The efficiency of Dye-Sensitized Solar Cell (DSSC) Improvement as a Light Party TiO$_2$-Nano Particle With Extract Pigment Mangostana Peel (*Garcinia mangostana*) with various solvents

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**Article Info**

| Article history: | Abstract |
|------------------|----------|
| Received May 2018 | The dye-sensitized solar cell (DSSC) is one of the photochemical electrical cells consisting of a photoelectrode, dye, electrolyte, and counter electrode. The purpose of using dyes in the DSSC is to extend the absorption spectrum to visible light because visible light has about 96% energy from sunlight. This article presents some experimental data on the nature of absorbance and the conductivity of natural dyes extracted from the plant as an application in the DSSC. Absorbance test using Spectrophotometer UV Visible 1601 PC and electrical properties test using Elkahfi 100 / Meter I-V. DSSC fabrication has been done using dye extract of mangosteen skin pigment (*Garcinia mangostana*) with a variety of coating technique of Spin Coating and Slip Casting. The results show that natural dyes from natural material extraction have an absorbance spectrum of 380-520 nm range and the greatest conductivity is owned by mangosteen fruit skin pigment (*Garcinia mangostana*). From the results of the test using AM Simulator 1.5G (100 mW / cm$^2$) diesel simulator, it was found that the volume of TiO$_2$ precursors affected the performance of DSSC solar cells and the overall conversion efficiency was 0.084% for the mangosteen skin dye by slip casting technique and 0.092% for the mangosteen skin dye by spin coating technique. |
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**Keywords:** Dye-Sensitized Solar Cell (DSSC); Spin Coating; Slip Casting; Absorbance; Conductivity

**INTRODUCTION**

Energy needs in the world are very large, in Indonesia and even in the world are incessant-the incessant of the researchers to find alternative energy sources, in lieu of fossil energy (Schiffer, 2016). One of the considerable alternative energy available in nature is solar energy. Solar energy in Indonesia, in particular, the amount is very abundant and is said to be large enough to serve as an alternative energy source. To realize that, then needed a system to convert solar energy into electrical energy. One of the utilization of solar energy is through the use of solar cells (solar cell) because this is a promising alternative.

This is what makes energy very important in meeting all the needs of life in the world, so the energy needs in the world increasingly day. Limitations of silicon solar cells are not only expensive, but the absorption spectra are too narrow. It is known that the energy distribution of sunlight consists of about 4% ultraviolet and 96% visible light. The main spectrum of silicon solar cell absorption is ultraviolet and purple. This shows that silicon solar cells cannot use nearly 96% of the energy from sunlight (Lin et al., 2007). Efforts to broaden the absorption spectra from the ultraviolet region to the visible light region are now applied as Dye-Sensitized Solar Cell (Grätzel, 2006), where dyes can assist DSSC to expand the absorption spectrum (Grätzel, 2003).
The absorption of light in the range 380-520 nm and the molar extinction coefficient greater than 105 makes the carotenoids as potential sensitizers in photovoltaic solar cells and other artificial photochemical devices (Gao et al., 2000). Carrots (Daucus carota), melinjo fruit (Gnetum genomon), and mangosteen peel (Garcinia mangostana) are natural ingredients that are widely consumed and contain carotenoids. But the carotenoid content may vary depending on the source.

DSSC is a photoelectrochemical solar cell so that the electrolyte is used as the transport medium of charge. DSSC is divided into sections comprising TiO$_2$ nanopores, dye molecules adsorbed on the surface of TiO$_2$, and catalysts all deposited between two conductive glass. The DSSC structure looks like Figure 1.

The working principle of DSSC begins with the excitation of electrons in the dye molecule due to the absorption of photons from the state of the ground state (S) to the excited state (S$^\ast$). Then the energy of the photon is sufficient to inject the electrons into the conduction band of TiO$_2$ leaving the dye molecule to the S$^\ast$ oxidation state. Then the electrons flow into the anode (negative electrode) through TiO$_2$ by the diffusion process. Next through the external load to the cathode (positive electrode). After that At the cathode, the electrons moving toward the triiodide on the electrolyte produce iodine. And the cycle is continued by reduction of dye by iodine on the electrolyte. As shown in Figure 2.

DSSC cannot be separated from Dye, therefore Dye is generally used and achieve the highest efficiency of ruthenium complex type. In addition, dye-photosintezer is an important factor in determining the performance of DSSC, such as its photosensitizer uptake properties, which directly determine the range of photosresponse of the solar cell. Dye function absorbs visible light, pumps electrons into the semiconductor, receives electrons from the redox pair in solution, and so on in a cycle, so the dye acts as a molecular electron pump. The dye must have high chlorophyll content, has a strong absorption in visible areas of light, high stability and reversibility in its oxidized form. The dye used in the DSSC has a conjugated chromophore group allowing for the transfer of electrons.

Technical difficulties of developing DSSC to extend the life of the DSSC and increase the absorption of the quantity of sunlight, because organic dyes will easily decay. All questions for dye are very interesting and worthy of study (Kalyanasundaram & Gra\'etzl, 1998). This study presents some experimental data on the carotenoid content of the mangosteen fruit skin pigment that can be used as a sensitizer. The material analysis was performed on the optical and electrical properties of organic matter from mangosteen fruit skin extract (Garcinia mangostana). The extracts from the natural ingredients used in the study showed a similar absorbance of β-carotene in the 380-520 nm range (Hardani et al., 2018). While the value of absorbance and optimum conductivity on the skin of mangosteen fruit. This study aims to analyze the optical properties and to know the electrical properties of the mangosteen skin pigment consisting of 3 stages: the extraction of the mangosteen skin pigment, the measurement of the absorption of the spectrum, and the measurement of the conductivity of the extraction results.
RESEARCH METHODOLOGY

Equipment and Materials
The materials used in this study include glass substrate Fluorine Doped Tin Oxide (FTO), Titanium (IV) dioxide (TiO2) nanopowder 21 nm, Polyethylene Glycol (PEG) 400, Potassium Iodide (KI), Iodine (I2), Ethanol, Pt (Hexachloroplatinic (IV) acid 10%), Isopropanol, 70% Alcohol, and Mangosteen Peel. Equipment used include digital multimeter, hot plate with a magnetic stirrer, hairdryer, ultrasonic cleaner, 10 ml, and 50 ml beaker, dropper dropped, 5 ml glass bottle, digital scales, filter paper Whatman no.42, mortar chromatography column, knife, furnace, and the spin coater.

Preparation
This preparation stage includes cleaning tools for the extraction and preparation of TiO2 paste. The preparation process for extraction is done by cleaning the tool in the form of mortar, Fluorine Doped Tin Oxide (FTO) glass, glass bottle, beaker, and dropper with ethanol solution and using the ultrasonic cleaner to be free from materials that can not be cleans with water only. Clean glass affects the test results of samples to be superimposed on the glass substrate.

FTO glass cleanup (Fluorine Doped Tin Oxide)
Alcohol 70% poured on the glass of chemical as much as 100 ml. The 2.5 x 2.5 cm FTO glass to be cleaned is inserted in a glass containing chemicals. Ultrasonic cleaner filled aquades to the specified limits. Chemical glass containing alcohol and FTO glass is inserted into ultrasonic cleaner at 30 minutes. After 30 minutes, the glass is dried using a hairdryer. Then measured resistance to the FTO glass using a digital multimeter.

Making of TiO2 Nano Pasta
TiO2 0.5 gram of nanopowder dissolved in 2 ml ethanol is then stirred using a stirrer vortex with a speed of 200-300 rpm for 30 minutes. The already formed TiO2 paste is fed into aluminum foil-covered bottles and stored in a spot that avoids direct sunlight to reduce the evaporation process.

Mangosteen Peel Extraction (Garcinia mangostana)
Mangosteen peel weighed using 25 grams of digital scales. Furthermore, the peel of mangosteen fruit crushed and mashed using mortar. The finely ground mangosteen peel was dissolved in 125 ml of ethanol solvent with the ratio (1: 5) and then stirred for 60 minutes using a stirrer vortex with a rotation speed of 300 rpm in 60°C. After the solvent is dissolved for 24 hours and filtered with filter paper Whatman no.42. The extraction results were then chromatographed by pouring in chromatographic columns and waited until dark red extraction.

Making Working Electrode
The working electrode is made of FTO conductive glass on which the TiO2 nano paste is deposited by the spin coating technique. In FTO glass measuring 2.5 x 2.5 cm formed an area for the deposition of TiO2 measuring 2 x 1.5 cm above the conductive surface. The FTO side taped the tape as a barrier. The TiO2 paste is dripped on the FTO glass that has been glued in the spinner, then in the stirrer with a speed of 200-300 rpm with a predetermined time. The coated TiO2 FTO glass is heated using a hotplate at 500°C for 60 minutes, then cooled to room temperature. The scheme of the TiO2 paste deposition area is shown in Figure 3.

Making of Electrolyte Solution
Potassium iodide (KI) of 0.8 grams (0.5 M) in solid form is mixed into 10 ml of polyethylene glycol 400 then stirred. Next to the solution was added Iodine (I2) of 0.127 grams (0.05 M) then stirred with a stirrer vortex at 300 rpm for 30 min. The finished electrolyte solution is stored in a sealed container coated with aluminum foil.
Making of Opponent Electrode

The counter electrode is an FTO conductive glass which has been coated with a thin layer of Platinum (Hexachloroplatinic (IV) acid 10%). The steps of making the opponent electrode are: 1 ml of Hexachloroplatinic (IV) acid 10% mixed with 207 ml of isopropanol and then stirred using vortex stirrer with a speed of 300 rpm for 30 minutes. The FTO glass was heated using a hotplate at 250°C for 15 minutes then spilled 3 ml of platinum solution onto the surface of the FTO glass substrate by the drop method. The glass that has been dropped platinum then cooled to reach the room temperature. The scheme of the Platinum deposition area is shown in Figure 4.

Dye Absorption On TiO₂ Layer

FTO conductive glass substrate which has been deposited TiO₂ layer then soaked in dye extract of mangosteen peel for 24 hours.

DSSC Sandwich Making

The arrangement of DSSC layers of FTO glass that has been coated with TiO₂ and has been immersed in the dye solution of extraction result is called the working electrode. The working electrode is dropped by an electrolyte solution and then covered with a platinum coated glass called the opposing electrode. Then the DSSC arrangement is clamped with a clamp on both sides of the right and left so as not to shift. The finished DSSC results are shown in Figure 5.

Absorption Analysis

A spectrophotometric method was used for the simultaneous determination of β-carotene (Alharbi & Kais, 2015). The spectrophotometric method shows potential for β-carotene analysis because Pigments can absorb radiation in the visible region (Shalini et al., 2015). The content of each extracted material was analyzed using Spectrophotometer UV Visible Shimadzu 1601 PC to determine the absorbance properties of the material. The wavelength range of absorption spectrum analysis in visible light is 300-800 nm from the result of measurement of absorbance characteristic then known the type of dye content from natural material.

Material Conductivity

The conductivity measurements using Elkahfi 100 / IV-Meter were performed in a dark state by covering all parts of the container using aluminum foil and under irradiation using a 100 W halogen light source and an energy intensity of 680.3 W / m². Halogen lamps are used because they have a full spectrum that resembles visible light with sunlight. From the result of measurement of I-V then determined conductivity (σ) various material. To determine the conductivity of the organic solution can use the equation:

\[ \rho = \frac{RA}{l} \]  \hspace{1cm} (1)

\[ \sigma = \frac{l}{\rho} = \frac{l}{RA} \]  \hspace{1cm} (2)

Where σ is the conductivity (ohm⁻¹.m⁻¹), R is the resistance (Ohm), l is the distance between the two electrodes (m) and A is the cross-sectional surface area of the electrode (m²).

RESULTS AND DISCUSSION

Research that uses natural ingredients to produce carotenoids extracts from the bark of the mangosteen which is extracted using a variation of solvent namely ethanol and acetone with proportions 1 gram of natural ingredients 2 ml of solvent. Then tested UV absorbance...
Figure 6. The absorbance of natural pigment extract of mangosteen peel skin with (a) ethanol solvents, (b) acetone solvents, using Spectrophotometer UV Visible Shimadzu 1601 PC.

Table 1. Resistivity (Ohm), Conductivity (Ohm$^{-1}$m$^{-1}$), and Flow (mA) of mangosteen peel.

| Organic Materials | solvents | Condition | R (Ohm) | $\sigma$ (Ohm$^{-1}$m$^{-1}$) | I (mA) |
|-------------------|----------|-----------|---------|-------------------------------|--------|
| Mangosteen skin   | Ethanol  | Bright    | $5 \times 10^8$ | $2.34 \times 10^{-5}$ | $3.46 \times 10^{-5}$ |
|                   | Aceton   | Bright    | $7.2 \times 10^8$ | $3.4 \times 10^{-5}$ | $2.89 \times 10^{-5}$ |

Figure 7. Keithley test results with ethanol solvents
Figure 8. Keithley test results with acetone solvents

Table 1 can be determined that it is currently in a State of light that flows to the second variation of the solvent has the distinction of barriers. While the conductivity for greater acetone solvents compared with ethanol solvent. However, the current flowing in the circuit between the two solvents have a slight difference. This is because current accepted in different cells and resistance are also different.
DSSC tested electrically with the measurement system 2602A Keithley. Current and voltage test results are shown in Figures 7 and 8.

Based on the graph of the test results Keithley in Figures 7 and 8, we can determine the current (Isc) and voltage (Voc). So based on the calculation that was done the efficiency of the mangosteen peel with solvent variation, shown in Table 2.

From Table 2, it can be seen that the efficiencies produced by the DSSC For Mangosteen Peel pigment with solvent ethanol are greater than with the solvent acetone. This shows that the difference in the solvent also equally affects the efficiency, which is using a solvent of ethanol has a good solvent stability and makes the transfer of electrons remain, then the generated greater efficiency.

### CONCLUSION

The measurement and analysis of the absorption spectra of natural dye extract of mangosteen peel have been done with the ratio of the mass of natural materials and the volume of solvent is kept steady. The results showed that the dye extracted from the natural material has an absorption spectrum similar to that of β-carotene having absorption at wavelengths between 380 - 520 nm and a wave peak in the 450 nm range.

Electrical current and conductivity measurements produced by mangosteen peel extracts, this makes the mangosteen fruit necessary for further investigation as a DSSC sensitizer.

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### Table 2 Mangosteen Skin Efficiency

| Solvents | Imax (Ampere) | Vmax (Volt) | Isc (Ampere) | Voc (Volt) | Fill Factor | Efficiency (%) |
|----------|---------------|-------------|--------------|------------|-------------|----------------|
| Etanol   | 0.00055       | 0.340       | 0.0007       | 0.550      | 2.4 x 10$^{-7}$ | 0.068          |
| Acetone  | 0.00001       | 0.370       | 0.0002       | 0.550      | 1.7 x 10$^{-7}$ | 0.032          |
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