Influence of Fe$_2$(SO$_4$)$_3$ doping concentration into Chlorophyll (Carica Papaya L.) dye on performance of Dye-Sensitized Solar Cells

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Abstract. DSSC consisted of FTO glass/ TiO$_2$/ dye/ electrolyte/ platinum/ FTO glass. The aims of the research are to obtain the optical properties (spectrum absorbance) and electrical properties (I-V Characterization) from DSSC based using chlorophyll dye doped metal of Iron (III) Sulphate/ Fe$_2$(SO$_4$)$_3$ with various concentration. Variation of Fe$_2$(SO$_4$)$_3$ concentration which doped to the chlorophyll dye were 10$^{-1}$M, 10$^{-2}$M, 10$^{-3}$M and 10$^{-4}$M. The I-V characterization was measured using Keithley Type 2602A with irradiation halogen lamp and the optical properties was tested using Spectrophotometer UV-Visible Lambda 25. The result showed that absorbance spectrum for all various dye at wavelength of 400 -500 nm and 640 -700 nm. I-V characteristic by DSSC without Fe$_2$(SO$_4$)$_3$ doping obtained $V_{oc}$ of 2,7 x 10$^{-1}$ V, $I_{sc}$ = 8,9 x 10$^{-5}$ A, $FF$ = 4,7 x 10$^{-1}$ and $\eta_{ef}$ was about 1,1 x 10$^{-2}$ %. After doped by Fe$_2$(SO$_4$)$_3$ with largest concentration of 10$^{-1}$M obtained $V_{oc}$ of 5,0 x 10$^{-1}$ V, $I_{sc}$ = 2,0 x 10$^{-4}$ A, $FF$ = 9,5 x 10$^{-1}$ and $\eta_{ef}$ was about 9,7 x 10$^{-2}$ %.

1. Introduction
Solar cells are semiconductor devices that can convert solar energy directly into DC electric energy / direct current [1]. The principle of converting solar light energy to electrical energy (photovoltaic) was discovered by Chapin and Fuller in the 1960s. Since then the development of photovoltaic is dominated by the fabrication technology of silicon solar cells (Si). This type of solar cell is called the first generation of solar cell. However, due to the expensive price of Si material, the second generation solar cell with thin film technology, such solar cells are made from Si, CdTe, CuInSe2 (CIS) and so on. Then the development of solar cell technology focuses on the type of solar cell with the utilization of abundant natural material, non-toxic, and can produce high efficiency and can be fabricated with an easy process [2]. Another type of solar cell is a third generation solar cell called organic solar cell. This technology was introduced by Professor Grätzel in 1991 so that this type of solar cell is often called the Grätzel cell or Dye-sensitized Solar Cells (DSSC). DSSC is a dye-based solar cell capable of absorbing light [3]. The working principle of DSSC is a combination of optical, electrical and chemical processes. DSSC is believed to produce alternative energy at a more affordable cost and simpler fabrication technology than its predecessor like silicon-based solar cells. However, until now the energy conversion efficiency generated by DSSC is still lower than that of silicon solar cells, but the DSSC is still highly potential to produce higher efficiency in the future [4]. In general, there are four main components in the DSSC. Namely dye, TiO$_2$ semiconductor layer, electrolyte solution, and catalyst. Dye acts as an electron donor, TiO$_2$ semiconductor as an electron acceptor, catalyst would draw electrons into electrolyte solutions resulting in oxidation-reduction reactions that produce electrons. So far dye is used as a sensitizer in the form of synthetic dye and natural dye. Although commercial DSSC uses synthetic dye, the ruthenium
complex has achieved an efficiency of more than 10%, but its availability and cost are very expensive [5]. This makes various other types of dye alternatives derived from natural ingredients that can be extracted from plant parts such as leaves, flowers, or fruit [6]. Different types of natural dye have been studied and developed for DSSC, but usually produce only less than 1% efficiency [7]. For example, the efficiency of DSSCs based on pomegranate leaves, red Sicilian orange, purple eggplant, Kerria japonica, and Rosa chinensis extracts was 0.597% [8], 0.66% [9], 0.48% [9], 0.22% [10], and 0.29% [9], respectively. This research used natural dye in the form of chlorophyll extract from papaya leaf. Chlorophyll is the main pigment as photosensitizer when the process of photosynthesis of green plants. Chlorophyll has a maximum absorbance at wavelengths in visible rays of about 670 nm [11]. To increase the efficiency of solar cells is relatively low estimated because of the nature of the natural dye has a low stability to light radiation, so in this study will examine the characteristics of natural organic dye and influence of iron metal (III) sulphate in papaya leaf extract (Carica Papaya L.) as dye photosensitizer.

2. Experimental Methods

2.1 Preparation of TiO$_2$ Solution
The TiO$_2$ solution is made by mixing 3 grams of TiO$_2$ with 3 ml of ethanol stirred using a magnetic stirrer of 300 rpm for 30 minutes until both are completely dissolved.

2.2 Extraction of Chlorophyll Dye from Papaya Leaf
The extraction is a separation process of a certain substance from its mixture by dividing a solute between two non-mixed solvents, in order to extract the solute from one solvent to another. This extraction process aim is to obtain chlorophyll from papaya leaf. 40 grams of papaya leaves washed first by using aquades, then cut into small pieces and mashed with mortar. Fine papaya leaves are dissolved in 500 ml ethanol and 50 ml distilled water on the erlenmeyer tube, then stirred with a magnetic stirrer at 300 rpm until the papaya leaves dissolves. After sitting for 24 hours, the solution is filtered with filter paper.

2.3 Fe (III) Sulphate Doping into Chlorophyll Dye
Fe$_2$(SO$_4$)$_3$.7H$_2$O powder of 10$^{-4}$ M, 10$^{-2}$ M, 10$^{-3}$ M and 10$^{-4}$ M that are respectively 1,32 gr; 0,132 gr; 0,0132 gr dan 0,00132 gr were dissolved into 10 ml of distilled water plus 10 ml of ethanol. Then each of all stirred for 2 hours with a rotation speed of 300 rpm. A metal solution of various concentrations was mixed into chlorophyll dye of 20 ml each.

2.4 Deposition of TiO$_2$ Layers
The process of depositing TiO$_2$ paste on the conductive side of FTO glass (1 cm x 1 cm) was using spin coating machine. The active area was dropped TiO$_2$ paste until the glass surface is completely closed and the edges were bordered with scotch tape. Then rotated at 1000 rpm for 60 seconds. The process is repeated 3 times to obtain 3 layers of TiO$_2$.

2.5 Preparation of Counter Electrode
The counter electrode in the form of platinum (Hexachloroplatinic (IV) acid 10%) was mixed with isopropanol (200 ml) and stirred of 300 rpm for 30 minutes. FTO glass is heated at 250°C for 15 minutes and then the solution was dropped on FTO glass with 1 cm x 1 cm active layer.

2.6 Annealing Process
FTO glass that has been coated with the TiO$_2$ paste then in annealing applies at temperature of 550°C with a holding time of 60 minutes and a heating rate of 15°C / min.

2.7 Dye Immersion
The working electrodes are then immersed in a dye solution for 24 hours.
2.8 DSSC Assembly
The working electrode and the counter electrode were arranged according to the sandwich structure. Firstly, counter electrode was initially given a seal using a piece of keyboard protector on the right and left side to avoid contact with the working electrode and dropped by electrolytes by 2 drops. Then the working electrode is placed on the counter electrode with the position of line of sight. Both are combined with 2 pieces of paper clips.

3. Results and Discussion

3.1 Optical Characterization
Figure 1 shows the UV-Vis absorption spectra of chlorophyll dye extracted from papaya leaf before and after doped by Fe (III) sulphate with various concentration in the visible light spectrum (400-800 nm). The first absorbance peak is in the wavelength range of 400-500 nm and the second peak occurs in the wavelength range of 640-700 nm. The values of absorbance (λ_max) are 441 nm and 668 with absorbance (A_max) of 0.728 a.u and 0.260 a.u. respectively. Figure 1 also shows absorption spectra of chlorophyll dye after doped by Fe (III) sulphate. The absorbance curves have changed. For the addition of Fe (III) sulphate with concentration of 10^{-2} M, 10^{-3} M and 10^{-4} M the peak absorbance decreased slightly. While Fe (III) sulphate concentration is 10^{-1} M, the absorbance peak was increased at wavelength of 414 nm and 664 nm with absorbance (A_max) 0.837 a.u and 0.363 a.u. This condition indicates that more photon energy can be absorbed and converted into electrical energy in solar cell applications.

3.2 DSSCs Performance
Figure 2 shows IV curve of DSSC with chlorophyll of papaya leaf with variation of doping concentration of Fe(III) sulphate. In that figure also shows IV curve DSSC at dark condition. At dark condition, the IV curve does not cross the quadrant 4. That means no electric current exits the DSSC. While at bright conditions show the electric current is indicated by the curve of each passing quadrant.

Figure 1. Absorption spectra of (a) Chlorophyll dye and Fe(III) sulphate solution (b)dye+Fe(III) sulphate
4. Because when the bright conditions DSSCs get light from Xenon lamps so that it can remove the electrical current that is the result electron excitation dye from HOMO energy level to LUMO.

![Figure 2. I-V curve of DSSCs](image)

**Table 1. Photovoltaic performance with chlorophyll dyes from various Fe(III) sulphate concentration**

| Characteristic | Without Fe | $10^{-1}$M | $10^{-2}$M | $10^{-3}$M | $10^{-4}$M |
|----------------|------------|-------------|-------------|-------------|-------------|
| $V_{OC}$ (Volt) | 2.7 x $10^{-1}$ | 5.0 x $10^{-1}$ | 4.2 x $10^{-1}$ | 2.9 x $10^{-1}$ | 3.2 x $10^{-1}$ |
| $I_{SC}$ (Ampere) | 8.9 x $10^{-5}$ | 2.0 x $10^{-4}$ | 2.3 x $10^{-4}$ | 4.5 x $10^{-5}$ | 2.6 x $10^{-5}$ |
| $V_{max}$ (Volt) | 1.5 x $10^{-1}$ | 3.2 x $10^{-1}$ | 2.4 x $10^{-1}$ | 2.4 x $10^{-1}$ | 1.7 x $10^{-1}$ |
| $I_{max}$ (Ampere) | 7.5 x $10^{-5}$ | 3.0 x $10^{-4}$ | 1.3 x $10^{-4}$ | 5.3 x $10^{-5}$ | 2.8 x $10^{-5}$ |
| $P_{max}$ (Watt) | 1.1 x $10^{-5}$ | 9.7 x $10^{-5}$ | 3.1 x $10^{-5}$ | 1.3 x $10^{-5}$ | 4.6 x $10^{-6}$ |
| FF | 4.7 x $10^{-1}$ | 9.5 x $10^{-1}$ | 3.2 x $10^{-1}$ | 9.9 x $10^{-1}$ | 5.5 x $10^{-1}$ |
| $\eta$ (%) | 1.1 x $10^{-2}$ | 9.7 x $10^{-2}$ | 3.1 x $10^{-2}$ | 1.3 x $10^{-2}$ | 4.6 x $10^{-3}$ |

The absorbance level of dye determines the value of short-circuit current ($I_{SC}$) [12]. According to Table 1, we can conclude that the highest efficiency is the chlorophyll dye doped by $10^{-1}$ M of Fe(III) sulphate. The value of efficiency is 9.7 x $10^{-2}$%. It is due to its $I_{SC}$ is one of the highest also with the absorbance (Fig. 1). Another doping concentrations also have a higher efficiency value compared with chlorophyll dye except the lowest doping ($10^{-4}$ M). It means that doping of Fe(III) sulphate on chlorophyll dye DSSC has the advantage of increasing efficiency and absorbance that can be used as photosensitizer in the DSSC.
4. Conclusion
From the results of this study concluded that the solar cell DSSC has been successfully created by using chlorophyll dye from papaya leaf and doped Fe(III) sulphate with various concentrations. The results of the absorbance dye showed that the value of wavelength these material are able to work on the Visible light. The greatest efficiency achieved by using the chlorophyll dye doped Fe (III) sulphate with concentration $10^{-1}$ M amount of $9.7 \times 10^{-2}$ %. The optimum conditions for chlorophyll dye is when its doped by Fe(III) sulphate with a concentration of $10^{-1}$ M because this concentration yielded the highest absorbance and efficiency.

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