

Visible Light Absorption and Photo-Sensitizing Characteristics of Natural Dye Extracted from Mangosteen Pericarps Using Different Solvents

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Abstract—Dye is an important factor in determining the efficiency of a dye-sensitized solar cell (DSSC) device. One of the dyes derived from natural resource is anthocyanin. At the same time, one of the natural resources containing anthocyanin is a tropical plant called mangosteen. In this work, the characteristics of anthocyanin extracted from mangosteen pericarps using different solvents have been examined. The anthocyanin was extracted from mangosteen pericarps using various different solvents, i.e. dry ethanol, ethanol containing 1% HCl, and ethanol containing 1% acetic acid. Absorption characteristic of dye extracted from different solvents was determined using ultraviolet-visible spectroscopy (UV-Vis). Fourier transform infrared (FTIR) was used to examine the functional groups of the extracted dye. Visible light absorption and photo-sensitizing characteristics of the extracted natural dye were then investigated through their applications in a DSSC device. The results from infrared characterization showed that all of the extracted dyes indicated the same tendency with the characteristic of anthocyanin. At the same time, the UV-Vis examination revealed that the dye extracted using solvent HCl 1% acidified ethanol was found to have a visible light absorption at a wavelength of 533 nm. This result indicated that HCl 1% acidified ethanol was the best solvent to extract anthocyanin from mangosteen pericarps. The activity of the DSSC device sensitized using the extracted dye through a photocurrent-voltage examination showed a power conversion efficiency of 0.23% and 0.18% for the device using the commercial dye and the mangosteen extracted dye, respectively. This result is quite convincing and promising for the next DSSC device development using natural dye extracted from mangosteen pericarps.

Keywords— anthocyanin; dye-sensitized solar cell; mangosteen; natural dyes; power conversion efficiency.

I. INTRODUCTION

Dye sensitized solar cells (DSSCs) are photo-electrochemical devices that mimics the effects of photosynthesis using a simple electrochemical principle, i.e. by capturing photon energy at the molecular level and directly convert it into electrical energy [1]. DSSCs have taken much attention especially because of their low cost in manufacturing process, ease of fabrication, flexibility, and at the same time maintains its relatively high-power conversion efficiency [2]. In general, a DSSC device consists of an electrode made of thin layer of porous semiconductor coated transparent conducting glass and a dye that serves as light sensitizer, an electrolyte layer, and a counter electrode made of graphite or platinum coated conducting glass [3], [4].

In a DSSC device, dye-sensitizer serves as a solar absorber and transforms it into electrical energy. Because of that, it is considered as an important portion of a DSSC device. Moreover, since the dye and its functional groups will help promoting electron injection into the semiconductor band, it surely will increase the efficiency of a DSSC device. Thus, the absorption spectrum of a dye would be an important factor in selecting a dye in order to increase a DSSC conversion efficiency [2], [3]. These dye molecules are what make DSSCs unique among other types of solar cells.

There have been many studies and researches to explore the dye molecules from alternative green sources such as from extracted plant parts, e.g. roots, bark, leaves, flowers, fruits, vegetables, and flowers called natural dye-sensitized

solar cells (N-DSSCs) [4]–[9]. Because the cost in obtaining the natural dyes are relatively low, while at the same time they are abundant in nature, easy to extract using cheap solvents, safe material handling, environmentally friendly, and fully biodegradable, these natural dyes would be a preferable choice for the green solar cell development [2], [5].

Dyes contain important compound that forms a pigment essential in the DSSC efficiency. A dye can be attached onto TiO_2 surface because of the presence of carbonyl ($\text{C}=\text{O}$) and hydroxyl (OH) groups in the dye. In addition, these carbonyl and hydroxyl group also can stabilize the excited states and resulted in the maximum absorption by having lower energy [2]. One of the natural dyes containing these functional groups is anthocyanin, which has been known to exhibit broad region of the visible light spectrum. This broad region is attributed to its charge transfer transitions [2], [10]. At the same time, one of the natural resources containing anthocyanin is a tropical plant called mangosteen (*Garcinia mangostana* L.) [11]. This plant is native to the Indonesia, specifically in Sunda and Moluccas. It has globular shape, purplish brown colour, a size similar to a small apple, and consists of edible white flesh and a dense, thick and purplish-brown pericarp that contains a dye [12].

It has been known that there are two major natural pigments found in mangosteen, namely α -mangostin and anthocyanin [13]. The chemical structures of the α -mangostin is shown in Fig. 1, whereas the chemical structure of the anthocyanin is shown in Fig. 2.

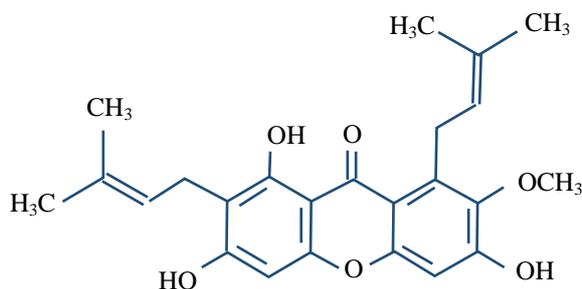


Fig. 1 Chemical structure of α -mangostin

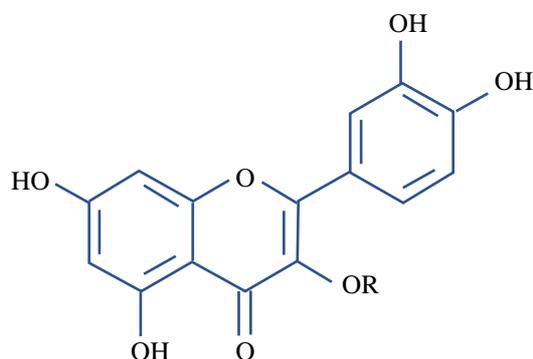


Fig. 2 Chemical structure of anthocyanin

Previous studies have shown that anthocyanin could be easily dissolved in ethanol solution because the dye molecules will have less aggregation [14]. Once extracted

and homogenized in a solution, it could be then used in a DSSC device. The dye compounds will attach to the surface of TiO_2 and when this dye absorbs sufficient photon in the visible range, the electron will be injected into the conduction band of the semiconductor TiO_2 through their functional groups. This injection will be followed by inducing electron transfer and forms electron loop in the DSSC device.

In this paper, anthocyanin was extracted from mangosteen using three different types of solvents, i.e. dry ethanol, ethanol containing 1% HCl, and ethanol containing 1% acetic acid. The natural dyes extracted from these different solvents were then characterized using UV-Vis for the absorption characteristic and FTIR for the functional groups of the extracted dye. The effects of the extracted dye to absorb photon energy in the visible light spectrum were studied. The results are given and discussed in detail.

II. MATERIAL AND METHOD

A. Materials

Fresh and fully ripened mangosteens were obtained from local market in Jakarta, Indonesia. The chemicals were titanium dioxide (TiO_2) nanoparticle (Degussa P25), platinum paste (Platisol, Solaronix), electrolyte KI (Iodolyte, Solaronix), ethanol and HCl were from (Merck KGaA, Germany), whereas acetic acid and polyethylene glycol (TRITON X-100) were purchased from Sigma Aldrich.

B. Dye Extraction

Mangosteen pericarps were obtained by emptying the sweet white flesh of edible parts out. The pericarps were washed thoroughly under running water and allowed to stand for some time to evaporate the remaining water before chopping them in a blender. The chopped pericarps were then air dried for 48 hours. The dried chopped pericarps were further ground using a blender and sieved to obtain a fine homogeneous powder.

A total of 10 grams of the fine powder was then put into an Erlenmeyer flask and was added with 100 mL of different solvents, i.e. dry ethanol, ethanol containing 1% HCl, and ethanol containing 1% acetic acid (Sigma Aldrich). The mixture was stirred using a magnetic stirrer at room temperature for 6 hours. After the stirring process, the supernatant was passed through a filter paper to separate the insoluble powder with the solvent. The filtered supernatant was allowed to stand for some time at ambient conditions to evaporate the solvent and to obtain a concentrated dye of about 10 mL.

The solution was then ready for characterization by using attenuated reflectance Fourier transform infrared (ATR FTIR, PerkinElmer Spectrum 2) and ultra violet-visible (UV-Vis, PerkinElmer Lambda 25). As a comparison, a commercial dye (Ruthenizer 535-bisTBA, Solaronix) dissolved using ethanol was also examined.

C. DSSC Fabrication

Firstly, TiO_2 nanoparticle paste was prepared by adding an amount of ethanol into commercial TiO_2 nanoparticle powder and stirred to form a gel-like paste. Two drops of TRITON X-100 were added into this paste and the stirring

process was continued until a homogeneous paste was obtained.

Secondly, two conductive glass substrates made of fluorine-doped tin oxide (FTO, Solaronix) were prepared. One of the glass substrates was drilled to create two tiny holes at one side for the electrolyte injection. The glass substrate was then dry cleaned using methanol and was kept for further use. The other FTO glass was also dry cleaned using methanol, tape masked, and attached to a flat layer. This substrate was then coated with TiO₂ nanoparticle paste using a doctor-blade method. The area under the coating was about 1 cm². After the coating, the substrate was dried for about an hour at 450°C and then allowed to cool down. After the cooling, the substrate containing TiO₂ paste was soaking it in the dye solution prepared from the extraction and air dried. As a comparison, the commercial dye (Ruthenizer 535-bisTBA, Solaronix) was also used as a reference.

Thirdly, the other perforated FTO glass substrate was coated with a platinum paste and dried for an hour at 450°C. Both the coated glass substrates were then attached to one another separated by a spacer. After the attachment, every edge of the substrate was sealed to avoid electrolyte leakage and allowed to dry. Once dried, the electrolyte was then injected through the two tiny perforations drilled at one side of the substrate. The two holes were also sealed before being ready for the characterization. Cell activity was measured by using a semiconductor parameter analyzer (SPA, Agilent 4155A) with a standard illumination of about 100 mW/cm².

III. RESULT AND DISCUSSION

The image of the mangosteen pericarps used for the extraction is given in Fig. 3. After extraction using different solvents, the different colours of the natural dye solutions were obtained as shown in Fig. 4.



Fig. 3 Mangosteen pericarps used as a source for natural dye

As seen in Fig. 4, after the extract was filtrated, a transparent yellowish red, red, and dark red solutions were obtained from the solvents using dry ethanol, ethanol containing 1% acetic acid and ethanol containing 1% HCl, respectively.

In order to be effectively adsorbed onto TiO₂ layer, a dye need to have specific functional groups. These functional groups can be examined using Fourier transform infrared (FTIR). In this work, the FTIR examination was carried out

to observe the functional group characteristic presented in the mangosteen extracted dye using different solvents. As a comparison, the characteristic of pure commercial dye was also examined. The infrared spectra obtained at wavenumber from 4000 – 400 cm⁻¹ are given in Fig. 5.



Fig. 4 The colour of the dye solution after mangosteen pericarps extraction using different solvent. Left to right: ethanol containing 1% HCl, ethanol containing 1% acetic acid, and dry ethanol

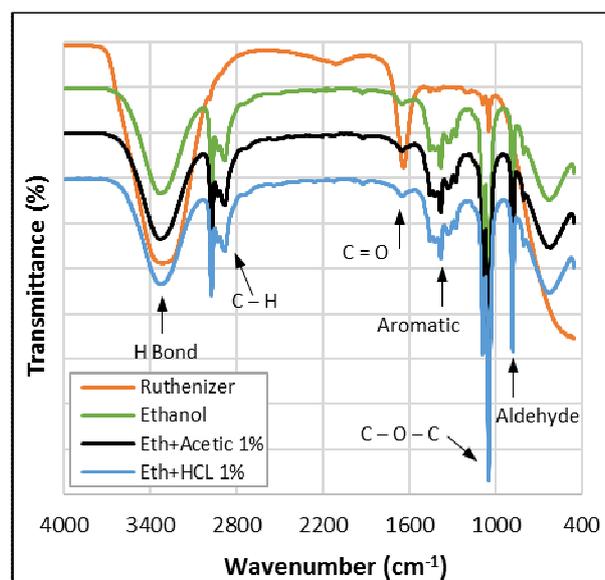


Fig. 5 Fourier transform infrared transmittance characteristics of the commercial dye and the mangosteen extracted dye using different solvents at wavenumber from 4000 – 400 cm⁻¹

As seen in Fig. 5, the spectra of the mangosteen extracted dye from different solvents show the same appearance with the same functional groups. All of the dyes, including the commercial one, show the hydrogen bonded OH stretching bands ranging from 3250 to 3450 cm⁻¹. However, different from the commercial one, the mangosteen extracted dye using different solvents show bands at around 2878 to 2973 that represent C-H groups stretching. Band at 1640 cm⁻¹ indicates C=O stretching vibration, only small peak exists for the extracted dye. The bands at 1423-1274 cm⁻¹ belong to aromatic compound (absent in the case of commercial dye), band at 1045 belongs to C – O, and stretching vibration of C–O–C esters is found at 1046 cm⁻¹. The extracted dye also has the presence of aldehydes in the wavelength between

880 cm^{-1} and 800 cm^{-1} due to the organic base natural dye. This finding is an indication that all of the extracted dye using different solvent show the presence of anthocyanin.

Absorption spectra of the extracted dyes using different solvents in the ultraviolet-visible region were examined using UV-Vis spectroscopy and the results are given in Fig. 6. This UV-Vis absorbance characteristics were obtained at wavelength from 400 – 700 nm.

As shown in Fig. 6, the absorption spectrum of the mangosteen extracted dye using HCl 1% acidified ethanol appears at 533 nm. This peak indicates at which the presence of anthocyanins that absorbs high number of photon energy from the visible light source. As a comparison, the absorption spectrum of a commercial dye shows the peak of absorption at 427 nm.

The influence of acidified extraction solvents on anthocyanin yield using HCl has been reported somewhere else [15]. In this instance, the addition of acid into the solvent used for the extraction may be explained in three different ways. First, it will increase the stability of the anthocyanins. Second, it will promote the dissolution of phenolic compounds via a hydrolysis. Lastly, it will improve the disintegration of the cell walls and facilitate the solubilization and diffusion of phenolic compounds from the plant material. Hence, in this work, the dye extracted using ethanol containing 1% HCl results in a specific wavelength.

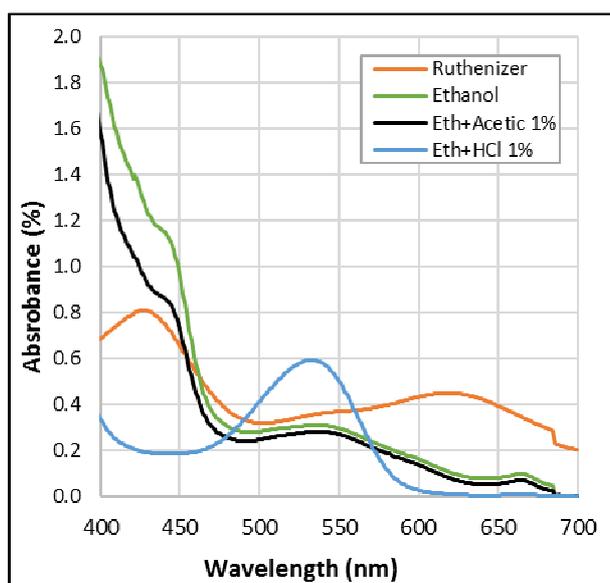


Fig. 6 Ultraviolet-Visible absorbance characteristics of the commercial dye and the mangosteen extracted dye using different solvents at wavelength from 400 – 700 nm

At the same time, the absorption characteristics of the mangosteen extracted dye using dry ethanol and acetic acid 1% acidified ethanol do not show a specific absorption characteristic as does by the HCl 1% acidified ethanol. Although anthocyanin is more soluble in ethanol solution [14], in this work, it seems that the natural dye from mangosteen pericarps will be better to be extracted using acidified ethanol in order to have a specific absorption wavelength in the visible region. However, while the use of

acid in the extraction solvent enhances anthocyanin recovery, it may vary with plant materials [15], [16].

When this dye is using as a sensitizer in the DSSC device, it will form bonds with the oxygen site of TiO_2 through functional groups of the natural dye such as carbonyl ($\text{C} = \text{O}$) and or hydroxyl ($\text{O}-\text{H}$) groups. For any successful bridging between TiO_2 semiconductor and the natural dye, the electrons will be promoted from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) state when an incident photon is absorbed by the natural dye [13]. This can be observed through a photocurrent activity.

Photocurrent-voltage activity of the extracted dye on TiO_2 nanoparticle assembled in DSSC device was examined through a J-V curve characteristic. The assembled DSSC device are shown in Fig. 7.

Among the natural dyes extracted using three different solvents tested for using as a sensitizer in the DSSC device, only the one extracted using HCl 1% acidified ethanol that shows good characteristic of a solar cell. This could come from the fact that, as has been explained previously, HCl 1% acidified ethanol was capable of extracting the natural pigment better than the others resulting in a specific absorption peak in the visible light wavelength. Because of that, only this extracted dye with the photocurrent-voltage characteristics is shown along with the commercial dye as a reference, and the results are given in Fig. 8.

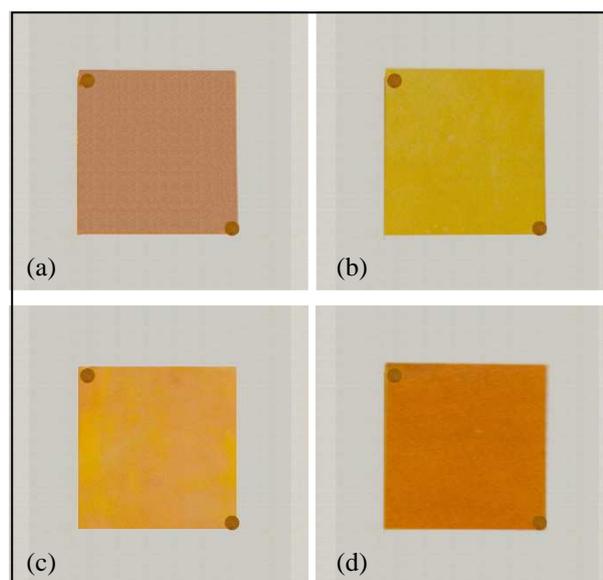


Fig. 7 Images of the DSSC device sensitized using (a) ruthenizer and mangosteen natural dye extracted using (b) dry ethanol, (c) acetic acid, and (d) HCl 1% acidified ethanol

As seen in Fig. 8, photocurrent-voltage characteristics of the natural and commercial dyes as sensitizer in DSSC device are around 0.45 and 0.55 volts, respectively, with a current density of around 0.97 mA/cm^2 . The power conversion efficiency (PCE) of the DSSC device was then calculated in according to the following formula [16]:

$$\eta = \frac{FF \times J_{sc} \times V_{oc}}{I_{in}} \times 100 \quad (1)$$

where J_{sc} is the short-circuit photocurrent density (mA cm^{-2}), V_{oc} is the open-circuit voltage (volts), I_{in} is the intensity of the incident light (W cm^{-2}) and FF is the fill factor defined as

$$FF = \frac{i_{max} \times V_{max}}{i_{oc} \times V_{oc}} \quad (2)$$

where i_{max} and V_{max} are the maximum photocurrent and voltage of the I-V characteristics and i_{oc} is the open-circuit current (mA).

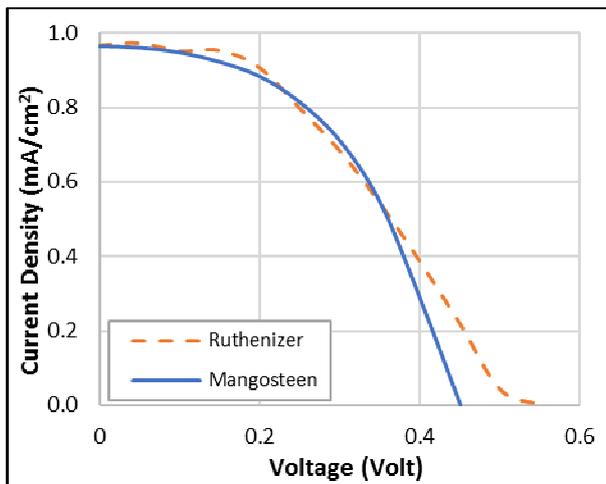


Fig. 8 Photocurrent-voltage characteristics of the DSSC with sensitizer from the commercial dye (dash line) and from the mangosteen extracted natural dye (solid line)

Based on the extrapolation of the graphs obtained from the photocurrent-voltage examination, the efficiency is found to be 0.23% and 0.18% for the device sensitized using the commercial dye and the mangosteen extracted dye, respectively. Detail of this calculation is given in Table 1. Although the efficiency is still low, the current result is still convincing and promising for the next development considering the abundant resources of this natural dye.

TABLE I
POWER CONVERSION EFFICIENCY (PCE) OF THE DSSC DEVICE SENSITIZED USING NATURAL DYE AND RUTHENIZER

	Natural Dye	Ruthenizer
V_{oc} (Volt)	0.45	0.55
I_{oc} (mA)	0.97	0.97
V_{max} (Volt)	0.20	0.25
I_{max} (mA)	0.89	0.92
FF	0.44	0.46
PCE (%)	0.18	0.23

IV. CONCLUSIONS

The results from infrared characterization showed that all of the mangosteen extracted dyes indicate have the same tendency with the characteristic of anthocyanin. However, the results from UV-Vis examination showed that HCl 1% acidified ethanol was found to have a visible light absorption at a wavelength of 533 nm, therefore it could be the best solvent to extract anthocyanin from mangosteen pericarps. The activity from the photocurrent-voltage examination showed a power conversion efficiency of 0.23% and 0.18% for the device using the commercial dye and the mangosteen extracted dye, respectively. This result is convincing and promising for the next DSSC device development using natural dyes.

NOMENCLATURE

DSSC	dye sensitized solar cells	
FF	fill factor	
FTIR	Fourier transform infrared	
I_{in}	intensity of the incident light	mW cm^{-2}
I_{max}	maximum photocurrent of DSSC	mA
i_{oc}	open-circuit current	mA
J_{sc}	short-circuit photocurrent density	mA cm^{-2}
PCE	power conversion efficiency	
UV-Vis	ultraviolet visible	
V_{max}	maximum voltage of DSSC	V
V_{oc}	open-circuit voltage	V
η	efficiency of DSSC	%

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