Studies on the Optical and Morphology Properties of DN-F01 Dye Hybrid Black Rice and Ag Metal as Dye-Sensitized Solar Cells (DSSC) Transparent

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Abstract. Dye-Sensitized Solar Cells (DSSC) is a set of solar cells based on photoelectrocomia, which involves the transfer of electric charge from one phase to another. This research aims to determine the optical and photoelectric properties of DN-F01 dye hybrid black rice and Ag metal as DSSC transparent. TiO₂ (DN-E0P3) was used which was coated on a conductive glass through a spin coating technique and as a photon absorbent was used DN-F01 dye with combination of DN-F01 dye hybrid anthocyanin dye from extracts black rice and DN-F01 dye doped Ag metal. Characterization of glass substrate that has been coated with TiO₂ using FESEM and EDS where with FESEM tools it is seen that TiO₂ on the surface of the glass is more evenly distributed and from EDS it is found that the dominant substance found on the glass surface is Ti. In the absorption of UV-VIS light characterization it is known that combination of DN-F01 dye can absorb the spectrum of light at wavelengths around 400-800 nm. When solar cells are illuminated with sunlight, solar cells can convert solar energy into electrical energy. The voltage, electric current, and highest efficiency produced by DSSC with optimizing the combination of DN-F01 dyes is DN-F01 hybrid Ag metal that is 805 mV, 1,234 µA and 2,145%.

1. Introduction
Solar energy is the largest source of energy, does not contain pollution, is not used up, and is free. Currently, solar energy has not been used as a primary energy source because energy supply still depends on various fossil fuel sources. As of 2002, the availability of fossil energy reserves around the world is running low [1]. To overcome the energy crisis and support human survival, solar energy can be converted into electrical energy. The conversion of solar energy into electrical energy takes place through a photovoltaic cell system. The photovoltaic effect is the event of the discharge of an electric charge in a material as a result of the absorption of light by that material [8]. One mechanism that works based on photovoltaic systems is solar cells. In solar cells, photons from solar radiation are absorbed and then converted into electrical energy. The solar cells that are widely used today are conventional solar cells based on silicon technology [10]. However, the cost of producing silicon is very expensive so that its consumption costs are more expensive than fossil energy sources. Besides the fabrication process of silicon solar cells also use hazardous chemicals [11].
DSSC is one of the non-conventional solar cell technologies that develops in line with the development of nanotechnology. DSSC consists of TiO$_2$ nanocrystals as photoelectrodes, dyes as light absorbers, and electrolytes as electron donors arranged in a sandwich structure [9]. Basically the working principle of DSSC is the reaction of electron transfer. The first process begins with the excitation of electrons in the dye molecule due to absorption of photons [12]. The second process occurs at the negative electrode (anode), which is the TiO$_2$ layer where the excited electrons are then injected into the TiO$_2$ conduction band so that the dye is oxidized. With an electron donor by an electrolyte, the dye molecule returns to its original state and prevents the recapture of the electron by the oxidized dye. In the third process, after reaching the ITO electrode, electrons flow into the counter-electrode which acts as a positive electrode (cathode) through an external circuit [14]. The next process, in the presence of a catalyst at the counter electrode, electrons are received by the electrolyte so that the holes formed in the electrolyte ($I_3^-$), due to electron donors in the previous process, combine with electrons to form iodide ($I^-$) [15,16,17]. The final process, iodide is used to donate electrons to oxidized dyes, to form an electron transport cycle. With this cycle there is a direct conversion from sunlight to electricity [2]. The advantage of DSSC is that it does not require materials with high purity so that the production costs are relatively low [3]. In contrast to conventional solar cells, in DSSC the absorption of light and the transfer of an electric charge occur in separate processes. Light absorption is carried out by dye molecules, while charge transfer is carried out by nanocrystal inorganic semiconductors which have relatively large bandgaps [13]. One of the most commonly used semiconductors is TiO$_2$ which is relatively inexpensive, commonly found and non-toxic [4].

In DSSC, TiO$_2$ must have a wide surface so that the dye is absorbed more so that it can increase the current output of solar cells. Dye as a sensitizer includes synthetic dyes and natural dyes. Commercial DSSC uses dye synthesis of ruthenium complex type with efficiency of 9.2% [7]. However, the availability and price are expensive so that an alternative substitute is the natural dye extracted from plant parts [5]. Various types of plant extracts have been used as photosensitizers in dye sensitized solar cell systems. Natural dye sensitizers that have been used in DSSC systems include anthocyanins, namely black sticky rice or black rice. The dye material used must be able to absorb a wide spectrum of light for example with using black rice dyes. I-V curve of solar cells using black rice has good efficiency, estimated $\eta$ value is 0.22% and FF value is 32.6% [23]. The dye material used black glutinous rice for 48 hours soaking obtain the highest efficiency is 0.437 x 10$^{-3}$ % [24]. The natural dyes are proven to be able to provide photovoltaic effects even though the efficiency is still much smaller than synthetic dyes [6]. Natural dyes that are available when combined with synthetic dye DN-F01 will occur in greater color absorption so it is expected to increase efficiency. So, in this study DN-F01 combined with Ag metal forms have a good structure in the FESEM test and EDS it is found that the dominant substance so that it is expected to produce high solar cell efficiency.

2. Experimental Methodology
2.1. Materials
Fluorine doped Tin Oxide (FTO) glass, TiO$_2$ (DN-E0P3), Ethanol (C$_2$H$_6$O), Polyethylene Glycol (C$_2$H$_{4}$nH$_{4}$n+2On+1), Citric Acid (C$_6$H$_8$O$_7$), and Potassium Iodide (KI), DN-F01, Screen Printable Pt Paste, Ag metal, Black Rice.

2.2. Methods
2.2.1. Preparation of Combination of DN-F01 Dyes
Black rice washed carefully. The finely ground black rice is then stirred with ethanol, acetic acid, and distilled water. 10 grams of black rice and 35 ml of the solvent in the ratio of 30: 4: 16 distirer for 2 hours, then leave it for 24 hours. After 24 hours, the extract was filtered and used as a dye. DN-F01 dye consists of 0.125% wt, 0.5% wt, 1% wt combined with natural dye (black rice). Black rice dye solution is then mixed with DN-F01 solution in a ratio of 1: 1.
2.2.2. Preparation of Photo Anode
FTO glass that has been thoroughly cleaned is deposited with TiO\(_2\) paste with the "Spin Coating" coating technique. For TiO\(_2\) paste (DN-E0P3) mixed with ethanol in a ratio of 1:1 ie 10 grams DN-E0P3 and 10 ml of ethanol. The protected cell layer is 2 × 2cm\(^2\). The thickness of the subsequent film is around 10-20 μm. After that, the FTO glass that has been coated with TiO\(_2\) is coated with temperature of 550, holding time is 60 minutes, heating rate is 15 minutes. The anneling process is carried out in the carbolite furnace.

2.2.3. Preparation of Electrolyte
0.8 gram of Potassium Iodide (KI) and 10 ml of PEG (Polyetilenglicol) stirrer for one hour until homogeneous then adding 0.127 grams of iodine (I\(_2\)) mixed until homogeneous [19]. This solution is used as an electrolyte and stored in black bottles coated by aluminum foil.

2.2.4. Cell Preparation
The FTO substrate which was coated by TiO\(_2\) thin film of about 10 cm\(^2\) was immersed in natural dyes, Ag solution and organic dyes DN-F01, each for 24 hours to make a working anode [20]. After that the color particles that have been adsorbed by TiO\(_2\) film are rinsed with ethanol for a few seconds to wash the dye that is not bound. Then the TiO\(_2\) glass is allowed to stand for about 10 minutes to dry. For counter electrodes or cathodes, the FTO glass is coated by a Screen-Printable Pt paste by dripping on a hot plate. FIGURE 1 shown about chemical structure Anthocyanin, DN-F01, and Ag molecule.

FIGURE 1. Chemical structure (a) Anthocyanin, (b) DN-F01, (c) Ag molecule [13]

The working electrode (anode) and counter electrode (cathode) are then arranged like a sandwich with a paper binder clip and the electrolyte solution is injected into the coated cell of the DSSC component [18].
3. Results and Discussion

3.1. Absorbance of the DN-F01 Combination

Absorbance of various extracts black rice, and Ag solution ingredients using a UV Visible shimadzu u 1601 PC Spectrophotometer. FIGURE 2 shows that the fixed ratio between various natural dyes and solvents produces different absorbances. FIGURE 2 also shows that the spectrum of dyes extracted from various natural materials has an absorption spectrum that ranges from 400 to 800 nm.

Variation organic dyes (DN-F01) with concentration 0.125% + Black Rice have two peak absorpsion spectra 420-510 nm and 510-570 nm. 0.5% DN-F01 + Black Rice has an absorpsion spectrum from 450-580 nm, 1% DN-F01 + Black Rice has an absorpsion spectrum from 400-530 nm, while variation DN-F01 + Ag solution has absorption spectrum that ranges from 480 to 600 nm.

3.2. I-V Performance of DSSC with Combination of DN-F01

FIGURE 3 shows that the efficiency of 0.125% DN-F01 as much as 2 ml combined with 2 ml of black rice dye obtained 0.996 %. Efficiency of 0.5% DN-F01 as much as 2 ml combined with 2 ml of black rice dye obtained 1.014 %, and 1% DN-F01 as much as 2 ml combined with 2 ml obtained 1.065 %.
while DN-F01 as much as 2 ml combined with 2 ml of Ag solution obtained the highest efficiency of all combinations dye, which is 2.145 %.

### TABLE 1. Efficiency of DSSC by optimization result

| Materials            | $V_{oc}$ (mV) | $I_{sc}$ (mA) | $FF$ | $\eta$ (%) |
|----------------------|---------------|---------------|-----|------------|
| 0.125% DN-F01 + Black Rice | 364           | 1.386         | 0.569 | 0.996      |
| 0.5% DN-F01 + Black Rice     | 394           | 1.279         | 0.579 | 1.014      |
| 1% DN-F01 + Black Rice      | 378           | 1.235         | 0.656 | 1.065      |
| DN-F01 + Ag              | 805           | 1.234         | 5.396 | 2.145      |

**TABLE 1** shows that the DN-F01 doped Ag solution obtained the highest efficiency of all combinations dye, which is 2.145 %. So, for the next step is to examine the structure of the working electrodes of DN-F01 dapped Ag solution.

### 3.4.1. FESEM structure of TiO$_2$ doped DN-F01

![FESEM images of TiO2 doped DN-F01](image1)

**FIGURE 4.** FESEM images of TiO2 doped DN-F01

FESEM analysis, results FESEM characterization with a magnification of 20,000 times was carried out to determine the TiO$_2$ doped DN-F01 microstructure on the ITO glass substrate. Based on the results of the analysis, it is known that the properties obtained have a nanorod structure but TiO$_2$ doped DN-F01 particles have not been spread evenly across the surface. The most visible nanorod structure is the nanorod structure between particles. The nanorod structure in the particle and surface profile cannot be known because of the limited resolution of the instrument and research data. The nanorod structure of the TiO$_2$ layer is an important characteristic of DSSC [21]. More porous layer morphology can increase the number of dye molecules absorbed on the surface of TiO$_2$ particles. The more nanorod volume formed, the more space can be occupied by dye molecules. This makes photon absorption easier, increasing the number of electrons injected into the TiO$_2$ surface, which in turn can increase the ability of solar cells. As for the immersion in the dye solution, on the immersion for 24 hours the TiO$_2$ layer doped DN-F01 has a nanorod structure but has not been spread evenly. The structure of the immersed TiO$_2$ layer doped DN-F01 can be seen in **FIGURE 4**.

![EDS analysis of TiO2 doped DN-F01](image2)

**FIGURE 5.** EDS analysis of TiO2 doped DN-F01
The EDS spectrum (FIGURE 5) exhibits a strong carbon peak which is in agreement with the high percentage of carbon in DN-F01. The EDS spectra also revealed peaks likely to be due to the other materials used or formed during the reduction process. A strong titanium peak shown in the spectrum originates from the copper grid used for FESEM analysis.

3.4.2. FESEM structure of TiO₂ doped DN-F01 + Ag

![FESEM images](image_url)

FIGURE 6. FESEM images of TiO₂ doped DN-F01 + Ag

The results of the sample scan by FESEM provide information related to morphology, including the shape, size and distribution of the sample [22]. Photo of FESEM structure of 50% TiO₂ doped with Ag 50% for 24 hours as shown in FIGURE 6. In the picture can be seen TiO₂ doped Ag structure that grows nanowires cross section. This figure also shows the diameter of the 50% TiO₂ doped Ag metal nanowires which is almost the same for three samples, which is between 63.16-210.50 nm. In this sample a high-density homogeneous structure is produced. High density in the sample will increase the amount absorbed, so that the absorption rate of the sample increases.

![EDS spectrum](image_url)

FIGURE 7. EDS analysis of TiO₂ doped DN-F01 + Ag

The EDS spectrum (FIGURE 7) exhibits a strong silver peak which is in agreement with the high percentage of silver in DN-F01 doped Ag. The EDS spectra also revealed peaks likely to be due to the other materials used or formed during the reduction process. A strong titanium and chlorin peak shown in the spectrum originates from the copper grid used for FESEM analysis.

3. Conclusion

From the research that has been done, it can be concluded that the combination of syntetic dyes has an influence on the efficiency of DSSC produced, where the highest efficiency is the concentration of synthetic dye DN-F01 doped Ag which is 2.145%. The dye absorption technique on TiO₂ can increase the efficiency of DSSC, where TiO₂ paste combined with DN-F01 doped Ag have higher efficiency than TiO₂ paste which is soaked with natural dye. After knowing the highest efficiency, it can be carried out a morphological
structure study as FESEM and EDS of working electrodes that have been soaked DN-F01 doped Ag ie the more volume of nanowires formed, the more space can be occupied by dye molecules. This causes the absorption of high photons so as to increase the ability of DSSC performance.

Acknowledgment
This research was supported by Institute for Research and Community service, Sebelas Maret University by Hibah Penelitian Unggulan Terapan UNS (PUT-UNS) with contract 516/UN27.21/PP/2019 and Research Management Centre (RMC), Universiti Tun Hussein Onn Malaysia (UTHM) JOHOR, 86400 Parit Raja, Batu Pahat Johor, Malaysia.

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