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# Layered co-sensitization for enhancement of conversion efficiency of natural dye sensitized solar cells



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# ABSTRACT

This paper describes a double layered co-sensitization in dye sensitized solar cells (DSSCs) by using natural pigments from Ixora flower (*Ixora* sp. (Rubiaceae)) and the outer dark purple skin of 'Kembayau' (*Canarium odontophyllum*) fruit. UV-vis absorption data revealed that both dyes were anthocyanins. Co-sensitization was done by first adsorbing the dye from *C. odontophyllum* into TiO<sub>2</sub> electrode by dipping, and then by removing adsorbed dye of the top layer of TiO<sub>2</sub> using a de-sorption solution before the *Ixora* sp. dye was allowed to adsorb. Power conversion efficiency of the co-sensitized solar cell was 1.55%. The conversion efficiencies of DSSCs sensitized with *Ixora* sp. , *C. odontophyllum* and the mixture of both dyes (1:1) were 0.96%, 0.59% and 1.13% respectively. The superior conversion efficiency achieved by layered co-sensitization is attributed to the high adsorption capacities of *Ixora* sp. *and C. odontophyllum*, and the homogeneous monolayer adsorption of *Ixora* sp. as revealed by Freundlich and Langmuir adsorption isotherms.

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# 1. Introduction

Even though the Dye sensitized Solar Cells (DSSCs) have attracted much attention in the recent pass, still the long term stability and the use of expensive dyes are some of the major draw backs of these DSSCs in popularizing them in the practical applications. To date, the most efficient DSSCs are made using ruthenium dye complexes; with reported power conversion efficiency of about 12% with the illumination of 100 mW cm<sup>-2</sup> (AM 1.5) [1–3]. The reliability factor implies the robustness of the device to maintain a reasonable performance after prolonged exposure to weathering elements.

Much research is geared towards the improvement of the power conversion efficiencies of DSSC. Different types of sensitizers, both natural and synthetic are being tested for their efficiencies. However, synthetically produced dyes are very expensive and they utilize large quantities of heavy metals to form complexes for efficient adherence onto the  $TiO_2$  film, a necessary component of DSSC [2]. The present of heavy metal complexes poses a challenge to DSSC production, where the environmental impact factor

*E-mail addresses:* roshan.kumara@gmail.com (N.T.R.N. Kumara), piyasiri. ekanayake@ubd.edu.bn (P. Ekanayake), anderylim@hotmail.com (A. Lim), 12m8360@ubd.edu.bn (L.Y.C. Liew), iskandar.petra@ubd.edu.bn (M. Iskandar), cheeming.lim@ubd.edu.bn (L.C. Ming), rsena@ifs.ac.lk (G.K.R. Senadeera). becomes an issue. This accounts for the interest in using natural dyes as effective sensitizers in DSSC. Natural dyes such as chlorophyll, carotene and anthocyanin are relatively easy to be extracted from plants, as compared to the production of synthetic dyes. However, the DSSCs consist of these dyes showed quite poor performances and instabilities. On the other hand natural pigments containing anthocyanins and betalains have shown overall solar energy conversion efficiencies of around 2% [4].

In this work, a common group of natural dyes abundant in flowers and fruits, namely anthocyanin, is tested for its performance in DSSCs. The natural dyes used in this work, were obtained from petals of dark red colored *Ixora* sp. (coded as 'IX') and outer dark skin of *Canarium odontophyllum* (coded as 'CMB').

Anthocyanins are natural components that mostly give redpurple coloration to fruits and plants, and they have light absorb in the range of 520–550 nm wavelengths [5,6]. The color of an anthocyanin depends on its chemical structure and the pH of the medium it exists. It is usually red in color in an acidic medium but turn into blue in less acidic condition.

Basic chemical structure of anthocyanin is shown in Fig. 1. It consists of seven different side groups carrying a hydrogen atom, a hydroxide or a methoxy group. Temperature, light and pH are the main factors that destabilize the anthocyanin molecular structure [7].

*Ixora* sp. is found in Tropical Asia and it blooms all the year round. The plant has leathery leaves and their flowers are small



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**Fig. 1.** The basic structure of anthocyanin,  $R_1 = OH$ ,  $R_2 = OH$ ,  $R_3 = H$ .

and grouped in large clusters. It consists of many species, with different shapes, sizes and colors.

*C. odontophyllum* is a fruit with dark purple skin and found only in Borneo. Its flesh is thin and has a sour taste. Analysis of the *C. odontophyllum* has been done using reversed phase high-performance liquid chromatography coupled with diode array detector, and has revealed the presence of two groups of phenolic acids, five groups of flavonoids, three groups of anthocyanidins, four groups of anthocyanins and ethyl gallate [8].

This paper describes the use of these two natural dyes in a single DSSC for double layered co-sensitization. Co-sensitization is a novel method employed in DSSC, with the aim of improving the absorption of light over a broader wavelength region [9-11] and thereby to improve the current output of these devices and the overall efficiency. Two different dyes are usually used as sensitizers by employing co-sensitization technique which makes light absorption more efficient when a shorter wavelength absorbing dye is positioned in series with a longer wavelength absorbing dye. Co-sensitization is expected to increase the efficiency of the DSSC. Our literature review has suggested that there are no works of this type being reported. The enhanced efficiency obtained through co-sensitization is explained using UV-vis absorption and adsorption capacities of these two natural dyes. The adsorption studies are done using Freundlich and Langmuir isotherms. The cyclic voltammetry (CV) and UV-vis absorption experiments data were used to determine the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) levels and band gaps of these natural dyes.

#### 2. Materials and methods

#### 2.1. Fabrication of photo-electrode

Photo electrodes were fabricated using TiO<sub>2</sub> paste from Dyesol (DSL 18NR-T). The TiO<sub>2</sub> paste was coated on pre-cleaned fluorine-doped conducting tin oxide (FTO) glasses (Nippon sheet glass  $10 - 12\Omega$  sq<sup>-1</sup>) by Doctor Blade method. Electrodes were pre-heated (~50 °C) using a hair-drier and sintered at 450 °C for 30 min. The thickness of the TiO<sub>2</sub> electrodes used for this investigation was ~15 µm (Dektak profilometer; Veeco, Dektack 3) [12].

## 2.2. Plant materials and pigment extraction

The *C. odontophyllum* fruits were obtained from a grown plant found in Brunei. The dye pigment anthocyanin was extracted from the outer dark skin of CMB by crushing with a minimum amount of 70% ethanol (diluted from Scharlau 99.9% with distilled water). The residual solids were filtered off and the extract was then centrifuged to separate any remaining solid content. The presence of anthocyanin was confirmed by UV-visible absorption spectroscopy (Shimadzu UV-1800) [13].

Twenty grams of fresh outer dark purple skin of CMB were used in the extraction to make 100 ml extract of anthocyanins. Same method was followed in extracting pigments from dark red Ixora flower petals. The extracted pigments CMB and IX were stored in amber glass bottles, wrapped with aluminium foil, to protect from direct light, and stored in a dry and cool place.

#### 2.3. Dye sensitized solar cell preparation

 $TiO_2$  electrodes were dipped in respective dye solutions (CMB, IX and their mixture) for 14 h in order to allow the dye molecules sufficient time for adsorption. The dye mixture was prepared by mixing CMB and IX in 1:1 ratio. Then  $TiO_2$  electrodes were taken out and rinsed with absolute ethanol and air dried. DSSCs were assembled by introducing the redox electrolyte containing tetrabutylammonium iodide (TBAI; 0.5 M)/l<sub>2</sub> (0.05 M), in a mixture of acetonitrile and ethylene carbonate (6:4, v/v) between the dyed TiO<sub>2</sub> electrode and platinum counter electrode [12]. The monochromatic incident photo-to-electron conversion efficiencies (IPCE) were evaluated using a commercial setup for IPCE measurement (PVE 300, TMc 300) [13]. These DSSCs were placed under irradiation of 1000 W/m<sup>2</sup> for about 4–6 h for better incorporation of electrolyte into the TiO<sub>2</sub> layer.

### 2.3.1. Co-Sensitization

Two dye layers were introduced to the  $TiO_2$  anode, consecutively, using a cosensitization procedure as described below.

First a dried TiO<sub>2</sub> layer was fully immersed in a CMB extract for 7 h. Then it was taken out and dried without heating. A desorption solution, which consists of tetraethyl ammonium hydroxide in methanol and ethylene glycol solution was introduced to the upper region of the TiO<sub>2</sub> electrode for 30 s, and then it was immediately washed away with ethanol for 20 s before drying. This process is called de-adsorption and was repeated 3 times. Each repeated de-adsorption event would affect the desorption depth. Then it was dipped into the second sensitizer of IX for another stage of adsorption for a period of 7 h. The cycle of the sensitization adopted is depicted in Fig. 2. The co-sensitization in brief: the TiO<sub>2</sub> layer was allowed to adsorb one dye followed by a de-adsorption procedure of the top layer and then dipped it in the second dye for the adsorption of next dye layer [10].

## 2.4. Cyclic voltammetry measurements

Cyclic voltammetry measurements were carried out in a three-electrode system consisting of a glassy carbon working electrode, platinum counter electrode and Ag/AgCl reference electrode at a scan rate of 50 mV/s (Solartron 1286). Few drops of the required dye solutions were placed on the glassy carbon working electrode and allowed to dry at room temperature before immersing the electrode in a supporting electrolyte. The supporting electrolyte was 0.1 M KNO<sub>3</sub> [14].

## 2.5. Adsorption equilibrium studies

The adsorption properties of CMB and IX onto TiO2 were studied using Freundlich and Langmuir adsorption isotherms. The pH differential method was followed to calculate the total monometric anthocyanin concentration of CMB and IX [15]. Equilibrium experiments were carried out by different initial dye (for both CMB and IX) concentrations with a given amount of TiO2. The stock solutions were prepared by adding CMB and IX original extracts into absolute ethanol (Analytical grade). Six samples of different dye concentrations of each CMB and IX were prepared by adding 100, 200, 300, 400, 500 µL and 600 µL volumes of original extract into 10 mL of absolute ethanol. The initial sample concentrations were calculated and UV-vis absorption (Shimadzu, UV-1800) data of these pigments were obtained before 0.05 g of TiO<sub>2</sub> (P25 Degussa) powder was added to each sample and left for 24 h at room temperature to reach equilibrium state. The samples were then centrifuged for about 10 min at a speed of 3000 rpm (SiGma 3-18 k) to separate the solid and the liquid phases. The UV-vis absorptions of these liquid phases were measured and the equilibrium concentrations were determined by using a calibration curve.



Fig. 2. Schematic diagram of the procedure for the layered co-sensitization.

# 3. Results and discussion

# 3.1. Optical properties

The absorption spectra of the CMB, IX and the mixture were measured by using a UV-vis spectrophotometer with ethanol as the solvent reference. Hydrochloric acid (HCl) was added to the dye solutions in order to increase the prominence of the absorption. These absorption data were used to verify the presence of anthocyanin pigments in the two dyes and the mixture of dye. At pH 1.0 the anthocyanin strongly absorbs light between 520 and 550 nm, see Fig. 3a. Fig. 3b depicts the UV-vis absorption of dyes which were already adsorbed onto TiO<sub>2</sub> electrode. The UV-vis absorption of TiO<sub>2</sub> electrode without dye is also shown for comparison. After the top layer of CMB was removed from the TiO<sub>2</sub> electrode, the absorbance was decreased as shown in Fig. 3b. However, when a layer of IX dye was adsorbed onto the top layer of TiO<sub>2</sub> electrode, the UV-vis absorption of this co-sensitized electrode was increased significantly.

IPCE of the individual pigments, their mixture and layered cosensitized DSSCs are shown in Fig. 4. The slight increment of IPCE in the mixture sensitized DSSC compared with individual dyes sensitized DSSCs is in agreement with the I-V data (see Table 3) as well as UV-vis spectra. IPCE of co-sensitized solar cell shows a



**Fig. 3.** (a) UV-vis absorption spectra of CMB, IX and the mixture (non-acidified and acidified with conc. HCl). A broad absorption peak was observed around 520–550 nm when the extracts were acidified with conc HCl (b) UV-vis absorption spectra of  $TiO_2$  electrode and the adsorbed dyes onto the electrode.



Fig. 4. IPCE spectra of co-sensitized DSSC and the DSSCs sensitized with CMB, IX and the mixture.

great improvement over the entire wavelength range which also in good agreement with I-V data of the co-sensitized solar cell.

# 3.2. Band gap and HOMO-LUMO calculations

The electrochemical behavior of the dyes was studied using cyclic voltammetry [16]. The cyclic voltammograms of CMB, IX and their mixture are shown in Fig. 5. Evaluation of optical band gaps of the CMB, IX and the mixture pigments using their UV-vis absorbance spectra (edge) was performed by employing the Tauc relation [16–18]. The graph plotted according to the Tauc relation and the reduction onset potential determined from cyclic voltammetry were used to calculate the band gaps and the HOMO and LUMO energy levels of the anthocyanin pigments of CMB, IX and the mixture. The results are shown in Table 1.

# 3.3. Adsorption isotherms

The equilibrium adsorption isotherms indicate the nature of dye adsorption and distribution on TiO<sub>2</sub> surface. In other words, it gives relations between sorbent and sorbate. The two linear isotherm models namely Freundlich and Langmuir that were used to investigate the adsorption properties of our natural dyes are summarized in Table 2. Fig. 6 shows the experimental data and



Fig. 5. Cyclic voltamograms of CMB, IX and the mixture.

## Table 1

The HOMO, LUMO energy levels and the band gap energies of CMB, IX and the mixture.

Compounds	HOMO level (eV) <sup>a</sup>	LUMO level (eV) <sup>a</sup>	Band gap (eV)
CMB	-7.78	-3.99	3.79
IX	-7.31	-4.28	3.03
Mixture	-7.19	-4.03	3.16

<sup>a</sup> Energy levels were calculated with respect to the vacuum level.

## Table 2

The isotherms used in this study and their linear forms.

Isotherm		Linear form	Plot	Reference
Freundlich	$q_e = K_F C_e^{1/n_F}$	$log(q_e) = log(K_F) + 1/n_F log(C_e)$	$\log(q_e)$ vs. $\log(C_e)$	[20]
Langmuir	$q_e = \frac{q_m K_a C_e}{1 + K_a C_e}$	$\frac{1}{a_0} = \left(\frac{1}{K_0 q_m}\right) \frac{1}{C_0} + \frac{1}{q_m}$	$\frac{1}{q_e}$ VS. $\frac{1}{C_e}$	[20]

*Ce*-equilibrium dye concentration, mg/L; *qe*-amount of dye adsorbed at equilibrium, mg/g; *KF*-Freundlich isotherm constant, (mg/g)(L/g)1/nF; *nF*-Freundlich exponent; *qm*-maximum adsorption capacity, mg/g; *Ka*-Langmuir constant related to energy of adsorption, L/mg.

#### Table 3

Photovoltaic parameters of co-sensitized cell and the mixture, CMB and IX sensitized DSSCs.

Sensitizer	$I_{SC}$ (mA cm <sup>-2</sup> )	$V_{OC}$ (mV)	ff	η(%)
1. CMB	2.45	385	0.62	0.59
2. IX	6.26	351	0.44	0.96
3. Mixture	6.26	384	0.47	1.13
4. Co-sensitization	9.80	343	0.46	1.55

the best fits for Freundlich and Langmuir models, and corresponding regression ( $r^2$ ) values. The regression values indicated that CMB and IX data fit with Freundlich isotherm whereas IX data fit Langmuir Isotherm. The Freundlich Isotherm is used to explain adsorption the capacity of dyes [19]. The good fit of CMB and IX equilibrium data with Freundlich isotherm indicates clearly that both of the pigments have high adsorption capacity on the TiO<sub>2</sub> surface. The Langmuir isotherm describes the monolayer and homogeneous surface properties [19]. The good fit of IX equilibrium isotherm data with Langmuir isotherm indicates this pigment favors a monolayer and homogeneous adsorption on the TiO<sub>2</sub> surface.

## 3.4. I-V Characteristics

Fig. 7 shows current–voltage characteristics of the co-sensitized solar cell and the DSSCs sensitized with CMB, IX and the mixture. The fill factor and the maximum conversion efficiency of the DSSCs were calculated using their respective current–voltage characteristics.

The maximum power conversion efficiency ( $\eta$ ) was then calculated using the following formula,

# $\eta = ff imes I_{ m sc} imes V_{ m oc}/P$

where  $I_{SC}$  is the short circuit photo current density (A cm<sup>-2</sup>),  $V_{oc}$  is open circuit voltage (V), *P* is the intensity of the incident light (W cm<sup>-2</sup>) and *ff* is fill factor of DSSC.

The fill factor ff was defined as the ratio of the maximum power  $P_{max}$  obtained from the DSSC and its theoretical maximum power. Hence,



Fig. 6. Freundlich and Langmuir isotherm plots for IX and CMB.



**Fig. 7.** Comparison of *I–V* characteristics of the co-sensitized DSSC and the DSSCs sensitized with CMB, IX and the mixture.

$$ff = (I_m V_m)/(I_{SC} \times V_{OC})$$

Here,  $I_m$  and  $V_m$  are current and voltage corresponds to the maximum power.

Using the information obtained from *I*–V characterization, the fill factor and overall conversion efficiency for the DSSCs were calculated and tabulated in Table 3. It was found that the best performance was exhibited by from the co-sensitized cell, which showed conversion efficiency ( $\eta$ ) of 1.55%, with open circuit voltage ( $V_{OC}$ ) of 343 mV, short circuit current density ( $I_{SC}$ ) of 9.80 mA cm<sup>-2</sup> and fill factor (*ff*) of 0.46, under the irradiance of 1000 Wm<sup>-2</sup>. Table 3 also represents  $I_{SC}$ ,  $V_{oc}$ , *ff* and  $\eta$  for the mixture and individual dyes, under the same irradiation conditions.

Experimental results show that the UV-vis absorption of IX is lower than that of CMB (Fig. 3a). However, I-V characteristics of IX sensitized DSSC, shown in Fig. 7 and Table 3, are better than that of CMB sensitized DSSC. This may be due to the fact that IX dye forms homogeneous monolayer on the TiO<sub>2</sub> as revealed by adsorption isotherms (Fig. 6). The monolayer adsorption optimizes the DSSC efficiency [21-23]. On the other hand, the estimated optical band gap of IX was less than that of CMB (see Table 1) that also contribute to the higher performance of IX sensitized DSSC. The mixture sensitized DSSC showed better *I–V* performance compared to the individual IX and CMB sensitized DSSCs. The high adsorption capacities of IX and CMB (as revealed by Freundlich isotherm), and high UV-vis absorption properties of CMB might resulted this enhanced I-V characteristics of the mixture sensitized DSSC. The highest I-V performance, compared to IX, CMB and the mixture sensitized DSSCs was obtained from the co-sensitized DSSC. Selective positioning of dyes on the DSSC anode paves a way to utilize inherent properties such as absorption and adsorption of individual dyes without any alterations or modifications. Therefore, the photon energy conversion mechanism is directed by both of the dyes individually sitting in two different layers of the TiO<sub>2</sub> anode. This was shown, from our experimental data, to be more efficient than the mixture sensitized DSSC. When IX and CMB mixed unfavorable intermolecular interactions such as dye aggregations may occur which restricts the utilization of original properties of individual dyes for efficient photo-energy conversion process.

# 4. Conclusions

Extracts of *Ixora* sp. (Rubiaceae) (IX) and *C. odontophyllum* (CMB) were used to co-sensitize DSSC. UV–vis data revealed that both of these extracts contain anthocyanin pigments. HOMO,

LUMO levels and optical band gaps of the pigments were determined by cyclic voltammetry and UV–vis absorption data. Equilibrium adsorption studies show high absorption capacities of both CMB and IX onto TiO<sub>2</sub> while IX also having the homogenous monolayer absorption capacity. The highest conversion efficiency,  $\eta = 1.55\%$ , was obtained from the co-sensitization. Conversion efficiency of the mixture was 1.13%. IX and CMB individually exhibited lower conversion efficiencies. This work shows the effectiveness of selective positioning of dyes on the DSSC anode to utilize inherent properties such as absorption and adsorption of individual dyes without any alterations or modifications. When IX and CMB were mixed, unfavorable intermolecular interactions such as dye aggregations may occur which restricts the utilization of original properties of individual dyes for efficient photo-energy conversion process.

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