Effects of HSQ$_4$ Concentration into dyes of *Carica Papaya* on the Performance of Dye-Sensitized Solar Cell

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Abstract. Organic dyes are very important in improving the performance of solar cells, at very low prices and friendly to the environment. DN-F15 transparent green is a squaraine dye with good stability on DSSC or with an alternative name HSQ$_4$. HSQ$_4$ is a synthetic dye that is very expensive, but sensitive to light so that it can improve the performance of solar cells. DSSC uses titanium dioxide (TiO$_2$) as a semiconductor, electrodes are used as substrates for the flow of electric charge. DN-EP01 is a thixotropic terpineol-based screen-printable Pt paste with a viscosity of 4-7 Pa.s at 10s$^{-1}$. In furnaces around 450°C will produce an even and transparent platinum particle layer which has high catalytic activity. The color of the platinum paste is straw or light yellow. Measurement of absorbance dyes solution using a spectrophotometer with a wavelength of 400 nm - 800 nm. Characterization of I-V DSSC Carica Papaya produced a $V_{oc}$ value of 560 mV, $I_{sc}$ 1.5 x 10$^{-4}$ A, fill factor 0.47 and efficiency of 0.43%. After doping with HSQ$_4$, the concentration of 1 resulted in a $V_{oc}$ value of 378 mV, $I_{sc}$ 4.0 x 10$^{-4}$ A, fill factor 0.49 and efficiency of 0.14%. An increase in efficiency in variation 3 is 0.24% and variation 5 is 0.35%, this shows the effect of HSQ$_4$ concentration on the coloring of papaya leaf extract can improve the performance of DSSC.

1. Introduction

Solar energy in Indonesia is the biggest energy potential to be used as an alternative energy source in solar cells. One technology that utilizes solar energy to convert into electrical energy is solar cells. Indonesia can receive more solar heat without cost, which is 4800 W/m$^2$ every day [1]. Dye-Sensitized Solar Cell (DSSC) has been developed since 1991. This began to emerge as an alternative energy source after the discovery of solar cell materials with the photoelectrochemical principle by Grätzel [2]. Synthetic dyes that are commonly used are Ruthenium (Ru) Complex, this type of dye has excellent performance and can produce high efficiency [3]. Basically, the working principle of DSSC converts light energy to electrical energy on a molecular scale in the form of reactions from electron transfers. The first process starts with electron excitation in the dye due to photon absorption. Where this is one of the roles
of the nature of TiO$_2$. When photons from the sun hit the working electrode on DSSC, the photon's energy is absorbed by the dye attached to the surface of TiO$_2$. So the dye gets the energy to be excited to carry the energy and is injected into conduction to TiO$_2$. TiO$_2$ acts as an electron acceptor. The dye molecules that are left behind are then oxidized. Furthermore, electrons will be transferred through the outer circuit to the opposite electrode. Electrolytes that act as electron mediators so they can produce cyclical processes in solar cells. Electrolytes capture electrons from external circuits with the help of platinum molecules as catalysts. The excited electrons reenter the cell and are assisted by platinum so that they can react with electrolytes in the electrons.

In this study, using synthetic dye HSQ$_4$ which has good absorbance absorption at a wavelength of 703 nm and a maximum of 720 nm [4-5]. Solar cells with synthetic dye HSQ$_4$ showed very stable work performance in increasing DSSC parameters [6]. Each green plant contains chlorophyll, which is based on each leaf in the plant has the same performance as a solar cell, which absorbs solar energy and converts it into electrical energy [7]. Chlorophyll is the main pigment that is effective as photosensitizer in the process of plant photosynthesis with maximum absorption at 670 nm [8]. In the selection of natural organic material, the chlorophyll must meet the requirements of the characteristics of the active ingredients of solar cells. Where chlorophyll must be able to be a carrier medium for photons absorbed [9]. In this study chlorophyll extract dye used from papaya leaves (Carica Papaya L.). Papaya plants originate from tropical regions in America. This plant has soft and unbranched stems, produces white sap and is filled with leaves that are long and wide [10-11]. The natural chlorophyll dye from Carica Papaya is used as a dye to be hybridized with DN-F15 [12-14]. To obtain conductivity, absorbance and voltage-current characteristics for DSSC performance.

2. Experiments
2.1 Material Preparation
FTO glass is cut into sizes 2 x 2 cm$^2$. This substrate is then put into a clean container and soaked in ethanol for 15 minutes. Ultrasonic Cleaner is used to clean dirt on FTO glass. After the cleaning process is complete, the substrate is dried using a tissue.

DN-EP03 is a paste type TiO$_2$ which is dissolved in ethanol and stirred for 60 minutes (1: 4). Deposition on the FTO substrate using the spin coating method to get a thin and even layer. This is useful for DSSC as a transparent layer. Layers in furnaces with a temperature of 450°C to 550 °C [15-16].

2.3 Dye extraction
To make synthetic dye HSQ$_4$, variations in the concentration of dyenamo transparent green contained 1% wt, 3% wt and 5 % wt then combined with natural dye and dissolved with 5 ml ethanol solvent. Stirred for 30 minutes. To make chlorophyll coloring from papaya leaves, washed with alcohol and then dried, Carica papaya are weighed as much as 10 grams, then crushed with a mortar until smooth and put in 50 ml of ethanol solvent. Stirred for 2 hours.

2.4 Preparation of Electrolyte
The electrolyte solution consisted of three materials that we used in this study. Namely Iodine, Potassium Iodide, and ethylene glycol. Weighed 0.1269 g of pure Iodine and 0.83 g of potassium Iodide and dissolved into 10 ml ethylene glycol [17].

2.5 Characterization
Keithley IV 2602A meters to determine the efficiency of DSSC. To determine efficiency, measurements are made of the current-voltage dense relationship (I-V) that forms a curve. Measurements are usually carried out in bright and dark conditions. $I_{SC}$ current density, open-circuit voltage ($V_{OC}$), and fill factor FF are the three parameters that determine the quality of a solar cell. Short-circuit current density ($I_{SC}$)
and open-circuit voltage ($V_{OC}$) are defined as the maximum current and voltage that can be obtained from solar cells. The efficiency of the solar cell is a factor that measures the quality of the performance of a solar cell. The greater the efficiency, the higher the performance of a solar cell that is obtained [18].

Characterization using UV-Vis Spectrophotometer 1601 Pc to determine the wavelength and peak absorbance of the dye. To find out the optical band gap, by applying the Tauc relationship as follows $(a hv)^2 = A (hv - E_g)$. Where the absorption coefficient is photon energy, $A$ is the constant and the optical band gap is $ahvE_g$ [19]. The electrical conductivity characteristics were tested by Elkahfi 100 /I-V meter.

The DSSC mechanism in Figure 1 shows the DSSC structure consisting of a substrate with transparent electrodes and titanium dioxide (TiO2) [20]. And in Figure 2 is the work cycle of DSSC.

![Figure 1. Components of solar cells](image1.png)

![Figure 2. DSSC working principle](image2.png)
3. Results and Discussions

Conductivity characterization is to measure the Carica papaya dye solution, HSQ₄, and natural and synthetic hybrid chlorophyll. The solution is in concentrations of 1, 3 and 5 HSQ₄. Measurement using ELkahfi 100 IV-Meter with halogen lamp beam radiation with an intensity of 1000 W/m². Electrical conductivity is the ability of a material to conduct electric current if a potential difference is placed at the ends of a conductor, electrons will move through the material. Measurement of Carica papaya dye conductivity and HSQ₄ was carried out using the two-electrode method in the dark and light conditions. Copper is a conductor, whose function can capture electrons, is also able to deliver electrons produced by the dye.

Table 1 shows the fact, the increase in conductivity value is proportional to the increase in the amount of HSQ₄ added to the Carica papaya dye. The conductivity value in the Carica papaya dye is greater, that is 0.003 Ω⁻¹m⁻¹, the conductivity value on HSQ₄ is very small but tends to be the same.

Table 1 shows the electrical conductivity of Carica papaya with HSQ₄ variations

| Material               | Conductivity of Dark Condition (Ω⁻¹m⁻¹) | Conductivity of Light Condition (Ω⁻¹m⁻¹) | Δ Conductivity (Ω⁻¹m⁻¹) |
|------------------------|------------------------------------------|------------------------------------------|-------------------------|
| Carica Papaya          | 0.011                                    | 0.014                                    | 0.003                   |
| HSQ₄: 1% Wt            | 0.00019                                  | 0.00021                                  | 2 x 10⁻⁵                |
| HSQ₄: 3% Wt            | 0.00011                                  | 0.00012                                  | 1 x 10⁻⁵                |
| HSQ₄: 5% Wt            | 0.00032                                  | 0.00034                                  | 2 x 10⁻⁵                |
| HSQ₄ 1% Wt: Carica Papaya | 0.0017                                  | 0.0021                                  | 0.0004                  |
| HSQ₄ 3% Wt: Carica Papaya | 0.0006                                  | 0.0013                                  | 0.0007                  |
| HSQ₄ 5% Wt: Carica Papaya | 0.0012                                  | 0.0030                                  | 0.0018                  |

Table 1 shows the electrical characteristics of the material in dark or light conditions. The graph shows that all materials can conduct electricity in dark or light conditions. The highest conductivity in bright conditions is HSQ₄ 5% Wt: Carica Papaya is 0.0018 Ω⁻¹m⁻¹. This shows that the material has good conductivity so that it can help improve DSSC performance.

Table 2. Characterization UV-Visible Spectrophotometer of Carica Papaya with HSQ₄ variations

| Material               | λ (nm) | Eg (eV) |
|------------------------|--------|---------|
| Carica Papaya          | 668    | 2.37    |
| HSQ₄: 1% Wt            | 706    | 2.40    |
| HSQ₄: 3% Wt            | 708    | 2.41    |
| HSQ₄: 5% Wt            | 716    | 2.41    |
| HSQ₄ 1% Wt: Carica Papaya | 704    | 2.39    |
| HSQ₄ 3% Wt: Carica Papaya | 706    | 2.42    |
| HSQ₄ 5% Wt: Carica Papaya | 708    | 2.43    |

Table 2 shows that the synthetic dye solution obtained from the combination of synthetic dyes and natural dyes was larger. The energy gap is the energy needed by an electron to move to the conduction band. A synthetic dye doping solution will help transfer electrons from the level (LUMO) to the conduction band (CB). From these results, it can be seen that the length of each variation shifts to a larger wavelength, indicating that the mixing of the dyes has been successful. The smaller the material gap...
energy, the higher the absorption of the sample from incoming light. The high absorption rate of the sample has an impact on the level of electron mobility so that the efficiency of the resulting DSSC increases.

Table 3. Characterization I-V Keithley of Carica papaya with HSQ₄ variations

| Material                  | V_{oc} (V) | I_{sc} x 10^{-4} (A) | Fill Factor | Efficiency % |
|---------------------------|------------|----------------------|-------------|--------------|
| Carica Papaya             | 560        | 1.5                  | 0.473       | 0.43         |
| HSQ₄: 1% Wt               | 621        | 3.0                  | 0.62        | 0.93         |
| HSQ₄: 3% Wt               | 575        | 3.5                  | 0.64        | 1.03         |
| HSQ₄: 5% Wt               | 530        | 5.1                  | 0.53        | 1.14         |
| HSQ₄ 1% Wt: Carica Papaya | 378        | 4.0                  | 0.49        | 0.14         |
| HSQ₄ 3% Wt: Carica Papaya | 394        | 2.1                  | 0.47        | 0.24         |
| HSQ₄ 5% Wt: Carica Papaya | 454        | 2.2                  | 0.45        | 0.35         |

I-V Keithley characteristics can be seen in Figure 5 and Table 3. From the table there is an increase in solar cells, the synthetic dye HSQ₄ obtained an efficiency value of 1.14% at a variation of 5% Wt. This shows that the combination of natural and synthetic dyes with increasing concentrations can improve DSSC performance [21].

Figure 3. Absorbance Spectrum of HSQ₄ and HSQ₄: Carica Papaya

Figure 3 shows the optical characteristics of the carica papaya dye, HSQ₄, and HSQ₄: Carica papaya. There are seven absorbance peaks located in the wavelength range of 400 nm - 800 nm. From the absorbance results, it can be seen that the increase in HSQ₄ concentration gives a greater shift in wavelength. If more light is absorbed, more electrons can be transferred and DSSC performance increases.
Figure 4. Electrical conductivity Characteristics for (a) HSQ₄ and (b) HSQ₄: Carica Papaya
The $I-V$ test resulted in the highest efficiency produced by cells with HSQ$_4$ working electrodes and TiO$_2$ from 0.93% to 1.14% and HSQ$_4$: Carica Papaya ie 0.14% to 0.35% showed an increase. So, it can be concluded that cell efficiency can increase greater by increasing the amount of concentration.

4. Conclusion
From the data generated it can be concluded that the performance of the platinum type DN-EP01 and TiO$_2$ type DN-EP03 is very good. Dye made from HSQ$_4$ powder which is easily soluble in ethanol can absorb and continue the visible light spectrum. Wavelengths are in the range of 400 nm - 800 nm. And the resulting energy gap is also in the range of 2.37 eV-2.43 eV, the smaller the gap of material energy, the higher the absorption of incoming light samples. The high level of sample uptake affects the level of electron mobility so that the efficiency of the resulting DSSC increases. Characterization of $I-V$ DSSC Carica Papaya produced a $V_{oc}$ value of 560 mV, $I_{sc}$ 1.5 x $10^{-4}$ A, fill factor 0.47 and efficiency of 0.43%. After doping with HSQ$_4$ the concentration of 1 resulted in a $V_{oc}$ value of 378 mV, $I_{sc}$ 4.0 x $10^{-4}$ A, fill factor 0.49 and efficiency of 0.14%. An increase in efficiency in variation 3 is 0.24% and variation 5 is 0.35%, this shows the effect of HSQ$_4$ concentration on the coloring of papaya leaf extract can improve the performance of DSSC.

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