

Study of the Enhancement of Cell Performance of Dye Sensitized Solar Cells Sensitized With *Nephelium lappaceum* (F: Sapindaceae)

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We have studied the performance of dye sensitized solar cells sensitized with pigments extracted from the fruit sheath of *Nephelium lappaceum* (F: Sapindaceae). The pH of the pigment solution used for impregnation was controlled by adding concentrated HCl (50:0.2 v/v). The UV-Vis spectroscopic results revealed that the extract consists of the pigment of Anthocyanin, with an additional absorption peak appearing around 540 nm at a lower pH of the pigment solution. Also the band gap of the pigment was reduced by 1 eV at low pH conditions. The solar cells fabricated with pigment extracted from the fruit sheath of *Nephelium lappaceum* showed photo-response with the conversion efficiency of 0.26%, with an open-circuit voltage (V_{OC}) of 453 mV, short-circuit current density (I_{SC}) of 1.17 mA cm⁻², and fill factor (ff) of 0.48. The conversion efficiency was significantly enhanced when pH of the pigment solution was lowered by adding concentrated HCl. The conversion efficiency of the dye sensitized solar cells (DSSCs) sensitized after HCl treatment of the pigment was increased to 0.56%, with an open-circuit voltage (V_{OC}) of 404 mV, short-circuit current density (I_{SC}) of 2.71 mA cm⁻², and fill factor (ff) of 0.35. The HOMO level of the pigment at low pH was shown to be shifted towards more positive values with respect to vacuum level, giving rise to an enhanced DSSC efficiency. The overall efficiency enhancement of the low pH pigment was due to the combined effect of increased UV-Vis absorption and efficient adsorption of dye molecules onto the TiO₂ semiconductor surface. [DOI: 10.1115/1.4023877]

Keywords: DSSCs, *Nephelium lappaceum*, HOMO, LUMO, Anthocyanin

1 Introduction

Dye sensitized solar cells (DSSCs) are devices that convert visible light into electricity based on the photosensitization of wide band-gap metal oxide semiconductors, such as TiO₂, and have attracted a lot of interest towards development and improvement of new families of dyes and metal complexes [1]. Most of the efficient DSSCs are sensitized with the dyes having ruthenium based complexes that have been shown to operate with power conversions up to 10% using nanoporous TiO₂ electrodes. Due to the high cost of ruthenium complexes and the long-term unavailability of these noble metals [2–4], there is a need to search for alternative photosensitizers for the use in TiO₂-based photovoltaic devices.

Preparation and development of synthetic dyes as a sensitizer of DSSC normally requires multistep procedures, which involves a variety of solvents and time consuming purification processes, making synthetic dye production very expensive [5]. Several studies have found the possibilities of using natural dyes as DSSC's sensitizer. DSSCs equipped with natural dyes as sensitizers have several advantages over rare metal complexes and other synthetic dyes, in that they can easily be extracted from fruits, vegetables, and flowers with minimal chemical procedures, thus attracting a

lot of interest in producing a low cost and yet easy to fabricate DSSCs as alternatives to silicon photovoltaics [6].

Natural pigments containing anthocyanins and carotenoids have shown overall solar energy efficiencies up to 1% [1,7]. Anthocyanins consist of a large family of widespread flavonoids in plants and they are responsible for many fruits and floral colors [8]. Its abundance in nature makes anthocyanins a convenient choice for natural pigment to be utilized in DSSCs. Availability in large quantities, convenient extraction into cheap organic solvents, ability of application without fine purification, environmentally-friendly, and low production cost of the devices are some of the competitive advantages of these natural dyes. These anthocyanin pigments are present in the fruit sheath (pericarp) of *Nephelium lappaceum* [9,10]. The pericarp of the cited fruit is normally discarded after the flesh is consumed, thus causing resource dissipation. Through this study, the anthocyanin pigments extracted from the pericarp of the *Nephelium lappaceum* has been found useful and has potential, value added economic benefits.

Nephelium lappaceum locally known as "Rambutan," is a native fruit tree of South East Asia that belongs to the family Sapindaceae. The flowering time of this fruit differs with localities and is usually in response to rain following a dry period, which accounts for two times per year between the month of March to July and June to November, and hence the fruits can only be found seasonally. The fruit is hairy and oval-shaped, which may appear greenish-yellow, orange, crimson or red in color, and 1–2 in. long [11,12].

To our knowledge, there has been no study of anthocyanin pigments from *Nephelium lappaceum* used in the DSSCs. The bright

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red colored pericarp of *Nephelium lappaceum* is chosen for the purpose of this study and tested for its potential as a sensitizer of DSSCs.

2 Materials and Methods

2.1 Fabrication of Photo-Electrode. Photo electrodes were fabricated using a TiO₂ paste Solaronix (nanoxide-T, colloidal anatase particles size: ~13 nm, ~120 m² g⁻¹ (BET), Switzerland). The TiO₂ was coated on precleaned fluorine-doped conducting tin oxide (FTO) glasses (Nippon sheet glass 10⁻¹² Ω sq⁻¹) by Doctor Blade method. Electrodes were preheated (~50 °C) using a hair dryer and sintered at 450 °C for 30 min. The thickness of the TiO₂ electrodes used for this investigation was ~9 μm (Dektak profilometer; Veeco, Dektack 3) [6].

2.2 Plant Materials and Pigment Extraction. *Nephelium lappaceum* fruits were obtained from an orchard grown plant found in Brunei.

The dye pigment anthocyanin was extracted from the pericarp of *Nephelium lappaceum* 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 using the UV-visible absorption spectroscopic techniques (Varian Cary 5 E UV-Vis-NIR) [3]. Twenty grams of fresh pericarp were used in the extraction to make 100 ml extract of anthocyanins.

2.3 Dye Sensitized Solar Cell Preparation. The TiO₂ electrodes were subsequently dipped in the extracted anthocyanins overnight. The electrodes were then removed, rinsed with absolute ethanol, and air dried. DSSCs were assembled by introducing the redox electrolyte containing tetrabutylammonium iodide (TBAI, 0.5 M)/I₂ (0.05 M), in a mixture of acetonitrile and ethylene carbonate (6:4, v/v) between the dyed TiO₂ electrode and platinum counter electrode [6]. Those DSSCs placed under irradiation of 1000 W/m² about 4–6 h after applying the electrolyte to obtain the best current, possibly due to slow incorporation of the electrolyte into the TiO₂ layer.

2.4 Cyclic Voltammetry Measurements. Cyclic voltammetry measurements were carried out in three-electrode systems 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 separately 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 KNO₃ in distilled water [13].

3 Results and Discussion

3.1 UV-Vis Absorption Spectra. Extracted dye from the pericarp of *Nephelium lappaceum* was run under a UV-Vis spectrophotometer and produced spectra as shown in Fig. 1. Many studies have shown that absorption spectra of anthocyanins were pH sensitive [14] and this was also observed in our experiments as acidified dye extract of *Nephelium lappaceum* produced a peak between 500 and 550 nm. The intense peak observed at 540 nm wavelength shown in Fig. 1 is attributed to the lowering of the lowest unoccupied molecular orbital (LUMO) of the anthocyanin and to the possible presence of impurities in the extract [14]. In addition, adsorbed pigments onto TiO₂ working electrode were also analyzed under the UV-Vis spectrophotometer and the resulted spectra are shown in Fig. 2. Upon chelation to TiO₂ film (see Fig. 3), the characteristics of the peaks of both nonacidified and acidified dye remain the same as in Fig. 1, except for a small shift to the left. Performance of DSSCs could also be affected by

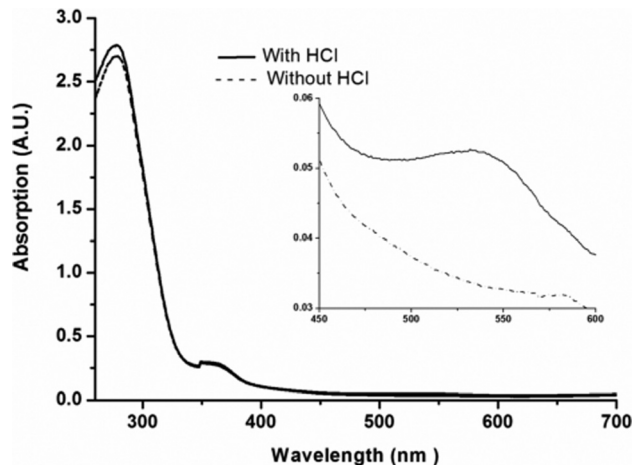


Fig. 1 UV-Vis absorption spectra of pigments extracted from *Nephelium lappaceum* (without and with concentrated HCl). A broad absorption peak was observed around 540 nm when pH of the extract *Nephelium lappaceum* was lowered. Inset shows an enlarged picture of the emerging absorption peak.

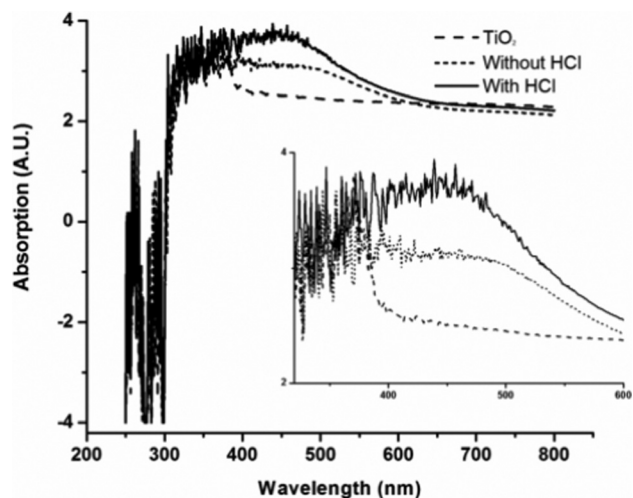


Fig. 2 UV-Vis absorption spectra of adsorbed *Nephelium lappaceum* pigments onto the TiO₂ film. Inset shows an enlarged picture of the emerging absorption peak of the analyzed sample.

the light absorption properties of the pigment. The broad absorption peak around 540 nm which emerged at low pH facilitated DSSCs to absorb even lower energy solar radiation from the visible spectrum increased the overall photovoltaic performance.

3.2 Current-Voltage Characteristics. The current-voltage characteristics of the DSSC prepared using *Nephelium lappaceum* extract as the natural dye sensitizer is shown as Fig. 4. Pretreated dye extracts with and without concentrated HCl acid were examined in the characterization. Maximum power conversion efficiency (η) was then calculated using the following formula:

$$\eta = ff \times I_{sc} \times V_{oc} / P$$

where, I_{sc} = short circuit photo current density (A cm⁻²), V_{oc} = open circuit voltage (V), P = the intensity of the incident light (W cm⁻²), and ff = fill factor of the DSSC.

The fill factor ff was defined as the ratio of the maximum power P_{max} obtained with the DSSC and the its theoretical maximum power of it.

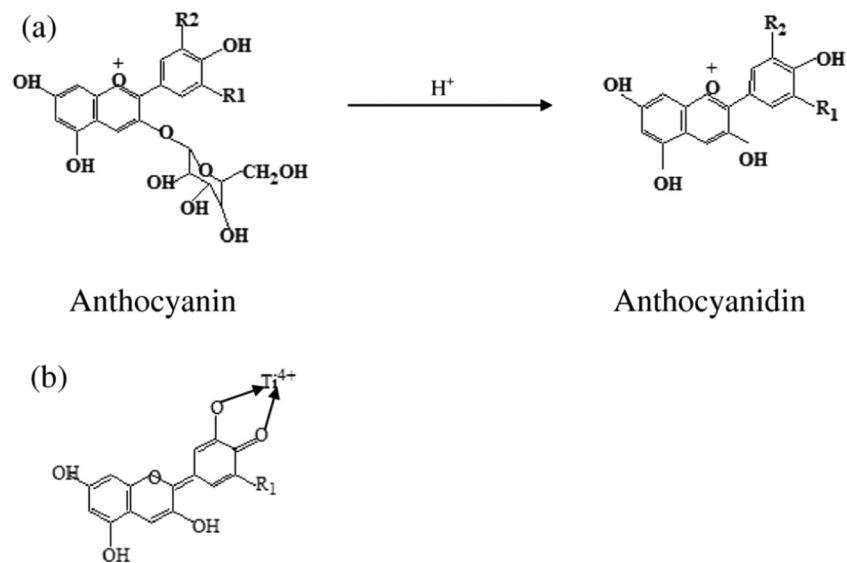


Fig. 3 (a) Chemical structures showing the transition of anthocyanin to anthocyanidin. (b) Chelation mechanism of anthocyanidin with TiO₂, here R₁ = -H; R₂ = -OH.

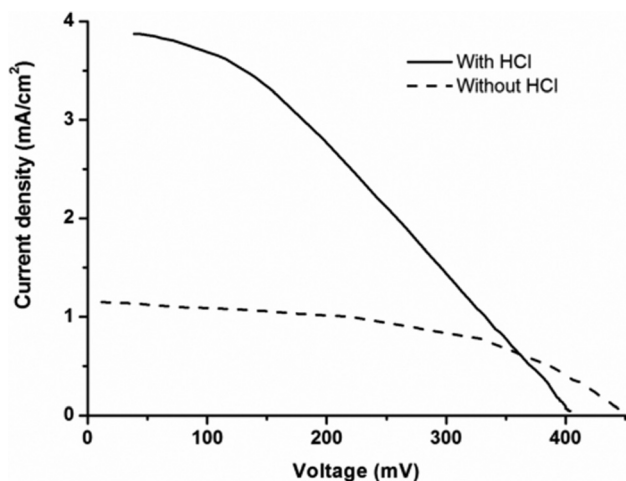


Fig. 4 Comparison of *I-V* characteristics of the DSSCs sensitized with pigment extracted from *Nephelium lappaceum* at two different pH

Hence,

$$ff = (I_m V_m) / (I_{sc} \times V_{oc})$$

Here, I_m and V_m are current and voltage related to maximum power point in the *I-V* curve.

The characteristics of the DSSCs determined by using dye extract from *Nephelium lappaceum*, with and without HCl were summarized in Table 1.

Table 1 Characteristics of DSSCs sensitized with the pigments extracted from *Nephelium lappaceum*. (Device: glass/FTO/TiO₂/dye/0.5 M TPAI, 0.05 M I₂, 3.6 ml EC, 1 ml acetonitrile/Pt/glass.)

Dye	I_{sc} (mA cm ⁻²)	V_{oc} (mV)	ff	$\eta\%$
With HCl	3.88	404	0.35	0.56
Without HCl	1.17	453	0.48	0.26

It was found that the best performance was observed from the DSSCs sensitized with acidified dye extract, which showed a conversion efficiency (η) of 0.56%, with open circuit voltage (V_{oc}) of 404 mV, short circuit current density (I_{sc}) of 3.88 mA cm⁻², and fill factor (ff) of 0.35, under the irradiance of 1000 W m⁻². Also illustrated in Fig. 4 was the current-voltage curve of DSSC sensitized with extract dye from *Nephelium lappaceum* without acidification (without adding concentrated HCl), which achieved the conversion efficiency (η) of 0.26%, with open circuit voltage (V_{oc}) of 453 mV, short circuit current density (I_{sc}) of 1.17 mA cm⁻², and fill factor (ff) of 0.48, under the same irradiation conditions.

The results obtained showed that acidification of the dye extract improved the photoelectric conversion efficiency of DSSCs.

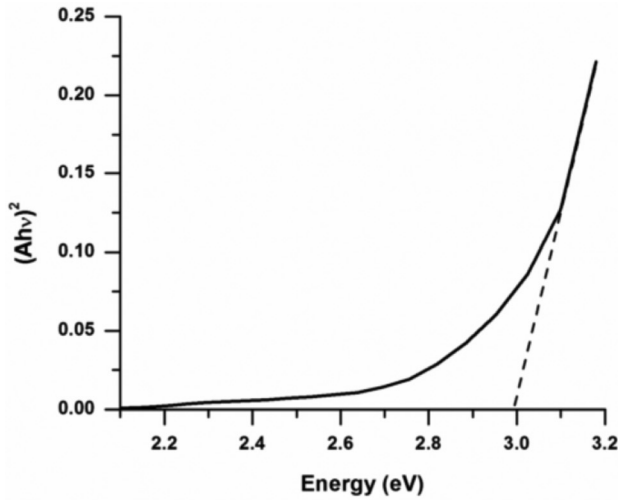
The main reason for comparatively low performance of the pigment in the nonacidified case was that the interaction between pigment molecule and TiO₂ would have been low. This interaction was affected by pigment structure. As the pigment molecule has longer side groups, steric hindrances affect bonding between the pigment molecule and the TiO₂ surface resulting in reduced electron transfer from the molecules to the TiO₂ conduction band. The glucose group in the anthocyanin structure was removed upon acidification and anthocyanidin was formed (see Fig. 3) [15]. Anthocyanidin has less steric hindrances compared to the original pigment molecule, anthocyanin, resulting a better bonding to the TiO₂ surface.

3.3 Optical Properties. The evaluation of the optical band gap of the pigment using UV-Vis absorbance spectra was done by using the Tauc relation [16–19]. Values of optical band were determined by the extrapolation of the linear region to zero absorbance from a plot that was drawn according to the Tauc relation (see below) when $n = 1/2$,

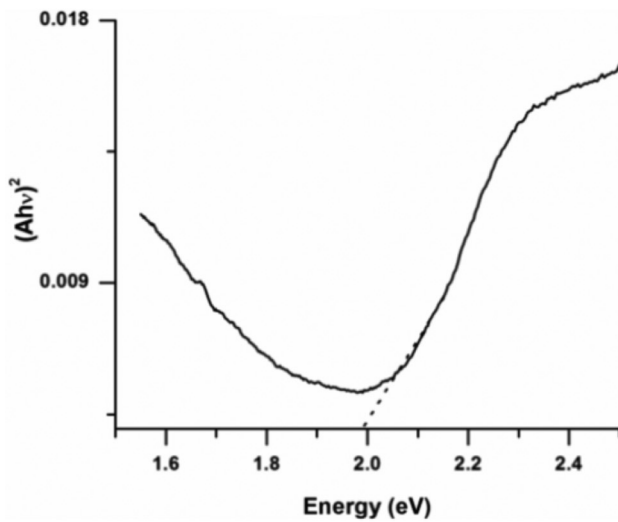
$$A h\nu \approx (h\nu - E_g)^n$$

where A is absorbance, E_g is band gap, and $h\nu$ is photon energy.

Plots of $(A h\nu)^2$ versus $h\nu$ were illustrated as Fig. 5(a) for the original pigment and Fig. 5(b) for the pigment with lowered pH. Optical band gaps for these two cases were determined to be 2.99 and 1.99 eV, respectively. The lowering of pH was seen to result in a lowering of the band gap by 1 eV. This facilitated DSSCs to absorb more radiation and hence to perform more efficiently.



(a)



(b)

Fig. 5 Absorbance squared $\{(Ah\nu)^2\}$ versus the photon energy $(h\nu)$ extrapolated to zero absorption allows determination of band gap energy of the dye extract from *Nepheium lappaceum* (a) normal pigment and (b) pigment at lower pH

3.4 Electrochemical Properties. The electrochemical behavior of the dye was investigated by using cyclic voltammetry (CV). The cyclic voltammograms of the extracted dye of *Nepheium lappaceum* without and with concentrated HCl was shown as Fig. 6. The electrons from the LUMO level could be injected to the conduction band (CB) of the TiO_2 effectively if the level of the LUMO of the dye was sufficiently more positive with respect to vacuum level than the level of the CB. The highest occupied molecular orbital (HOMO) level is affected by an electron donor. The electron donor with strong donating ability would shift the HOMO level towards more positive with respect to vacuum level [20]. In addition, electron recombination losses were reduced when the HOMO level is positively shifted resulting in a higher cell performance [21]. The onset potentials for the reduction of dye in the CV experiment were observed to be -0.37 eV and -0.22 eV with respect to saturated calomel electrode (SCE) for dye extract without and with the addition of concentrated HCl, respectively. Calculations of LUMO for both cases follow collections of the method extracted from the literature [16–18].

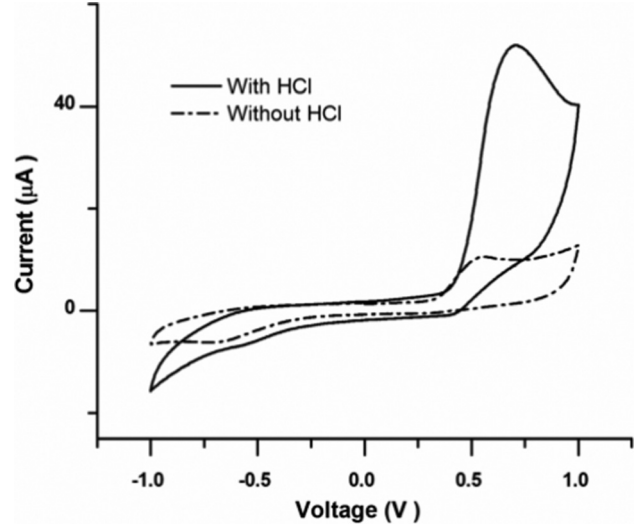


Fig. 6 Cyclic voltammograms of anthocyanins extracted from *Nepheium lappaceum*, with and without concentrated HCl

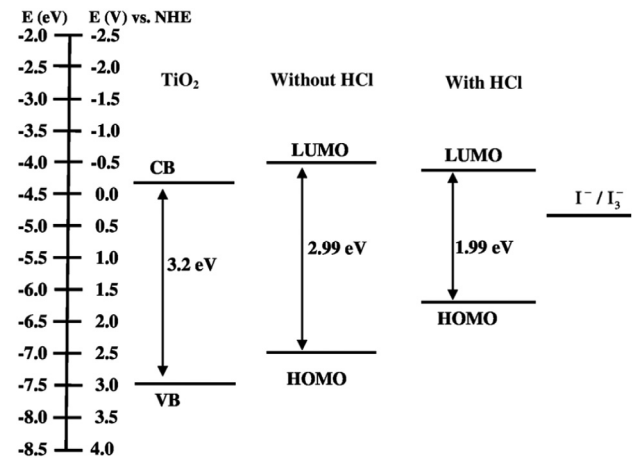


Fig. 7 Schematic diagram showing the calculated positions of HOMO and LUMO levels of anthocyanins extracted from *Nepheium lappaceum*, with respect to the vacuum level and NHE, at two different pH of pigment solution. Edges of the conduction and valence bands of TiO_2 are also shown.

An illustration of positions of the calculated HOMO and LUMO levels of the pigment were shown in Fig. 7. The HOMO level of the low pH pigment solution was more positive, and therefore in acidified dye extract the electron donating ability was more effective compared to that of normal pigment, exhibiting higher performance in DSSC, as discussed above. Moreover, details of energy levels for CB and valence band (VB) of TiO_2 , HOMO, and LUMO of the dye extract, as well as the energy level of the redox mediator was also illustrated in Fig. 7.

4 Conclusions

DSSCs fabricated using natural dye extracted from the pericarp of *Nepheium lappaceum* as a photosensitizer and the performance of the dye were reported.

Best overall energy conversion efficiency of 0.56% was obtained from the extracted pigments at low pH. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the *Nepheium lappaceum* extract were calculated and determined using data from UV-Vis

absorption spectra and cyclic voltammetry. It was revealed that the energy band gap of *Nephelium lappaceum* pigment was reduced by 1 eV upon lowering the pH of the pigment solution resulting in improved energy harvesting capability. The pigments at low pH have demonstrated an improved overall conversion efficiency due to a possible improvement of both absorption and adsorption properties of the pigment.

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