The co-pigmentation of anthocyanin isolated from mangosteen pericarp (Garcinia Mangostana L.) as Natural Dye for Dye-Sensitized Solar Cells (DSSC)

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Abstract. Study of color stability of anthocyanin from extract mangosteen pericarp (Garcinia mangostana L.) with co-pigmentation method has been conducted. Malic acid and ascorbic acid used as a co-pigment to stabilize the anthocyanin structure through formation of new binding between anthocyanin. Anthocyanin from mangosteen pericarp were isolated by several steps, including maceration, extraction, and Thin Layer Chromatography (TLC). Anthocyanin separation was conducted by TLC, while the identification of functional groups of those compound, were used FTIR (Fourier Transform Infrared Spectroscopy) for spectra analysis. Ultraviolet-visible absorption spectra have represented differences absorbance and color intensity in various pH. Copigmentation with malic acid and ascorbic acid in many composition and temperature were also well described. Meanwhile, anthocyanin-malic acid and anthocyanin-ascorbic acid have color retention higher than that of pure anthocyanin. Maximum color retention has been achieved at a ratio of 1:3 and 1:5 for ascorbic acid and malic acid, respectively. Therefore, the addition of ascorbic acid and malic acid as a co-pigment shows the ability to protect color retention of anthocyanin (mangosteen pericarp) from degradation process. The better efficiency of DSSC (η) have been achieved, whereas η of controlled anthocyanin, anthocyanin-ascorbic acid, and anthocyanin-malic acid were 0,1996%, 0,2922%, 0,3029%, respectively.

1. Introduction
Based on the manufacture of materials, there are two kinds of solar cells. The first solar cells are made of silicon. However, the fabrication of silicon solar cells is costly. While the new type of solar cells is dye-sensitized solar cells (DSSC), a device for the conversion of visible light into electricity based on the sensitization of wide band gap semiconductors [1]. The first DSSC was pioneered by Grätzel et al. in the early nineties, called Grätzel cells [1,2], these have attracted considerable attention due to their environmental friendliness and low cost [3]. The performance of the cell mainly depends on a dye used as a sensitizer. The important parameters of the efficiency of the cells are determined by the absorption spectrum of the dye and the anchorage of the dye to the surface of TiO₂ [4]. So far, the highest efficiency of DSSC by transition metal coordination compound (ruthenium polypridyl complexes) absorbed on nanocrystalline TiO₂ reached 8.7% [5]. However, ruthenium polypridyl complexes contain heavy metal which is undesirable for environment aspect and a limited amount of
ruthenium hence their costly production [6]. Alternatively, natural dyes are being developed due to their availability, low cost [3], easy to prepare, nontoxic, and biodegradable [7].

By far, several of natural dyes that have been used as a sensitizer in DSSC system such as tannin [8], chlorophyll [9], anthocyanin [10], cyanine [11], and carotene [12]. Anthocyanin is very large group of red-blue pigments that can be found in flowers, fruits, fruit juice, leaves, stem, and root of the plants. One of them can be obtained from mangosteen (Garcinia Mangostana L.) pericarp. Anthocyanin in isolated from mangosteen pericarps has been studied before[13], but they have the weakness especially in the color stability and labile pigment due to very easily degraded. The efforts to enhance the stabilization of anthocyanin is co-pigmentation, an interaction between anthocyanin with other molecules such as metal (Al\(^{3+}\), Fe\(^{3+}\), Sn\(^{2+}\), Cu\(^{2+}\)) and other organic molecules such as flavonoid compounds (flavonoids, flavanones, flavonols), and more. Their action of co-pigmentation tends to increase the color stability and protect from oxidation [14].

Based on the description above, this research focuses on co-pigmentation anthocyanin with malic acid and ascorbic acid. These extracted dyes were characterized by Thin Layer Chromatography (TLC), Infrared spectroscopy (IR), and UV-Vis absorption spectra. The photovoltaic properties of DSSC by purified product were studied.

2. Experimental

2.1. Sample preparation
Mangosteen pericarp was dried in an oven with temperature ± 40 °C. And then dried sample changed into a powder.

2.1.1. Sample maceration and extraction. Extraction of mangosteen pericarp powder used ethanol 96% and HCl 1M as a solvent with ratio 1:4 in 24 hours. Residue and filtrate were separated with vacuum filtration. Then filtrate was evaporated to remove the solvent with a rotary evaporator, yielded concentrated extract. Characterization concentrated extract was conducted with UV-vis spectrophotometry, Thin Layer Chromatography (TLC), and Fourier Transform Infrared (FTIR).

2.1.2. Characterization of anthocyanin extracts in various pH. Measurement of the color intensity of anthocyanin extract was performed on six pH conditions (1, 3, 5, 7, 9, 11). Each solution was measured at the maximum wavelength with a spectrophotometer at range 200-800 nm.

2.1.3. The color retention characterization of anthocyanin in co-pigmented with ascorbic acid. In this step, anthocyanin was diluted with ethanol than mixed with ascorbic acid in several ratio; 1:0, 1:1, 1:2, and1:3 (w/w). Then co-pigmented-anthocyanin was conducted in several of temperature (30, 40, 50, and 60 °C) to observe the effect of temperature in color stabilization. Then the result was characterized with UV-visible spectrophotometry in wavelength 520 nm.

2.1.4. The color retention characterization of anthocyanin co-pigmented with malic acid. In this step, anthocyanin was diluted with ethanol than mixed with ascorbic acid in several ratio; 1:5 and 1:10 (w/w). Then co-pigmented-anthocyanin was conducted in various of temperature (60 °C, 80 °C, 100 °C, 120 °C and 140 °C) to observe the effect of temperature in color stabilization. Then the result was characterized with UV-vis spectrophotometry in wavelength 520 nm.

2.2. Fabrication of DSSC
A fluorine-doped tin oxide (FTO) glass was used. The conductive glass substrate was first cleaned and coated with a layer of TiO\(_2\) paste (0.5 g TiO\(_2\) was added 2 mL ethanol and stirred until homogeny) by slip casting and dried at 400 °C for 30 min. After that, the glass substrate coated TiO\(_2\) was immersed into anthocyanin dye overnight. To prepare the counter electrode, a platinum paste was deposited on the conductive substrate glass and dried at 400 °C for 30 min. The working electrode and counter
electrode were assembled into a cell. A drop of electrolyte solution containing I-/I3-injected in the cell and the hole in the counter electrode was sealed using a sealing spacer. Therefore, DSSC arrangement was FTO|TiO\textsubscript{2}|Anthocyanin (or co-pigmented-anthocyanin)| I-/I3-|Pt|FTO.

2.2.1. Characterization and measurement of photoelectrochemical. Solar energy conversion efficiency (the photo current-voltage (I-V) curve) was measured by Keithley multimeter under illumination. Based on I-V curve, the fill factor (FF) is defined as equation (1):

\[
FF= \frac{I_{\text{max}} \times V_{\text{max}}}{I_{\text{sc}} \times V_{\text{oc}}}
\]  

(1)

Where \(I_{\text{max}}\) and \(V_{\text{max}}\) are the photocurrent and photovoltage for maximum power output (\(P_{\text{max}}\)), \(I_{\text{sc}}\) and \(V_{\text{oc}}\) are the short-circuit photocurrent and open-circuit photovoltage, respectively. The overall energy conversion efficiency (\(\eta\)) is defined as equation (2)

\[
\eta= \frac{I_{\text{sc}} \times V_{\text{oc}} \times FF}{P_{\text{in}}}
\]

(2)

where \(P_{\text{in}}\) is the power of incident light.

3. Result and Discussion

3.1. Absorption of anthocyanin

Figure 1(a) shows the UV-Vis absorption spectrum of mangosteen extract. It was found that the absorption peak of mangosteen extract is about 520 nm. About 320, 340, and 450-520 nm indicate the presence of anthocyanin compounds. The present anthocyanin also depends on pH value. Figure 1(b) shows the absorption spectrum of anthocyanin shift to a greater wavelength in base condition or pH increase. Overall the spectrum shows a peak of anthocyanin at range 400-600 nm.

![Figure 1. (a) Spectrum UV-Vis Anthocyanin.](image)

![Figure 1. (b) Effect of pH.](image)

Besides using UV-Vis, characterization of extract mangosteen was performed also with Thin Layer Chromatography (TLC) and infrared spectroscopy (IR). The purpose of using Thin Layer Chromatography (TLC) is to determine patterns of separation and purity of the compounds. Butanol:acetic acid: water used as eluent with a ratio of 4:1:5. The retention factor (Rf) obtained
0.255, this value related to the previous result that the Rf of anthocyanin approximately 0.1 to 0.4 [15]. While the characterization of anthocyanin using IR spectroscopy to determine the molecular structure of compounds (figure 2).

![Figure 3. Spectra IR of Anthocyanin.](image)

The FTIR spectra of these compounds show benzene groups vibration peaks between 455.22-929.7 cm\(^{-1}\). The double bond C=C vibrations at 1100-1300 cm\(^{-1}\). Two adjacent peaks at 1604-1634 cm\(^{-1}\) indicate carbonyl group (C=O). In addition, the peak appearing at 2932-2937 cm\(^{-1}\) for C-H stretching. While the wide uptake 3362 cm\(^{-1}\) indicate the presence of OH group and hydrogen bonding that occurs as intermolecular interaction of anthocyanin. All of these function groups establish the structure of anthocyanin that consist of benzene ring, double bond, a carbonyl group, C-H bond, and OH group.

### 3.2. Copigmentation anthocyanin: ascorbic acid

Figure 3 shows the effect of increasing temperature to color stability of anthocyanin-ascorbic acid co-pigmentation. Increasing absorbance of anthocyanin-ascorbic acid co-pigmentation followed by increasing mass ratio of ascorbic acid were added. The co-pigmentation of anthocyanin-ascorbic acid with ratio 1:3 have the greatest absorbance rather than ratio 1:1 and 1:2. However, there is an irregularity curve at ratio 1:2 caused by influence of heat that make the anthocyanin-ascorbic acid degraded quickly. High heating temperatures relatively can damage the structure of anthocyanin. Heating an anthocyanin-ascorbic acid cause an impact to their color stability due to degradation that may occur. Figure 5 represent that increasing temperature of heating anthocyanin-ascorbic acid was followed by degradation of color retention (color stability).
3.3. Copigmentation anthocyanin: malic acid
Figure 4 shows the effect of increasing temperature to color stability of anthocyanin- malic acid co-pigmentation. The color stabilities anthocyanin-malic acid with ratio 1:0, 1:5, and 1:10 are 74.32; 92.89; and 98.64%, respectively. High heating temperatures relatively can damage the structure of anthocyanin. Heating an anthocyanin-malic acid cause an impact to their color stability due to degradation that may occur. Increasing temperature of heating anthocyanin-malic acid was followed by degradation of color retention (color stability).

3.4. Photoelectrochemical properties of DSSC with natural dye
Photovoltaic test of DSSC using co-pigmentation of natural dyes as sensitizers were performed by measuring the current-voltage (I-V) curve by solar simulator. The performance of DSSC was evaluated by energy conversion efficiency (η). The efficiency of anthocyanin, anthocyanin-ascorbic
acid, and anthocyanin: malic acid are 0.199; 0.292; 0.303%, respectively. The result shows that co-pigmentation potentially increase the efficiency of DSSC from 46.40% to 51.75%. The polymerization that may occur between anthocyanin and co-pigment be able to stabilize the color of anthocyanin.

4. Conclusions

The anthocyanin was successfully extracted from mangosteen pericarp by maceration method. The characterization using TLC, UV-Vis, and FTIR shows the characteristic of anthocyanin, compared by the standard of anthocyanin. The efficiency of anthocyanin, anthocyanin-ascorbic acid, and anthocyanin-malic acid are 0.199; 0.292; 0.303%, respectively. The co-pigmentation with ascorbic acid and malic acid be able to increase the efficiency of DSSC from 46.40% to 51.75%.

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