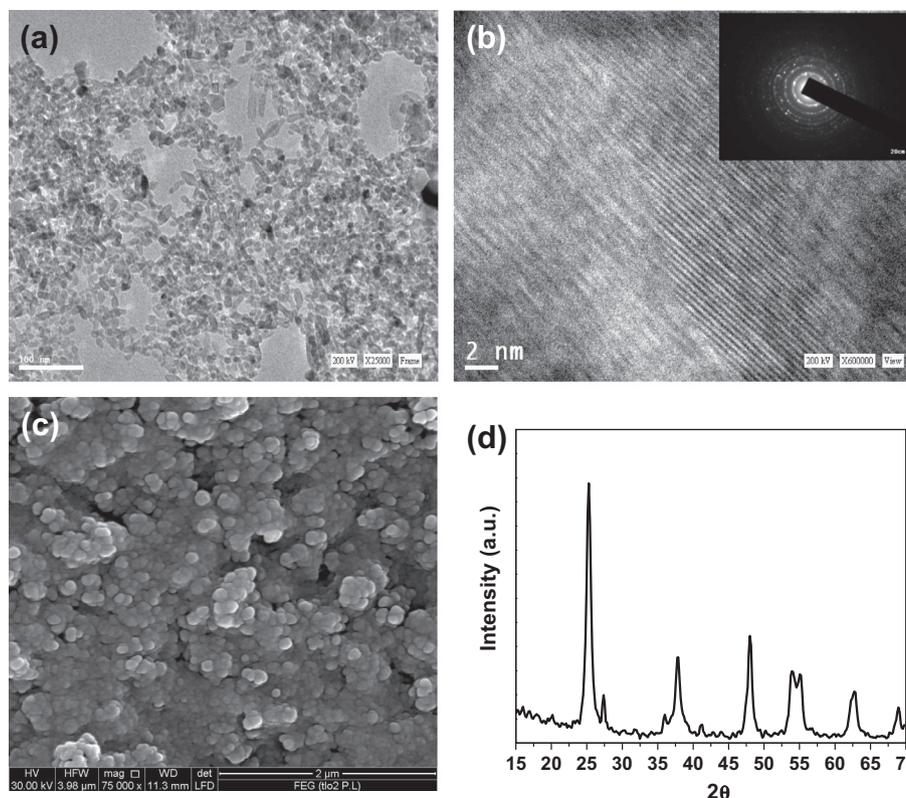
Fig. 1. Chemical structures of the dyes.

Fig. 2. (a) TEM; (b) HR-TEM; (c) SEM images and (d) XRD pattern of the TiO_2 film electrode.
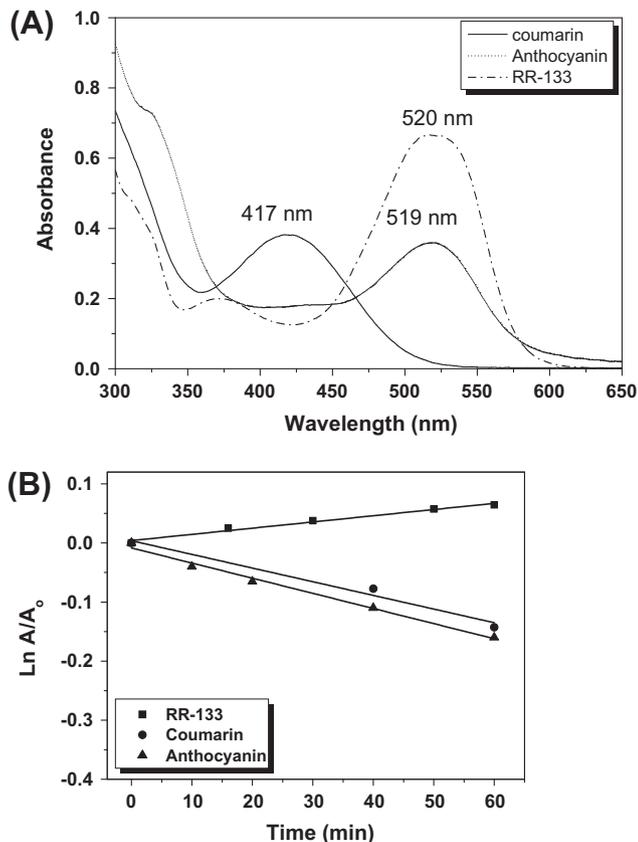

Fig. 3. (A) Light absorption spectra of dye solutions of: (a) anthocyanin; (b) RR RB-133; and (c) coumarin. (B) Photostability rate kinetics of pure aqueous solutions of; (■) 4×10^{-5} M RR, (●) 1×10^{-4} M coumarin, and (▲) 0.5 g/l anthocyanin dyes under 100 W cm^{-2} UV–Vis light.

cell at 1sun light intensity of 100 mW/cm^2. A dual-channel Keithley (K2635, USA) source-measure meter computerized with Lab-View software adjusted by ETC (Egyptian Centre for Technology), National instruments certified alliance partner, was used for I–V curve measurements and cell parameters calculations. The current–voltage source and measure ranges of K2635 are (20 fA–1.5 A) and (1 μV–202 V), respectively. TENMARS Solar power meters (TM 206, Taiwan) certified by ISO 9001, was used to measure the solar radiation intensity in mW cm^{-2}.

Typical parameters from the J–V curves were taken from 0 V to −0.7 V and back to 0 V with a scan rate of 50 mV S^{-1}. The overall efficiency (η) was calculated from the current density–voltage (J–V) curves using the following equation:

$$\eta = P_{max}/P_{input} = (J_{sc} \cdot V_{oc} \cdot FF)/P_{input} \tag{1}$$

where the P_{max} is the maximum power output point in the J–V-curve yielding maximum product of current and voltage, P_{input} is the radiation power incident on the cell, J_{sc} is short circuit current density generated under illumination, and V_{oc} is the open-circuit voltage. FF is the fill factor calculated from the following equation:

$$FF = (I_{mp} \cdot V_{mp})/(I_{sc} \cdot V_{oc}) \tag{2}$$

Results and discussion

Characterization of the TiO$_2$ film electrode

Generally, the photovoltaic performance of DSSCs is closely related to the surface characteristics of the TiO$_2$ semiconductor nanoparticles. The particle sizes and surface potential of the oxide nanoparticles control the amount the dye adsorbed on the photoanode, which determines total number of photogenerated carriers and hence the photovoltaic efficiency of the DSSCs [13].
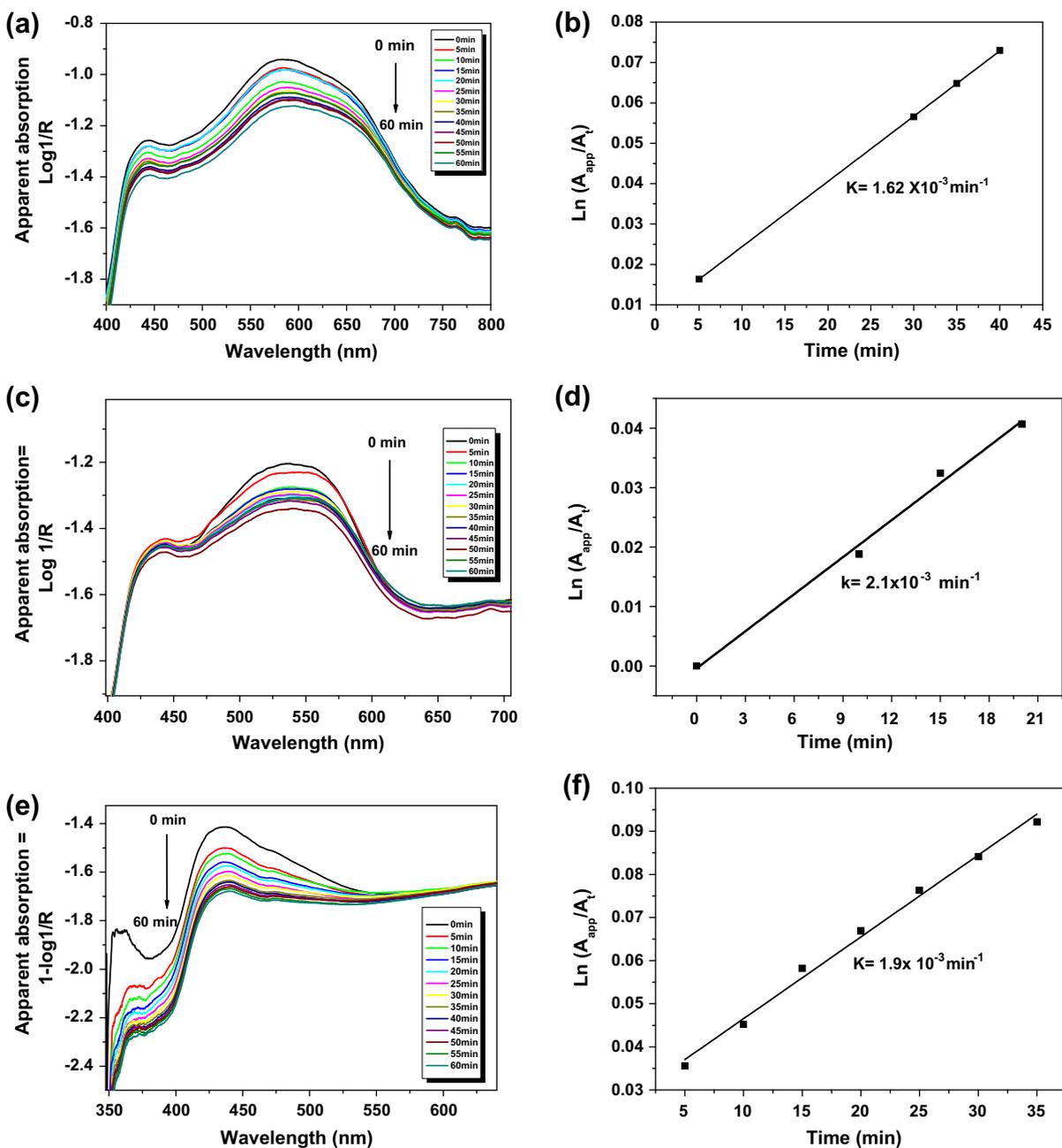
Fig. 4. Effect of light irradiation on the diffuse reflectance color change and the calculated rate kinetics of: (a and b) anthocyanin; (c and d) RR-133; (e and f) coumarin dyes adsorbed on TiO_2 thin film electrodes.

The detailed morphology of the TiO_2 thin film electrode used in DSSCs fabrication was characterized by scanning electron microscope (SEM) and transmission electron microscope (TEM) (Fig. 2a–c). The TEM images (Fig. 2a and b) of the titania paste used in electrode preparation show two uniform sizes of TiO_2 nanoparticles; viz., (8–10 nm) and (20–40 nm). This mixed morphology enables a well interconnected porous network structure of the titania film electrode needed for efficient dye absorption [14]. The high resolution TEM image (Fig. 2b) and the selected electron diffraction pattern (SEAD) (Inset in Fig. 2b) confirm the lattice finger pattern of the TiO_2 anatase structure.

The SEM image (Fig. 2c) of the film electrode shows a uniform morphology from TiO_2 nanoparticles without any cracks in the fabricated film electrode.

Table 1
The kinetics of degradation/decolorization of the diffuse reflectance color change of the three dyes adsorbed on TiO_2 thin film electrodes.

Dye	$k \times 10^{-3} \pm 0.05$ (min^{-1})
Anthocyanin	1.62
RR-133	2.10
Coumarin	1.90

The XRD pattern of the TiO_2 film electrode (Fig. 2d) confirms that all the diffraction peaks are assigned to anatase and rutile phases (JCPDS No. 84-1285 fpr anatase and 87-0920 for rutile) with
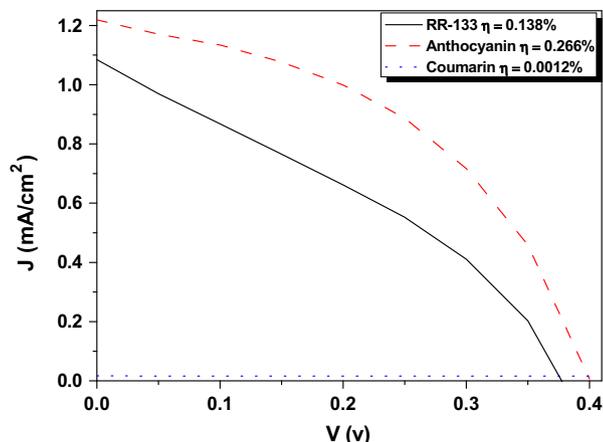
Fig. 5. *J–V* characteristics of the DSSCs based on the three dyes under investigation at 1 sun irradiation, 100 mW cm^{-2}.

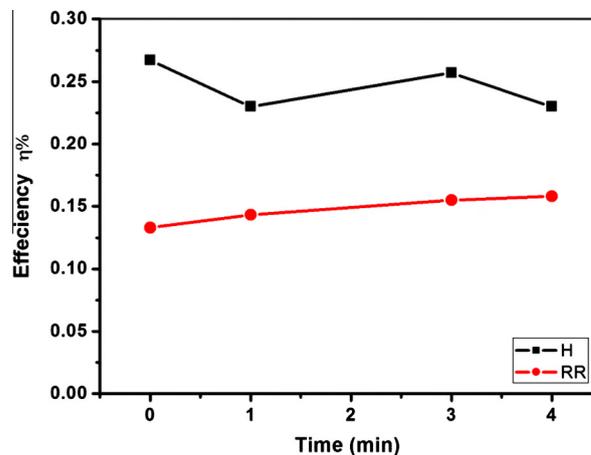**Fig. 6.** Photostability tests of the DSSCs based on the three dyes under investigation at 1 sun irradiation, 100 mW cm^{-2}.

an average crystal size for anatase and rutile phases equal to 14 and 38 nm respectively. Moreover, the peaks are rather sharp, which indicates that the obtained TiO_2 has relatively high crystallinity [15]

Photostability of the dyes

Fig. 3a shows the UV–VIS absorption spectra of the three dyes. It was found that the absorption peak of anthocyanin compounds is about 519 nm while those of RR-133 and coumarin dyes are about 520 and 417 nm.

Fig. 3b shows photostability rate kinetics of the three dyes under UV–Vis light irradiation of 100 mW cm^{-2} for 1 h. The three dyes are clearly resistant to direct photolysis by UV–Vis irradiation, reflecting a high photostability of the three dyes.

Photostability of the dye-sensitized titania film electrodes

The photostability of all the sensitized dyes on the TiO_2 thin film electrode has been investigated under exposition to UV–Vis irradiation by diffuse reflectance spectroscopy (Fig. 4a–f). The rate kinetics of the photostability curves are well fitted first order rate kinetics (Fig. 4b, d, and f): Ln (A_{app}/A_o) were plotted against time t. where R = reflectance at time t; A_o = absorbance at zero time. The calculated degradation/decolorization rate constants k (Table 1), were k = 1.6, 2.1 and 1.9×10^{-3} min^{-1} for anthocyanin, RR and coumarin sensitized dyes, respectively. These would be useful information for selecting the anthocyanin derivative as the most stable dye, also giving the best DSSC performance.

Stability and performance of the DSSCs

The current–voltage (*I–V*) characteristic curves of the DSSCs based on the three dyes are given in Fig. 5 and the photovoltaic characteristics are listed in Table 2.

Anthocyanin dye shows a high short-circuit current (J_{sc}) of (0.203 mA cm^{-2}) when compared to remazole red and coumarin (0.173 mA cm^{-2} and 0.003 mA cm^{-2} respectively) (Table 2). This can be attributed to the better light harvesting ability of anthocyanin when compared to remazole red and coumarin. The open circuit voltage (V_{oc}) of anthocyanin dye (0.5 V) is lower than that of remazole red and coumarin (0.4 V and 0.2 respectively). This can be the result of either the lower number of acidic protons in anthocyanin dye versus remazole red or coumarin, and/or due to the acceleration in the recombination rate of injected electrons with the electrolyte in the case of anthocyanins [16].

As a conclusion, the anthocyanin dye showed the maximum current efficiency η = 0.27% followed by remazole red η = 0.14%, but coumarin showed the least current efficiency η = 0.0012%. The results of the coumarin based dye could be explained on the basis of weak adsorption of the coumarin dye on the surface of the TiO_2 film and the mismatch between its excited S_1 state and the conduction band of TiO_2 (see Table 2). Moreover, a DSSC based on coumarin dye is active only in a limited operating spectral range (see Fig. 3), giving a consequent smaller efficiency, indicating the importance of the dye spectral profile in light to electricity conversion. Furthermore, S_1-state light energy dissipation via the strong fluorescence of the coumarin-based dye in the solid state [11] strongly competes, or prohibits, charge generation and electron transport to the TiO_2 photoanode.

The evolution of the photo-to-current efficiency (η) with the time for the DSSCs based on anthocyanin and remazole red dye sensitizers is presented in Fig. 6. The performance of the cells shows a relatively stable efficiency over a period of 4 h of continuous illumination. Wax was not used here to seal cells to allow rapid comparative studies on stability for longer times should be obtained after sealing. This leads to a conclusion to the relatively good stability of the dyes as sensitizers over the TiO_2 film electrode which means that it could be used as stable dye sensitizers in DSSCs applications.

Table 2
The solar cell parameters obtained from the *I–V* characteristics for DSSCs fabricated by using the three dyes:

Dye	V_{oc} (mV)	J_{sc} (mA/cm^2)	Fill factor FF (%)	Efficiency[a] (η) (%)
Anthocyanin	0.5	0.203	0.42	0.27
RR-133	0.4	0.173	0.32	0.14
Coumarin	0.2	0.003	0.38	0.001

[a] ±0.02 for anthocyanin and RR dyes.

Conclusion

Some natural pigments and synthetic dyes such as; anthocyanin dye extracted from rosella (*Hibiscus sabdariffa* L.) flowers, Remazole Red RB-133 (RR) and merocyanin-like dye based on coumarin are used as dye sensitizers in DSSCs showed relatively good photostability at the TiO_2 film electrode. However, their stability was not the determining factor in obtaining high efficiencies, which were only 0.27%, 0.14% and 0.001% for the anthocyanin, RR and coumarin dyes, respectively. The limited absorption spectral range of coumarin-based dye compared to those of the anthocyanin and RR dyes may play an important role in the measured DSSC light-to-electricity conversion efficiency. Additionally, strong fluorescence of coumarin-based dye competes significantly with charge generation and transport, leading to inefficient conversion. The performance of the cells based on anthocyanin and RR showed a constant efficiency over a period of continuous illumination, indicating a promising stability/conversion efficiency of DSSCs based on natural dyes.

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