Dye characteristics of *Zingiber officinale var rubrum*, *Cinnamomum zaylanicum*, *Curcuma longa L.*, *Oryza sativa L. Indica* in dye sensitized solar cell (DSSC)

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Abstract. The aims of the research to were know performance of DSSC using the dye of *Zingiber*, *Cinnamomum*, *Curcuma*, and *Oryza* as a photosensitizer with a variation of dye deposition area with spin coating techniques. The structure of the samples as a sandwich consisting of the working electrode (TiO₂), dye, electrodes of platinum (Pt) and the electrolyte sandwiched between two electrodes. Test absorbance dye using UV-Visible Spectrophotometer Lambda 25, using a two-point conductivity test probes El Kahfi 100 and characterization test I-V using a Keithley 2602A. For *Zingiber* results showed that absorbance at 243 nm and 279 nm, photoconductivity of 0.29 Ω⁻¹ m⁻¹ and the efficiency is 0.015% on 0.5 cm². *Cinnamomum* results showed that absorbance at 253 nm and 403 nm, photoconductivity of 0.11 Ω⁻¹ m⁻¹ and the efficiency is 0.002% on 3 cm². *Curcuma* results showed that absorbance at 243 nm and 403 nm, photoconductivity of 0.177 Ω⁻¹ m⁻¹ and the efficiency is 0.072% on 3 cm². *Oryza* results showed that absorbance at 240 nm and 423 nm, photoconductivity of 0.21 Ω⁻¹ m⁻¹ and the efficiency is 0.04% on 2.25 cm². Best absorbance value was obtained from *Oryza* dye; the highest photoconductivity was obtained from *Zingiber* dye, and the highest efficiency was obtained from *Curcuma* dye.

1. Introduction

The third generation of solar cells which can be an alternative to cell conventional solar silicon is DSSC. Materials of DSSC was used because the cost of purchasing a cheap, easy in production, but the efficiency is still small [1]. There are four main components in DSSC, which is a semiconductor as working electrode (TiO₂), a dye sensitive to the absorption of light, an electrolyte and a counter electrode such as platinum (Pt). Studies with ruthenium complex dyes was achieved an efficiency of 11.1% [2]. Price and availability is limited so switch to the organic, such as *Zingiber*, *Cinnamomum*, *Curcuma*, and *Oryza*.

**TiO₂** nanoparticles in FTO serves as the electron catcher for providing the hole. The function of counter electrode is a catalyst while transferring electrons to the electrolyte. Electrolyte generates electron when the redox reaction, which will be forwarded to fill the hole in the dye. The use of glass to work forward light so that the light energy absorbed by electrons in the dye atoms, then towards the hole of TiO₂ layers. Furthermore, electrons move to the FTO layers and external circuit, then the electrons towards the platinum layer and electrolyte.

To improve the performance of DSSC, using the more dye and more variation to limit the highest efficiency. Energy gap (Eg) of TiO₂ rutile and TiO₂ anatase is 3.0 eV and 3.2 eV. Eg anatase is the...
highest because the active surface area is larger and more photocatalyst [3]. The counter electrode is a
double function, the first; it can stream of electrons from the external circuit (lamp) back to the redox
system (electrolyte) and the second as a mediator to catalyze the redox reaction [4]. The counter
electrode of platinum (Pt) has been the material of choice because it is an excellent catalyst for
reducing triiodide [5]. Platina serves to decrease the resistance of the FTO glass. Electrolytes used in
this study is a mixture of iodine (I\textsubscript{2}) with Potassium Iodide (KI) or Sodium Iodide (NaI) into the
polyethylene glycol (PEG). Electrolytes were used as the electron mediator between the working
electrode and the counter electrode. The efficiency value for electrolyte KI is the greatest then NaI, and
TEAI each mixed into I\textsubscript{2} [6].

This study aims to determine the absorbance value, conductivity and efficient of DSSC.
Determination of absorbance in this study in accordance the law of Lambert-Beer, with The Increase
value of absorbance of a material which suggested a linear relationship between concentration and
absorbance according to the equation 1.

\[ A = \varepsilon . b . c \]  
(1)

Where \( A \) is the absorbance and \( \varepsilon \) is the molar absorptivity coefficient (molar\textsuperscript{-1}.L\textsuperscript{-1}), then \( b \) is
the thickness of the medium through which the beam (cm), and \( c \) is the concentration of the sample
solution (ppm) [7]. Determination of the conductivity of a material can be calculated by equations 2.

\[ \sigma = \frac{d}{R.A} \]  
(2)

With \( \sigma \) is the conductivity (\(\Omega \text{m}^{-1}\)) and \( R \) is the resistance of materials (\(\Omega\)). While \( d \) is the distance
between the two electrodes (m) and \( A \) is the cross-sectional area (m\textsuperscript{2}).

Performance solar cells are the ability to convert light into electrical energy. Determination of
performance solar cells is measured using Keithley 2602A to find the value of short circuit current (\( I_{sc} \))
and open circuit voltage (\( V_{oc} \)). The value of \( I_{sc} \) is determined based on the data in which the voltage
value starts from a negative to a positive. Similarly for the value of \( V_{oc} \) is determined by the current
value starts from a negative to a positive value. Then the value maximum voltage (\( V_{in} \) and maximum
current (\( I_{in} \) are obtained by multiplication of voltage and current. Determine of performance solar
cells can by comparing maximum power from multiplication result \( V_{in} \) and \( I_{in} \).

2.  Experiment

2.1.  Preparation of TiO\textsubscript{2} Solution
TiO\textsubscript{2} used in this study is Titanium (IV) Oxide nanoparticle (anatase) with 99.8% trace metals basis.
TiO\textsubscript{2} solution of 0.5 grams dissolved in 3 ml of ethanol, then stirred at 500 rpm for 30 minutes.

2.2.  Preparation of Natural Dyes Sensitizer
This study using a dyes extract from black rice (\textit{Oryza sativa L. indica}), red ginger (\textit{Zingiber officinale
var rubrum}), cinnamon (\textit{Cinnamomum zaylanicum}) and turmeric (\textit{Curcuma longa L.}). Then taken as
many as 10 grams was crushed to a fine powderusing a blender. Then the materials were dissolved in
ethanol, acid acetate and distilled water used to have a ratio of 25:4:21 so that the high value
absorbance of the solution because the best anthocyanin concentrate [8]. Then stirred (300 rpm) at
30°C for 30 minutes. Materials was allowed to stand for 24 hours, and it were filtered with a filter
paper 103. Then dyes were filtered with a filter paper 103, it were tested of absorbance using UV-Vis
Spectrometer Lambda 25 and conductivity using El Kahfi \textit{I-V meter} 2602A. Dyes said to be able to
work if it has absorption in the ultraviolet and visible area, while the conductivity states how large can
pass an electric current.

2.3.  Preparation of Electrolyte
The mix of Potassium iodide (KI) solids of 0.8 grams and 10 ml of polyethylene glycol, then stirred at
300 rpm for 30 minutes. Then was added iodine (I\textsubscript{2}) of 0.127 grams and stirred at 300 rpm for 30
minutes.
2.4. Preparation of Counter Electrode
The counter electrode in the form of platinum (Hexachloroplatinic (IV) acid 10%) and it was mixed with isopropanol (207 ml) was stirred at 300 rpm for 30 minutes. Then the solution was dropped on FTO glass with the variation of the deposition area of 0.5 cm$^2$, 1 cm$^2$, 1.5 cm$^2$, 2.25 cm$^2$ and 3 cm$^2$ and the side was masking tape affixed, then the FTO glass was heated at 250$^0$C for 15 minutes, and the solution of 3 ml was dropped on FTO.

2.5. Preparation of TiO$_2$
The TiO$_2$ solution was deposited on the FTO conductive with spin coating techniques. At the FTO glass with the variation of the deposition area of 0.5 cm$^2$, 1 cm$^2$, 1.5 cm$^2$, 2.25 cm$^2$ and 3 cm$^2$, and FTO side was masking tape affixed. Pasta TiO$_2$ dripped on FTO glass that has been glued in the spinner, then stirring with a speed of 200-300 rpm. The next is it was heated using a hotplate at 500$^0$C for 60 minutes, then cooled at room temperature.

2.6. Assembly of Sandwich DSSC
The composition of the DSSC in the form of glass FTO that has been coated with TiO$_2$ and has been soaked in dye, and then called the working electrode. The working electrode is etched with an electrolyte solution and then it was covered of platinum layer or called the counter electrode. Then the composition of DSSC is clamped on both sides of the right and left. Once formed system Sandwich DSSC then characterized current and voltage (I-V), which indicates how much the DSSC capable of converting light energy.

3. Result and Discussion

3.1. Absorption Spectra of natural dye doped Cu
The data of absorbance using UV-Vis Spectrometer lambda 25 with a wavelength range between 200-800 nm. Figure 1 shows that the maximum absorbance of Zingiber dye from 243 nm to 279 nm, Cinnamomum dye approximately from 253 nm to 403 nm, Curcuma dye from 243 nm to 422 nm, while Oryza dye from 240 nm to 423 nm. From the figure 1, the widest range of absorption is Oryza dye, so that Oryza can absorb more energy ultraviolet and visible light.

![Figure 1. The absorption spectrum of dye.](image)
Absorbance on figure 1 can work in the ultraviolet (UV) and visible (VIS) light, which is the area of energy absorption to excite electrons in the dye molecule. The result will be more electron are released from Higher Occupied Molecular Organic (HOMO) to the bandgap and then headed to Lower Unoccupied Molecular Organic (LUMO) in the dye molecule. The result will be formed holes in the HOMO and free electron in the LUMO, then the free electron flow to conducting TiO$_2$. The conduction band of TiO$_2$ can be the trapping of electrons from the dye. Increase the value of absorbance in accordance with the law of Lambert-Beer (equation 1).

3.2. Conductivity of dye+Cu

Characterization is electrical conductivity using El-kahfi 100 / IV-Meter with irradiation from halogen lamp of 680.3 W/m$^2$. The electrical conductivity is the ability of a material to conduct electricity when a potential difference was placed at the ends of a conductor, then the electron move through the material.

The TiO$_2$ is a conductor, which has functions can delivering electron generated by the dyes. Figure 2 shows that the Zingiber conductivity value by using the equation two, worth of 0.29 Ω$^{-1}$m$^{-1}$, Cinnamomum of 0.11 Ω$^{-1}$m$^{-1}$, Curcuma of 0.177 Ω$^{-1}$m$^{-1}$, and Oryza dye of 0.21 Ω$^{-1}$m$^{-1}$. From the four materials, the ability of Zingiber dye to conduct electrons is the best, so it increase of power solar cells. The greater of conductivity value is indicates that the resistance it worth getting smaller, so the produce of electrons can increased.

3.3. 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 in under irradiation with a halogen light 1000 W/m$^2$. The test with immersion 24 hours in FTO area of 0.5 cm$^2$, 1 cm$^2$, 1.5 cm$^2$, 2.25 cm$^2$ and 3 cm$^2$.

The highest light energy was absorbed by the dye, it is proportional to the number of excited electros. Excitation electron of dyes molecule occur from HOMO to band gap and then passed to LUMO. After that, the electron will flow to the TiO$_2$, or forwarded to the working electrode. Working electrode layer is TiO$_2$, that functioning as an electron acceptor from the dye. Besides being able to
forward the generated electrons dye, TiO$_2$ semiconductor can also produce electron as a result of absorbing light energy, but relatively small so that it was ignored.

![Figure 3. I-V curve of Curcuma longa L. Dye.](image)

The thickness of TiO$_2$ on FTO glass rather FTO will influence of electrons flow. TiO$_2$ is a kind of a semiconductor with a band gap value of 3.2 eV which is suitable for use in solar cells. TiO$_2$ will produce a hole and will function as an electron dye trap. The hole will catch or pass on electrons from the dyes. If the thickness is too thin, the amount of TiO$_2$ little hole, then the electrons will be forwarded to an external circuit is not optimal. With proper TiO$_2$ coating thickness, hence maximizing the trapped electrons with the electrons flowed, so the current flow will also be the maximum, that will produce the highest efficiency. If too thick, the electrons trapped too many, then flow to the external circuit, so that electron flow to the external circuit is not optimal. From Figure 3, found that the efficiency ($\eta$) of organic dyes is presented in Table 1.

| Dye         | $V_{OC}$ (mV) | $I_{SC}$ (mA) | $V_{MAX}$ (mV) | $I_{MAX}$ (mA) | FF | $\eta$ |
|-------------|--------------|---------------|----------------|----------------|----|--------|
| Zingiber    | 0.370        | 5.9 x 10$^{-5}$ | 0.175          | 4.7 x 10$^{-5}$ | 0.38 | 0.006  |
| Cinnamomum  | 0.230        | 7.9 x 10$^{-5}$ | 0.140          | 4.5 x 10$^{-5}$ | 0.35 | 0.002  |
| Curcuma     | 0.580        | 8 x 10$^{-4}$  | 0.370          | 5.8 x 10$^{-4}$ | 0.46 | 0.072  |
| Oriza       | 0.430        | 3.3 x 10$^{-4}$ | 0.310          | 2.8 x 10$^{-4}$ | 0.61 | 0.039  |

The result can conclude that the DSSC that produces the best performance in Curcuma longa L dye with efficiency is 0.072%, while Cinnamomum dye only 0.002%. The value efficiency of the material of organic compounds is still small (under 1%). For increase the performance DSSC, we can be using different counter electrode with polyaniline (PANI), because PANI was increased efficiency from 6.90% (platinum) to 7.15% using PANI [9], using of electrolyte which has viscosity is smaller than iodine such as PEO polymer gel [10].

4. Conclusion
The results were showed that the Zingiber dye has a maximum absorbance from 243 nm to 279 nm, photoconductivity of 0.29 $\Omega^{-1}$m$^{-1}$ and the efficiency is 0.005% on 0.15 cm$^2$. While Cinnamomum dye were showed absorbance from 253 nm to 403 nm, photoconductivity of 0.11 $\Omega^{-1}$m$^{-1}$ and the efficiency is 0.002% on 3 cm$^2$ area. In Curcuma longa L dye were showed absorbance from 243 nm to 422 nm,
photoconductivity of 0.177 Ω⁻¹ m⁻¹ and the efficiency is 0.072% on 3 cm². The *Oryza sativa L. indica* dye were showed absorbance from 240 nm to 423 nm, photoconductivity of 0.21 Ω⁻¹ m⁻¹ and the efficiency is 0.039% on 2.25 cm². So it can be concluded that the best absorbance value is in the *Oryza sativa L. indica* dye, the highest photoconductivity is in *Zingiber* dye, and the highest efficiency is in *Curcuma longa L.* dye.

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