The effect of Cu doping into *Oriza sativa L. indica* dye as photosensitizer for dye sensitized solar cell (DSSC)

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Abstract.The aims of the research to are know the effect of Cu doping into natural dye in increasing the efficiency of DSCC, to determine of the optical and electrical characteristic of natural dye Cu doping. Sandwich structures formed in the sample consisted of working electrode pair Titanium Oxide (TiO_2) and the counter electrode Platina (Pt). Absorbance test is measure by using UV-Visible spectrophotometer Lambda 25, conductivity test by using a two-point probe *El Kahfi/I-V Meter*, and characterization of current and voltage (*I-V*) by using a Keithley 2602A. The Cu doping into dye was increasing the efficiency of 71%.

1. Introduction

DSSC is the third generation of solar cells which can be an alternative to cell conventional solar silicon. DSSC material purchase costs are cheap, easy in production, but the efficiency is still small [1]. There are 4 main components in DSSC, which is a semiconductor as working electrode (TiO_2 and Cu metal), a dye sensitive to the absorption of light, an electrolyte and a counter electrode such as platinum (Pt). TiO_2 nanoparticels in FTO and Cu metal serves as the electron catcher for providing hole. The counter electrode which serves as a catalyst while transferring electrons to the electrolyte. Electrolyte generate electrons for their redox reactions are repeated, 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 atoms of dye towards the hole of Cu and TiO_2 layers. Furthermore, electrons move to the FTO layers and to external sircuit, then the electrons towards the platinum layer and electrolyte. Dye used comes from Black Rice. Sianidin 3 glucoside is black rice anthocyanin type of this role to give the red color purple or dark red. Black rice has anthocyanin content of (105.11 ± 7.76) mg / 100 g [2].

To improve the performance of DSSC, using metal inserted into the dye. The synthetic form of Cu metal was used is copper (II) sulphate pentahydrate ($CuSO_4.5H_2O$), because it was easily to found [3]. Titanium dioxide (TiO_2) is material used as the working electrode in DSSC. Energy gap (Eg) from TiO_2 rutile and TiO_2 anatase is 3.0 eV and 3.2 eV. Eg anatase is the highest because the active surface area is larger and more effective photocatalysts [4]. 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 [5]. The counter electrode of platinum (Pt) has been the material of choice because it is an excellent catalyst for reducing triiodide [6]. Platina serves to reduce the resistance on the FTO glass. Electrolytes used in this study is a mixture of iodine (I_2) with Potassium Iodide (KI) or Sodium Iodide (NaI) into the polyethylen glycol (PEG). Electrolytes

are 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_2 [7].
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.

$$A = \varepsilon .b.c \qquad (1)$$

Were A is the absorbance and ε is the molar absorptivity coefficient ($molar^{-1}.L^{-1}$). While b is the thickness of the medium through which the beam (cm), and c is the concentration of the sample solution (ppm) [8]. Determination of the conductivity of a material can be calculated by equations 2.

$$\sigma = d/R.A \qquad (2)$$

With σ is the conductivity (Ωm^{-1}) and R is the resistance of materials (Ω). While d is the distance between the two electrodes (m) and A is the cross-sectional area (m^2).
Performance solar cells is 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. Simillary 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. Performance solar cells is determined by comparing maximum power from multiplication result V_{oc} and I_{sc}.

2. Experiment

2.1. Preparation of TiO_2 Solution

Titanium (IV) Oxide nano particle is anatase Titanium Dioxide powders, 99.8% trace metals basis. Pasta TiO_2 of 0.5 grams dissolved in 3 ml of ethanol, then stirred of 500 rpm for 30 minutes.

2.2. Preparation of Natural Dye Sensitizers and Doping Copper (Cu)

10 grams of *Oriza sativa L. indica* was crushed using a blender. Then the materials was dissolved in ethanol, acid acetate and distilled water used to have ratio of 25:4:21 so that the value high absorbance of the solution because the best anthocyanin concentrate [9]. Then stirred of 300 rpm at 30°C for 30 minutes. Materialis was allowed to stand for 24 hours and it was filtered with a filter paper quality no.42. Then the dye black rice was mixed with solution of Cu. The solution made of copper sulfate pentahydrate ($CuSO_4.5H_2O$) with mass variation of 0.01 grams, 0.1 grams, 1 grams, 2 grams, 3 grams, and 4 grams. Then was dissolved in ethanol, acid acetate and distilled water then stirred of 300 rpm at 30°C for 60 minutes. Then it was filtered with a filter paper quality no.42. Dye and dye+Cu then tested of absorbance using UV-Vis *Spectrometer Lambda 25* and conductivity using El Kahfi *I-V meter 2602A*. Dye said to be able to work if it has absorption in the ultraviolet and visible, while the conductivity states how large are able to pass an electric current.

2.3. Preparation of Electrolyte

Potassium iodide (KI) solids of 0.8 grams are mixed into 10 ml polyethylen glycol then stirred at 300 rpm for 30 minutes. Then was added iodine (I_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 of 300 rpm for 30 minutes. Then the solution was dropped on FTO glass with size 1x1cm and the side masking tape affixed. FTO glass with size 1x1cm is heated at 250^0C for 15 minutes and then the solution of 3 ml was dropped on FTO.

2.5. Preparation of TiO_2

The working electrode is made of glass on which the FTO conductive paste deposited TiO_2 nano with spin coating techniques. At the FTO glass with size 1x1cm and FTO side masking tape affixed as a barrier. Pasta TiO_2 dripped on FTO glass that has been glued in the spinner, then stirring with a speed of 200-300 rpm. FTO glass that has been coated with TiO_2 is 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 a dye or dye+Cu, and then called the working electrode. The working electrode is etched with an electrolyte solution and then covered with glass that has been coated with platinum, and then 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* lamda 25, and in Figure 1 the maximum absorbance of dye *Oriza sativa L. indica* is 0.1646 a.u at wavelength (λ) 232 nm and 0.018 a.u at λ 531 nm. While maximum absorbance for dye+Cu 4 grams (0.73 M) to shifted between the value of 1.405 a.u (242 nm) and 0.126 a.u (531 nm). Then the maximum absorbance of TiO_2 is 0.069 a.u (341 nm), and the greatest absorbance of TiO_2+dye+Cu 4 grams is 0.33 a.u (324 nm).

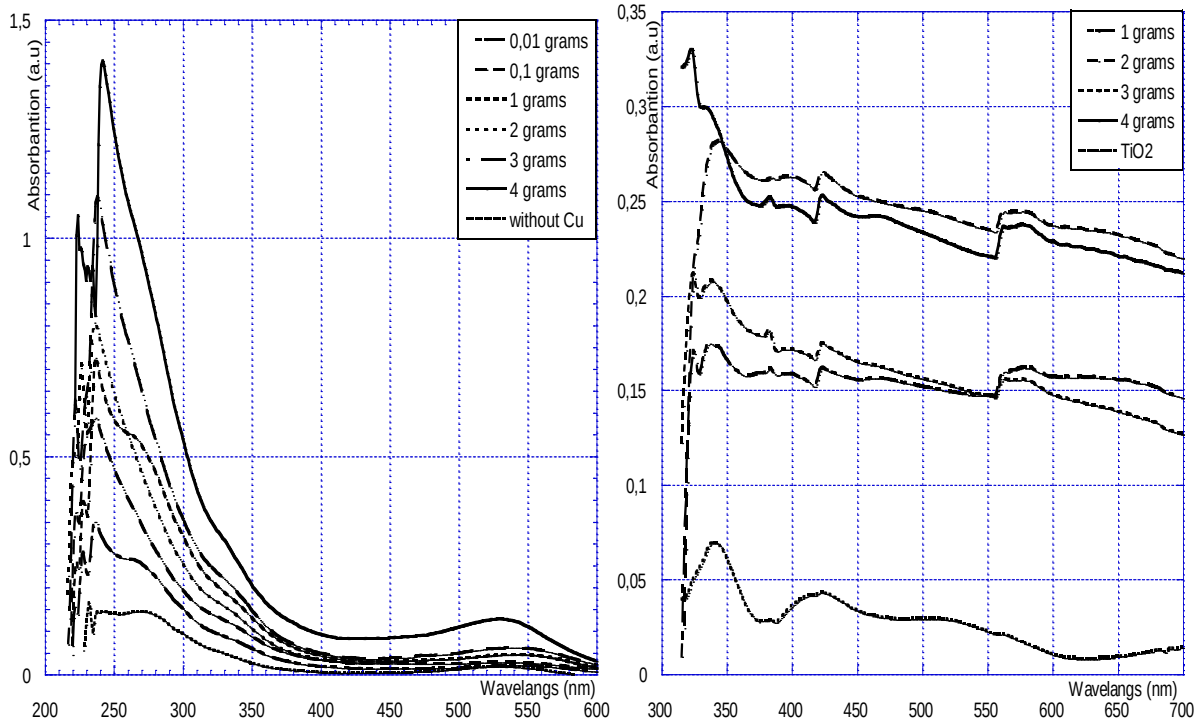

Figure 1. Absorption spectrum of (a) dye+Cu and (b) TiO_2+dye+Cu

Absorbance on figure 1 are able to work on the ultraviolet (UV) and visible (VIS) light, which is the area of energy absorption to excite electrons in the dye molecule. For figure 1(a) and figure 1(b) with the addition of Cu into the dye (dye+Cu), so it will be able to absorb the light energy is greater. The result will be more electrons are released from Higher Occupied Molecular Organic (HOMO), to the bandgap and then headed to Lower Unnocopied Molecular Organic (LUMO) in the dye molecule. The result will be formed holes in the HOMO and free electrons in the LUMO. Free electrons that which will then be forwarded to conducting Cu and TiO_2. But the electrons from the dye can also go directly to the conduction band of TiO_2 because the dye can be attached directly to TiO_2. The conduction band of TiO_2 can be trapping of electrons from the dye or from Cu. So that the number of Cu was affected the electrons can be captured and then channeled to the external circuit. Increase value of absorbance in accordance with the law of Lambert Beer (equation 1). In figure 1(b) the absorbance values of TiO_2 with dye+Cu 3 grams smaller than 2 grams, this is because the sample is less homogeneous when tested, but overall, Figure 1 shows the absorbance value at 4 grams of Cu is the highest, in λ 320 nm.

3.2. Conductivity of dye+Cu

Characterization is electrical conductivity using Elkahfi 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 is placed at the ends of a conductor, electrons move through the material.

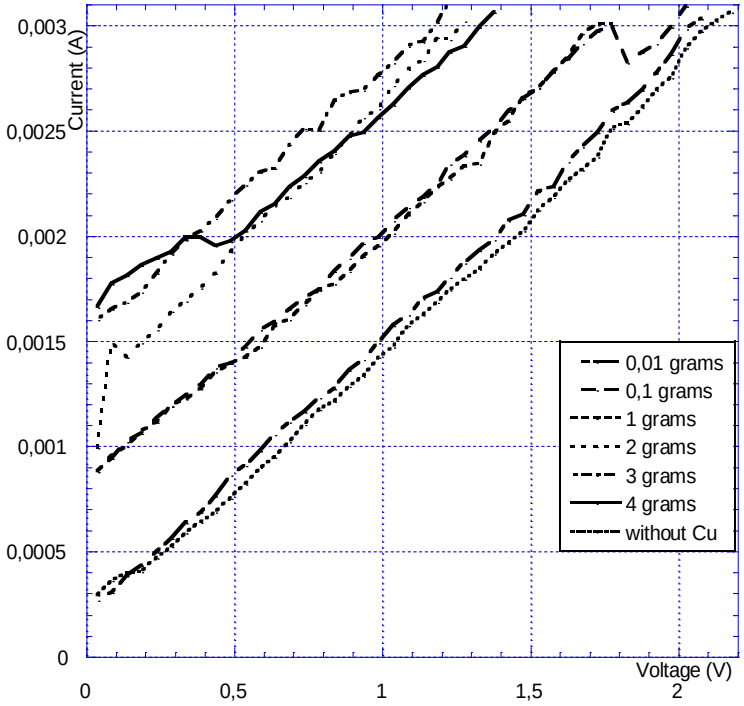

Figure 2. Conductivity Curve for dye with Cu

The Copper is a conductor, which has functions can delivering electrons generated by the dye. Figure 2 shows that the tendency of increase in the value of the conductivity is proportional to the increasing mass of Cu were added in the dye. By using the equation 2, conductivity of dye+Cu 3 grams worth 0.2509 $\Omega^{-1}m^{-1}$, then in the dye+Cu 4 grams only worth 0.2339 $\Omega^{-1}m^{-1}$. Values of 4 grams look smaller then 3 grams, it could be due to a mixture of dye+Cu solution with the solvent is not homogeneous, so the resulting in resistance value solution is still greater then the rate of flow in the solution inhibited. While the value of conductivity for dye is only 0.0669 $\Omega^{-1}m^{-1}$. The results of 3 grams and 4 grams have great conductivity, when compared to the other insertion conductivity values. This suggests that the ability to conduct electrons at the insertion of 4 grams is still the best. The greater of conductivity

value is indicates that the resistent it worth getting smaller, so the electrons that are drawn will be more.

3.3. Photovoltaic Properties

Characterization of the current-voltage (I-V) is a method to determine how much ability DSSC can convert light in to 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 1 cm^2. The dye+Cu 4 gram in 4 layers the largest value of efficiency, because the value of V_{in} intercept at 3.4 x 10^{-1} mV and the value I_{in} intercept at 2.5 x 10^{-4} mA. (See in Figure 3 and Table 1).
The mass of the copper used, it appears that the test absorbance on insertion 4 grams of Cu generate the highest value. Insertion of Cu into a dye, producing the highest absorbance value for the light energy will be absorbed by the dye, and is proportional to the number of excited electrons. Excitation electrons occurs from HOMO to band gap and then passed to LUMO. After that, electron will flow to the Cu, subsequently forwarded to the working electrode. Working electrode layer is TiO_2, that functioning as an electron acceptor from Cu or from the dye. The electrons from the dye can also go directly to the TiO_2, because dye can be attached to TiO_2.

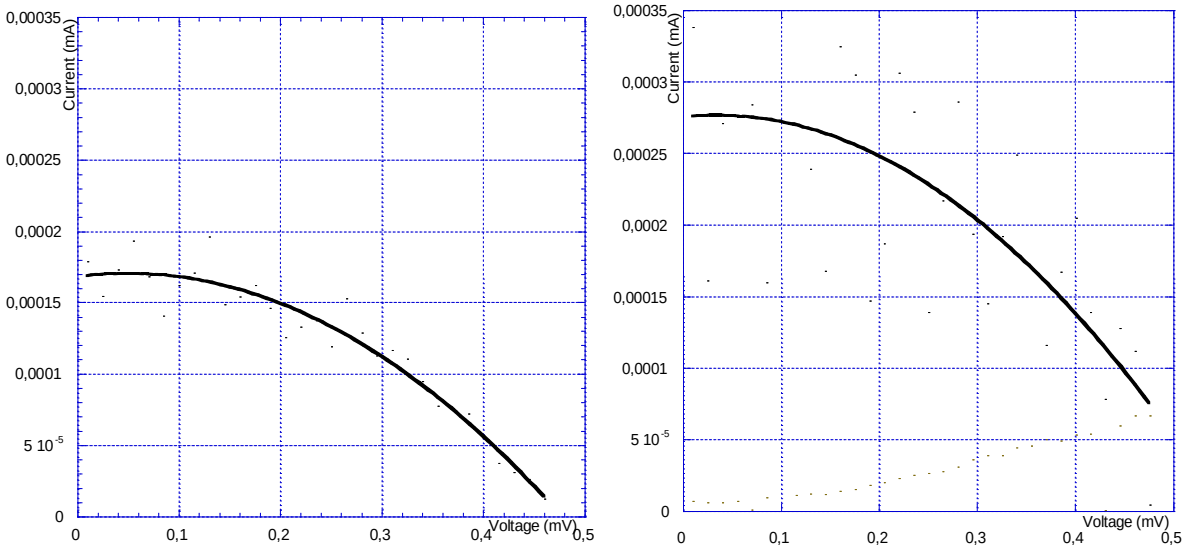

Figure 3. I-V curve with 4 layers of TiO_2 for (a) dye, (b) dye+Cu 4 gram

Besides being able to forward the generated electrons dye, TiO_2 semiconductor can also produces its own electron as a result of absorbing light energy, but relatively small so that it can be ignored. Likewise with dye+Cu conductivity are large, so the ability to transfer electrons from the dye will be faster in proportion to the amount of Cu is inserted in dye. Then the electrons will flow to the Cu and moved toward the working electrode to an external circuit.

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 be functions as an electron dye trap. Hole will catch or pass on electrons from the dye, or from Cu. 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, before they could be forwarded to the external circuit, so electrons will be forwarded to an external circuit is not optimal. (See Table 1 and equation 1).

Table 1. Photovoltaic performance with natural dyes from different doping Cu

Dye Source	*Iin (mA)*	*Vin (mV)*	*Isc (mA)*	*Voc (mV)*	*(%)*
Without Cu (4 layers)	0.00014	0.34015	0.00022	0.47521	0.04961
0.01 grams (3 layers)	0.00014	0.32504	0.00013	0.50513	0.04473
0.1 grams (3 layers)	0.00010	0.37007	0.00019	0.50515	0.03797
1 grams (3 layers)	0.00007	0.37008	0.00013	0.43010	0.02574
2 grams (3 layers)	0.00009	0.31006	0.00004	0.44512	0.03051
3 grams (3 layers)	0.00010	0.26508	0.00011	0.47565	0.02774
4 grams (3 layers)	0.00013	0.40003	0.00007	0.46009	0.05169
4 grams (4 layers)	0.00025	0.34026	0.00034	0.53531	0.08460
4 grams (5 layers)	0.00023	0.23507	0.00033	0.46021	0.05419
4 grams (6 layers)	0.00017	0.25002	0.00021	0.44517	0.04167

To improve efficiency need to insert a metal, in this case $CuSO_4.5H_2O$ produce good conductivity, increase absorption, and can reduce the electron hole recombination. The result can be concluded that the DSSC that produces the best performance in 4 layers at the dye+Cu of 4 grams with efficiency is 0.08460%, while the dye only 0.04961%. The value efficiency of the material of organic compounds is still very small (under 1%). For increase the performance DSSC, we can be using different counter electrode with polyaniline (PANI), because PANI can increase efficiency from 6.90% (platinum) to 7.15% using PANI [10], using of electrolyte which has viscosity is smaller than iodine such as PEO polymer gel [11].

4. Summary

The results of the absorbance these material are able to work on the UV-Visible light and the highest value of dye+Cu of 4 grams. The largest conductivity value is dye+Cu of 3 grams. Where as the greatest efficiency in achieved by using dye+Cu of 4 grams (0.73 M) in 4 layers in the amount of 0.0846%, the Cu doping into dye was increasing the efficiency of 71%.

5. Acknowledgement

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