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Enhanced Performance of Dye-Sensitized Solar Cells Using Melinjo Peel (*Gnetum gnemon*) Dye as Sensitizer

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ABSTRACT

It has been successfully done research using a dye Melinjo peel (Gnetum gnemon). Dye-sensitized solar cells (DSSCs) are widely studied for safe and reliable energy supply and cheaper than conventional solar photovoltaic, can be a potential energy resource for the future. The dye-sensitized solar cell (DSSC) is one of the photochemical electrical cells consisting of a photoelectrode, dye, electrolyte, and counter electrode. The dye extraction process (Dye) of the melinjo was stirred for 1 hour and then left for 24 hours at room temperature. Dye-sensitized solar cell (DSSC) is one of the photochemical electrical cells consisting of a photoelectrode, dye, electrolyte, and counter electrode. 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 melinjo (Gnetum gnemon) with a variety of immersion technique of drops and soak. 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 melinjo (Gnetum gnemon). 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 0.03% for the melinjo (Gnetum gnemon) dye by drops technique and 0.009% for the melinjo (Gnetum gnemon) dye by soak technique.

Introduction

The daily energy needs of the world continue to increase. This underlies the researchers to find alternative sources of energy as a substitute for fossil energy. One of a fairly large alternative energy available in nature is the Sun's energy [1]. Solar energy in Indonesia in particular is very abundant in number and is said to be large enough to serve as an alternative energy source [2]. The problem that can be solved by utilizing solar energy is that it can inhibit the rate of global warming. To realize it, then it needs a system to convert solar energy into electrical energy. One of solar energy utilization is through the use of solar cells (solar cell), because this is an alternative that is promising.

This is what makes energy very important in meeting all the needs of life in the world, so the daily energy needs of the world continue to increase. Limitations of silicon solar cells are not only expensive, but the absorption spectra are too narrow [3]. It is known that the energy distribution of sunlight consists of about 4% ultraviolet and 96% visible light [4]. 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 [5]. Efforts to broaden the absorption spectra from the ultraviolet region to the visible light region are now applied as Dye-Sensitized Solar Cell [6], where dyes can assist DSSC to expand the absorption spectrum [7].

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 [8]. Carrots (Daucus carota), melinjo (Genetum genemon), and mangosteen peel (Garnicia mangostana) are natural ingredients that are widely consumed as foods which also 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.

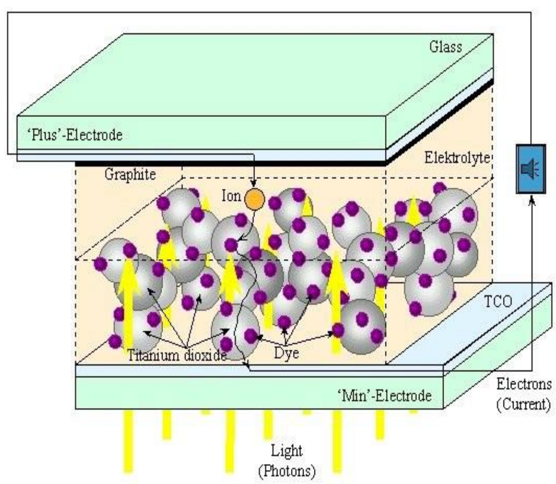


Figure 1 DSSC Scheme [9]

Basically, the working principle of DSSC converts light into electrical energy in a molecular scale in the form of electron transfer reactions. When photons of sunlight impinge on the working electrode DSSC, the photon energy is absorbed by the electron dye attached to the surface of TiO_2. So, the electrons are recorded to gain energy. Photoexcitation of the dye results in the injection of the electron into the conduction band of TiO_2. TiO_2 acts as an electron acceptor and dye act as an electron donor. Furthermore, the electrons are transferred past the outer circuit to the reference electrode of the platinum layer. Electrolytes containing I^-/I_3^-

which acts as an electron mediator so that it can produce in the cell cycle process. Triodide ions capture electrons originating from outside the circuit with the help of platinum molecules as the catalyst. Excited electrons back into the cell and aided by the platinum that can react with the electrolyte which causes the addition of iodide ions on the electrons. Then one of the iodide ions in the electrolyte to deliver electrons that carry the energy to the oxidized dye. Electrolytes provide replacement electrons to oxidized dye molecules. So that the dye back to its initial state. As shown in Figure 2.

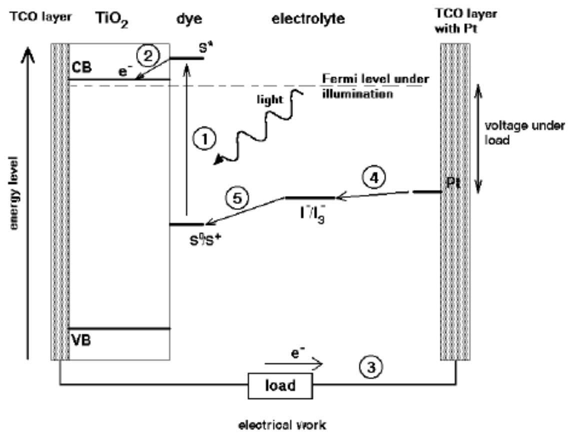


Figure 2 Working Principles of DSSC [10]

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 photoresponse 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 [11]. This study presents some experimental data of the carotenoid content of the melinjo fruit peel pigment that can be used as a sensitizer. The material analysis was performed on the optical and electrical properties of organic matter from melinjo peel extract (Gnetum gnemon). The extracts from the natural ingredients used in the study showed a similar absorbance of β-carotene in the 380-520 nm range. While the value of absorbance and optimum conductivity on the peel of melinjo in the range of 300-400 with absorbancy value is 0.058. This study aims to analyze the optical properties and to know the electrical properties of the melinjo peel pigment consisting of 3 stages: the extraction of the melinjo peel pigment, the measurement of the absorption of the spectrum, and the measurement of the conductivity of the extraction results. The novelty of previous research conducted by Nurussaniah et al [12] is still in research using the method of deposition soak but in my research using the method of deposition drops and soaking.

As for the standard method used in the application of dye depotsistion at DSSC is the immersion method. This method is often used in the manufacture of DSSC, as it is an easy-to-do method and simply soak the sample into dye until the TiO_2 changes color according to the dye used. However, this study used two methods of immersion method and method of drop. The goal is to compare the advantages of both methods. From the results obtained that using the Drop method resulted in higher efficiency than using the immersion method.

Experimental Method

Nano Pasta Preparation

TiO_2 0.5 gram of nano powder 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 TiO_2 paste is fed into aluminum foil-covered bottles and stored in a spot that avoids direct sunlight to reduce the evaporation process.

Melinjo Peel Extraction (Gnetum gnemon)

Melinjo peel weighed using 25 grams of digital scales. Furthermore the peel of Melinjo fruit crushed and mashed using mortar. The finely ground Melinjo peel was dissolved in 125 ml of ethanol solvent with ratio (1: 5) and then stirred for 60 minutes using a stirrer vortex with a rotation speed of 300 rpm in 60^{o}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.

Electrolyte Solution Preparation

Pottasium 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 (I_2) 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.

Natural Dye Extraction

The study used ethanol solvent to dissolve the carotenoid extracted from Melinjo peel pigment. The ingredients to be extracted were cleaned with water, then as much as 25 grams of Melinjo peel pigment smoothed and after finely mixed 50 ml of ethanol stirred for 60 minutes 200 rpm using a magnetic stirrer at room temperature. After stirring and then sample stand for 24 hours and filtered using Whatman no filter paper. 42. After filtration, the solution is stored in a sealed container and protected from sunlight.

DSSC Preparation

Fluorine Doped Tin Oxide (FTO) cleaning.

Alcohol 70% poured on 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 hair dryer. Then measured resistance to the FTO glass using a digital multimeter.

Electrodes Preparation

The working electrode is made of FTO conductive glass on which the TiO_2 nano paste is deposited by spin coating technique. In FTO glass measuring 2.5 x 2.5 cm formed an area for the deposition of TiO_2 measuring 2 x 1.5 cm above the conductive surface. The FTO side taped the tape as a barrier. The TiO_2 paste is dripped on the FTO glass that has been glued in the spinner, then distirrer with a speed of 200-300 rpm with a predetermined time. The coated TiO_2 FTO glass is heated using a hotplate at 500°C for 60 minutes, then cooled to room temperature. The scheme of the TiO_2 paste deposition area is shown in Figure 3.

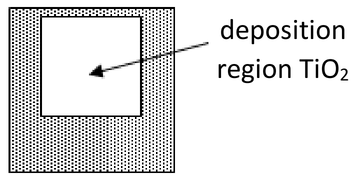


Figure 3. Schematic area of TiO_2 paste deposition

Counter Electrode Preparation

The counter electrode is a FTO conductive glass which has been coated with a thin layer of Platinum (Hexachloroplatinic (IV) acid 10%). The steps of making the opponent electrode is 1 ml of Hexachloroplatinic (IV) acid 10% mixed with 207 ml of isopropanol and then stirred using vortex stirrer with speed 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.

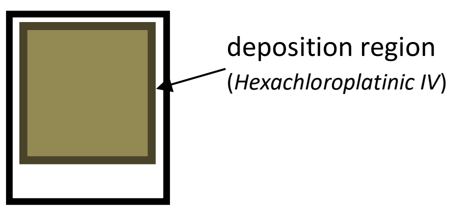


Figure 4. Platinum deposition area scheme

Adsorption of Organic Dye On TiO_2 Layer

FTO conductive glass substrate which has been deposited TiO_2 layer then soaked in dye extract of Melinjo peel for 24 hours.

DSSC Sandwiching

The arrangement of DSSC layers of FTO glass that has been coated with TiO_2 and has been immersed in dye solution of extraction result is called 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.

Figure 5. Results of DSSC Compilation

UV-Visible Characterization

A spectrophotometric method was used for the simultaneous determination of β-carotene [13]. The spectrophotometric method shows the potential for β-carotene analysis because Pigments can absorb radiation in the visible region [14]. 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[15].

Electrical Conductivity of Material

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 / m^2. Halogen lamps are used because they have a full spectrum that resembles visible light with sunlight[16]. From the result of measurement of I-V then determined conductivity (σ) various material. To determine the conductivity of organic solution can use the equation:

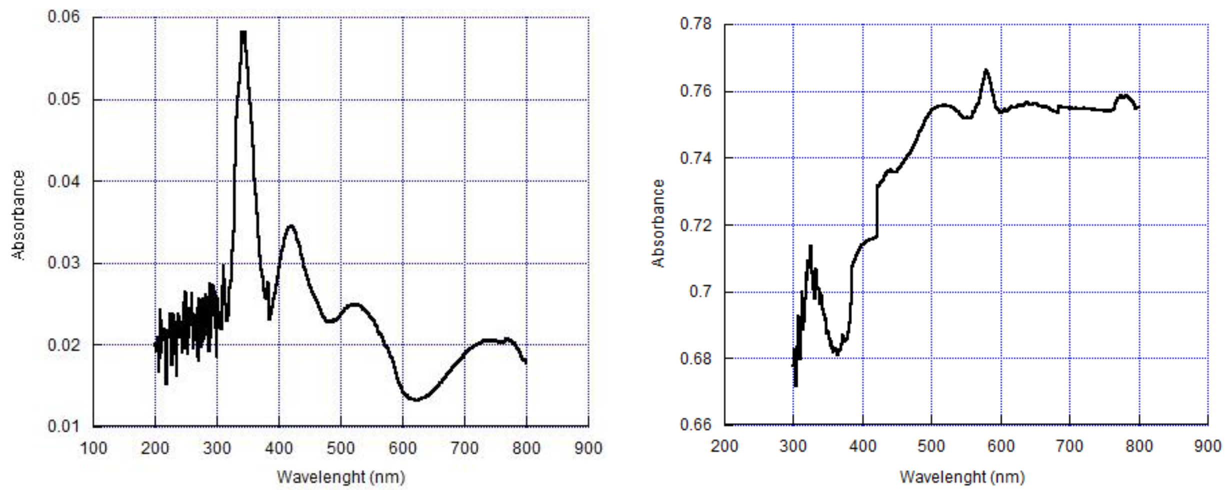
$$\rho = RA / l \tag{1}$$

$$\sigma = 1 / \rho = l / RA \tag{2}$$

here 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 (m^2).

Result and Discussion

Research using natural ingredients to produce a carotenoid extract from the peel of Melinjo extracted using ethanol with a fixed ratio of 1 gram of natural materials 2 ml of solvent. Then tested the absorbance using Spectrophotometer UV Visible Shimadzu 1601 PC and determined the Voltages using I-V meter / elkahfi 100 of I-V can be seen the value of dye conductivity made from the peel of Melinjo.



(a) (b)

Figure 6 Absorbance of extract of Melinjo peel with (a) soak method and (b) drop method.

Based on Figure 6, the absorbance of the Melinjo dye shows a considerable wavelength, with a sufficiently high absorbance ability, which allows the melinjo peel to absorb good sunlight and maximize the performance of the DSSC[17].

Figure 6 shows that a fixed ratio between melinjo peel extracts yields different absorbance values from both methods. Figure 6 also shows the dye spectrum of the peel of the melinjo fruit having an absorption spectrum similar to β-carotene[18], on the soak method which has a major absorption wave at 340-520 nm, with a successive wave peak 340 nm, 415 nm and 520 nm. While on the Drop method has a major absorption wave at 320-580 nm, with a successive wave peak 320 nm, and 580 nm.

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

Organic Materials	Condition	R(Ohm)	σ ($Ohm^{-1}m^{-1}$)	I (mA)
Melinjo peel	Dark	5.0×10^9	6.15×10^{-6}	3.27×10^{-5}
	Bright	5×10^8	3.34×10^{-5}	3.48×10^{-5}

The conductivity value of the Melinjo peel can be presented in Table 1. Table 1 can be determined that the current in the bright state is greater than in the dark. While the conductivity is greater in the dark than in the light.

DSSC was tested electrically with a Keithley 2602A measurement system. The current and voltage test results are shown in Figure 7 and Figure 8.

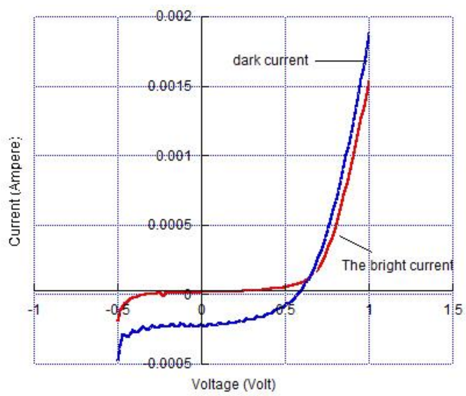


Figure 7. Keithley test results with Drops method

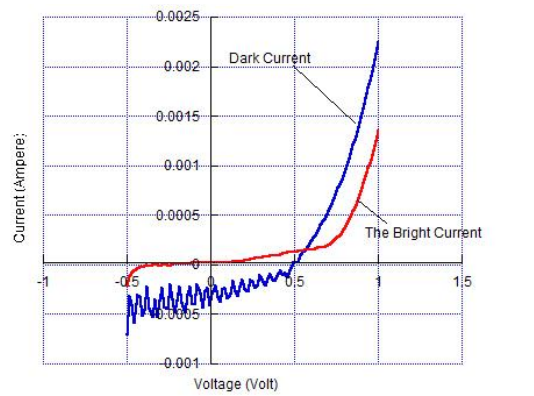


Figure 8. Keithley test results with Soak method

Based on the graph of Keithley test results in Figures 7 and 8, we can determine the current (Isc) and voltage (Voc). So based on calculations that have been done the efficiency of pigment peel extract of melinjo fruit, shown in table 2.

Table 2. Specification of Dye Melinjo Peel

Method	Imax (Ampere)	Vmax (Volt)	Isc (Ampere)	Voc (Volt)	Fill Factor	Efficiency (%)
Drops	0.00187	1.00018	0.00019	0.595	5.7×10^{-7}	0.03
Soak	0.00048	0.457	0.0003	0.550	$1.2x \times 10^{-7}$	0.009

From Table 2, it can be seen that the efficiency produced by DSSC for melinjo peel pigment with drops method is greater than with soak method. This suggests that the method of coating technique and engineering soaking drops almost equally affect the efficiency of the, where the spin coating method has a flat layer and makes the electron transfer fixed, then the resulting efficiency is greater.

Based on the results of previous studies, extraction from various natural materials such as tomatoes (Solanum lycopersiand), Pumpkin/Waluh (*Cucurbita*), carrot (*Daucus carota*), corn (*Zea mays*), and Melinjo peel (*Genetum gnemon*) produce dye with value Absorption of about 380-520 nm. The absorbance value is similar to the value of absorbance in beta-carotene. And from various materials, the highest absorbance value is on the Melinjo with red skin. Dye of the material is able to work on the range of absorption light visible (visible light) so that the natural materials can serve as a photosensitizer and can be used as dye in DSSC. I-V Meter measurements on various materials indicate that the material can work on visible light, this is due to changes in voltage and current when the material is measured in dark and bright conditions.

Conclusion

The measurement and analysis of the absorption spectra of natural dye extract of melinjo 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 melinjo peel has an absorption spectrum similar to that of β-carotene having absorption at wavelengths between 340 - 520 nm and a wave peak with a successive wave peak 340 nm, 415 nm and 520 nm. Measurement I-V Meter / Elkahfi used the same voltage source of 9 volts produces an electric current from the extract of the peel of the larger melinjo fruit. The current in the dark gives 3.27×10^{-5} mA, while under irradiation gives 3.48×10^{-5} mA.

Measurements of the I-V meter also show the conductivity value of the extract of melinjo fruit in the dark is 6.15×10^{-6} $Ohm^{-1}.m^{-1.}$ The conductivity under irradiation is 3.34×10^{-5} $Ohm^{-1}.m^{-1}$. Electrical current and conductivity measurements produced by melinjo peel extracts, this makes the melinjo fruit necessary for further investigation as a DSSC sensitizer.

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