Dye *Oriza sativa glutinosa* doped Fe as a active element of Dye Sensitized Solar Cell (DSSC)

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**Abstract.** The aims of the research are to determine the effect of doping Fe (III) Sulphate into dye *Oriza sativa glutinosa* on the characteristics parameters of solar cells, to determine the optical characteristic, functional group and electrical characteristic of dye *Oriza sativa glutinosa* doped Fe (III) sulphate. TiO₂ nano size as much as 0.5 gr dissolved in 3 ml ethanol. 100 gr black sticky rice (*Oriza sativa glutinosa*) was immersed in 80 ml ethanol solution (95%) and kept at room temperature without exposing to light. Then it was filtered with a filter paper no.42, and the extracted result was process with chromatography. Furthermore, it was doped with Fe (III) sulphate respectively of 10⁻¹ M, 10⁻² M, 10⁻³ M. The characteristic of dye solution was measured using UV-Visible *Spectrophotometer Lambda 25* for absorbance, *Elkahfi 1000/I-V meter* for conductivity and *Keithley 2602A* for characterization of current and voltage (I-V). The result showed that the area of dye *Oriza sativa glutinosa* doped Fe (III) sulphate with concentration 10⁻¹ M the largest, because the value of *Vₜₙₙ* intercept at 6.40 × 10⁻¹ mV and the value *Iₘₚ* intercept at 1.89 × 10⁻³ mA, with efficiency value is 0.148%.

1. Introduction

Dye sensitized solar cells (DSSC) is one type of solar cells which is attractive to be studied and development as an alternative way to substitute the conventional solar cells based on silicon semiconductor over the last decade. There are some advantages of DSSC, easy to fabricate, low cost and environmental friendly [1]. A DSSC is composed of a nanocrystalline porous semiconductor electrode-absorbed dye, a counter electrode, and an electrolyte containing iodine and triiodide ions. [2]. The principle of operation of DSSC is based on sensitization of a wide band-gap metal oxide semiconductor to the visible light region by an adsorbed molecular dye. When the metal oxide semiconductor film is immersed in the dye, a monolayer of the dye is anchored onto its surface. Excitation of atoms by sun light occurs in the dye and the photogenerated charges are separated at the interface between the dye and metal oxide [3]. The DSSC sensitized by Ru-containing compounds are reaching, 11-12% the highest efficiency as reported by Chiba and Islam [1]. However, noble metals limited in amount, and costly in production. Therefore, alternative organic dyes such as natural dyes have been studied intensively. Although its absorbance ability is lower than dye synthetic, such as ruthenium complex, but the findings of Hao et al. [4] and Yuliarto et al. [5] showed that extracts of black rice can be used as photosensitizer in DSSC. Furthermore, Hao et al. [4] also report that the dye of black rice extract is the best natural dye be caused, this kind of dye can absorb wavelength in wide spectrum. The anthocyanin pigments contained in black rice was over 80% of cyaniding-3-glucoside, the other minor pigments were peonidin-3-glucoside, malvidin-3-glucoside, and cyanidin-3-rhamnoglucoside [6]. Saehana et al. [7] reported that a conversion efficiency of 0.17% was obtained
using black rice dye as sensitizer. Until now, variations of the optimization is done by many researchers to improve the efficiency and stability of performance dye sensitized solar cell. Therefore, various engineering has been carried out such as by modifying the TiO2 electrode, electrolyte and, dye used [8]. This research studied the effect of doping Fe (III) Sulphate into dye Oryza sativa glutinosa as photosensitizer for dye sensitized solar cells. Selection of iron complex is based on ferrous metals located in the transition metals in which the electron configuration d6 as ruthenium and Osmium (used as dye solar cells), have quantum relatively high to produce sensitization of nanocrystalline TiO2, soluble in polar solvents, and its wavelength at visible region is 551 nm.

2. Experiment Methods

2.1. Preparation of TiO2 Solution
TiO2 nano powders as much as 0.5 gr dissolved in 3 ml of ethanol, then stirred using a vortex stirrer with a speed of 300 rpm for 30 minutes. TiO2 paste was stored in closed container lined with aluminium foil.

2.2. Preparation of Natural Dye Sensitizers and Doping Fe (III) Sulphate
100 gr Black sticky rice (Oriza sativa glutinosa) was immersed in 80 ml ethanol solution (95%) and keep at room temperature without exposing to light [9]. Then it was filtered with a filter paper no.42, and the extracted result was process with chromatography. Furthermore, it was doped with Fe (III) sulphate. Fe2(SO4)3.7H2O respectively of 10^-1 M, 10^-2 M, 10^-3 M which was dissolved in 40 ml of ethanol and each stirred for 2 hours at 60°C to form a solution of Fe (III) sulphate for each concentration. The solution of Fe (III) sulphate with various concentrations was mixed in 40 ml for each dye extracted from black rice, ratio of Fe (III) sulphate and extracted dye (1:1), while stirred for 2 hours.

2.3. Preparation of Electrolyte
Natrium iodid (NaI) of 2 grams are mixed into 3.68 ml acetonitrile added 1 ml propylene carbonate. Further to the solution is added polyethylene glycol then stirred. Further to the solution is added iodine (I2) of 0.2 grams was stirred with a vortex stirrer at 300 rpm for 30 minutes. Electrolytes solution was stored in closed containers lined with aluminum foil.

2.4. Preparation of Counter Electrode
To prepare platinum catalyst coated on FTO glass substrate, 1 ml hexachloroplatinic acid solution in 207 ml isopropanol was spread on the FTO conducting surface. The Pt-coated FTO counter electrode was then heated in a furnace at 250°C for 15 minutes.

2.5. Preparation of the TiO2/Dye Electrode
The FTO glass (1 × 1 cm²) was cleaned with distilled water and ethanol to remove impurities. The cleaned FTO surface was coated with TiO2 paste using spin coating techniques. The FTO/TiO2 electrodes were sintered at 450°C for 30 minutes. The electrode were immersed in the dye solution for 24 hours. The white TiO2 film will change color when dye is absorbed.

2.6. Fabrication of Natural Colorant-Sensitized Solar Cells (DSSC)
Natural colorant-sensitized solar cells with active area about 1 cm² were fabricated by sandwiching the electrolyte between TiO2/dye electrode and Pt counter electrode. The I-V characteristics of DSSC were obtained under light illumination (1000 W/m²) using keithley 2602A source meter.

3. Result and Discussion

3.1. Absorption Spectra of Black Sticky Rice doped Fe (III) Sulphate
Before being used as a sensitizer, extract black sticky rice and extract black sticky rice doped Fe (III)
sulphate, first characterized using UV-Visible Spectrophotometer Lambda 25. Absorbance spectra measured in the wavelength range of 400-800 nm.

![Graph showing absorbance spectra](image1)

**Figure 1** Absorption Spectrum of dye and dye doped Fe (III) sulphate

Figure 1 shows that absorbance maximum extract black sticky rice without doped Fe (III) sulphate at 0.432 a.u with wavelength 553 nm. Extract black sticky rice doped Fe $10^{-3}$ M at 0.379 a.u with wavelength 595 nm, extract black sticky rice doped Fe $10^{-2}$ M at 0.406 a.u with wavelength between 601 nm, and extract black sticky rice doped Fe $10^{-1}$ M at 0.419 a.u with wavelength 660 nm. Absorbance dye of the fourth materials showed that the value of wavelength of these material are able to work on the UV-Visible light. From Figure 1, doping Fe (III) sulphate into the dye causes peak absorbance by dye shifted from wavelength 553 nm becomes 595 nm, 601 nm, and 660 nm. In this case there has been a process of intermolecular copigmentation between anthocyanin extract of black sticky rice with copigmen compound of Fe (III) sulphate which is characterized by a bathochromic shift. Bathochromic shift causes absorption peak shifts towards larger wavelengths.

3.2. Fourier Transform Infrared (FT-IR) Analysis

FTIR spectroscopy is a characterization methods for identification of functional groups by measuring the absorbance at all wavelengths of IR. FTIR spectra of each sample can be shown in the figure 2

![Graph showing FTIR spectra](image2)

**Figure 2** FTIR spectral analysis of dye and dye doped Fe (III) sulphate
Figure 2 shows the different functional groups of extract black sticky rice and black sticky rice doped Fe with concentrations $10^{-1}$ M, $10^{-2}$ M, $10^{-3}$ M. Extract black sticky rice without doped Fe (III) sulphate have the absorbance at wavenumber 3440.19 cm$^{-1}$, 2925.17 cm$^{-1}$, 2853.81 cm$^{-1}$, 1745.65 cm$^{-1}$, 1632.81 cm$^{-1}$, 1464.03 cm$^{-1}$, and 1164.09 cm$^{-1}$ which is a compound of the O-H stretching, C-H (alkane), C=O stretching, C=C stretching, C-H (alkane), and C-O stretching. In the extract black sticky rice doped Fe (III) sulphate with concentrations $10^{-1}$ M, $10^{-2}$ M, $10^{-3}$ M have a functional groups that is almost the same forms as in extract black sticky rice but different values of the wavenumber and transmittance. In other words, doping Fe (III) sulphate into extract black sticky rice make widen the area of light absorption of dyes to larger wavelengths. In extracts of black sticky rice doped Fe (III) sulphate, O-H bond alcohol stretching formed from the value of spectral shifts to shorter wavenumber. This absorption band shift caused by the interaction of the ligand OH on black sticky rice cyanidin molecule with a central atom of Fe (III) sulphate. These interactions multiply the occurrence of hydrogen bonds that make the absorption band widening. In spectra 2925.17 cm$^{-1}$ and 2853.81 cm$^{-1}$ showed the C-H bonds (alkanes) in an area stretching hydrogen, the intensity of absorption that form C-H bonds (alkanes) to be reduced due to vibration in the catchment area occurs with changes in dipole moment that is smaller because no polar OH covalent bonds with Fe (III). In spectra 1745.65 cm$^{-1}$ showed the C=O stretching in the double bond with a very high intensity of absorption. Therefore carbonyl group in black sticky rice extract is very polar, so this stretching bond is produced change dipole moment is quite large. Then the intensity of absorption form C=O stretching bond is reduced because doping Fe (III) sulphate into extract of black sticky rice change molecular structure of the carbonyl group in ketones which causes the frequency of C=O stretching vibration become lower.

3.3. Conductivity characteristics

Further characterization is conductivity testing of dye using Elkahfi 100/I-V meter under irradiation of the halogen lamp 250 mW/cm$^2$

![Conductivity Curve for dye and dye doped Fe (III) sulphate](image)

Figure 3 shows the conductivity value of the extract black sticky rice without doped Fe (III) sulphate is $3.20 \times 10^{-3}$ ohm$^{-1}$.m$^{-1}$, for black sticky rice doped Fe (III) sulphate with concentrations $10^{-1}$ M, $10^{-2}$ M, $10^{-3}$ M obtained conductivity values of each of $6.27 \times 10^{-3}$ ohm$^{-1}$.m$^{-1}$, $4.48 \times 10^{-3}$ ohm$^{-1}$.m$^{-1}$ and $3.67 \times 10^{-3}$ ohm$^{-1}$.m$^{-1}$, respectively. The result shows that the tendency of increase conductivity value is proportional to the increasing molarity of Fe (III) sulphate were added into the dye.
3.4. Photovoltaic Properties

Characterization of the current-voltage (I-V) is a method to determine how much ability DSSC can convert light into electrical energy. Measurements using Keithley 2602A conducted in the dark and the light that is under irradiation with a halogen light intensity of 1000 W/m². The test results I-V with 24 hours immersion.

![Figure 4](image)

**Figure 4** Current-Voltage curve for DSSC extract black sticky rice and black sticky rice doped Fe (III) sulphate

Based on the graph in Figure 4, it can be shown that the dye extract black sticky rice doped Fe $10^{-1}$ M has the largest area, because the value of $V_{oc}$ intercept at $6.40 \times 10^{-4}$ mV and the value $I_{sc}$ intercept at $1.89 \times 10^{-1}$ mA. Therefore, it has the largest value of efficiency. In generally, the results of the efficiency of the extract black sticky rice without Fe (III) sulphate and black sticky rice doped Fe (III) sulphate with concentrations $10^{-1}$ M, $10^{-2}$ M, $10^{-3}$ M, are shown in Table 1.

| Dye Source          | $V_{oc}$ (mV) | $I_{sc}$ (mA) | $I_{max}$ (mV) | $I_{max}$ (mA) | Fill Factor | Efficiency (%) |
|---------------------|---------------|---------------|----------------|----------------|-------------|---------------|
| Black Sticky Rice   | 0.385         | $4.03 \times 10^{-4}$ | 0.385          | $4.23 \times 10^{-5}$ | 1.71 $\times 10^{-8}$ | 0.016         |
| Doped Fe (III) sulphate $10^{-1}$ M | 0.640         | $1.89 \times 10^{-3}$ | 0.640          | $2.31 \times 10^{-4}$ | 4.37 $\times 10^{-7}$ | 0.148         |
| Doped Fe (III) sulphate $10^{-2}$ M | 0.625         | $1.64 \times 10^{-3}$ | 0.625          | $2.33 \times 10^{-4}$ | 3.84 $\times 10^{-7}$ | 0.145         |
| Doped Fe (III) sulphate $10^{-3}$ M | 0.625         | $1.55 \times 10^{-3}$ | 0.625          | $1.0 \times 10^{-4}$ | $1.55 \times 10^{-7}$ | 0.062         |

From Table 1 and figure 4, we can be concluded that the dye extract of black sticky rice doped Fe (III) sulphate with concentration $10^{-1}$ M has the largest value of efficiency (0.148%). The result shows that doped Fe (III) sulphate into the dye extract black sticky rice widens absorption spectrum and increase the conductivity of the dye. The presence of a metallic contact layer becomes the path for electrons to flow faster toward the substrate FTO. In general, the value efficiency of these material is still very
small (under 1%). There are two kind of efforts to increase the performance DSSC. The first, using different counter electrode with polyaniline (PANI), because PANI can increase efficiency from 6.90% using platinum to 7.15% using PANI [10]. The second, using the kind of electrolyte which has viscosity is smaller than PEG electrolyte such as PEO polymer gel [11].

4. Summary

From the results of this study concluded that the solar cell DSSC has been successfully created by using dye extract black sticky rice and extract black sticky rice doped Fe with various concentrations. The results of the absorbance dye showed that the value of wavelength these material are able to work on the UV-Visible light. The largest conductivity value is dye extract black sticky rice doping Fe (III) sulphate with concentration 10^{-1} M, whereas the greatest efficiency in achieved by using the extract black sticky rice doped Fe (III) sulphate with concentration 10^{-1} M on 24 hour immersion in the amount of 0.148%.

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