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Krokot (*Portulaca oleracea*. L) As a Natural Sensitizer for TiO_2 Dye-sensitized Solar Cells: The Effect of Temperature Extract

Reyza Anni Mufidah, Khamidinal, Endaruji Sedyadi and Didik Krisdiyanto*
Department of Chemistry, Faculty of Science and Technology, UIN Sunan Kalijaga
Jl. Marsda Adisucipto No 1 Yogyakarta 55281, Indonesia. Tel. +62-274-540971, Fax. +62-274-519739

Author correspondency*:
didik_kris@yahoo.com

Abstract

The solar cell is formed by a sandwich structure, in which two electrodes flank the primary electrolyte that is containing redox I^-/I_3^- based on PEG (Polyethylene Glycol). The working-electrode which is TiO_2 layer on an ITO glass substrate is sensitized with krokot dye as the electron donor. The counter electrode is a layer of carbon. The fabrication cell is immersed with the krokot dye with 40°C, 50°C, and 60°C extract temperature. The result of the UV-Vis shows that the absorption of wave-length from dye extract of krokot is located in the visible region with the absorbance peak in 420.5 nm and 665.5 nm which are the peak of chlorophyll. For the UV-Vis solid system, there are the highest band gap in 50°C extract temperature that make the capability of absorption toward UV spectrum is large. Furthermore, in the functional group analysed by FT-IR, there are shiften-carbonil and hydroxyl group after they are sensitized. From the current and voltage test with I-V meter keithley 2400 is resulted that on the 50°C extract temperature produces the highest efficiency of reaches which is 2.63 x 10^{-3} %.

Keywords: Dye Sensitized Solar Cell (DSSC), krokot dye, chlorophyll, TiO_2

Introduction

The solar cell is one way to harness solar energy in which the device is able to convert the sunlight energy into electrical energy. In principle, the solar cell work is similar to the photosynthesis work in plants. Light energy is used to produce free electrons. Solar cell uses free electron to generate electrical energy while the plant uses the free electron to produce chemical energy (Yuwono. *et al*. 2011).

The development of solar cells based on dye sensitized began in 1991 when for the first time Grätzel and O'Regan designed the basic forms of solar cell based on film of titania semiconductor that is known as dye-sensitized solar cell (DSSC) in which these systems can convert solar energy into electrical energy (O'Regan & Gratzel, 1991). This mechanism shows the optical absorption and charge separation processes through the association of a sensitizer as a light absorber with a nanocrystal semiconductor that has a wide bandgap (Gratzel, 2003).

A DSSC consists of a pair of coated glass TCO substrate (Transparent Conducting Oxide) as the electrode and the counter electrode, the redox electrolyte that contains iodide and triiodide ion (I^-/I_3^-) carbon layer as the catalyst, porous TiO2 nanocrystal as fotoanoda, and a dye photosensitizer (O'Regan & Gratzel, 1991). All components are arranged in front of the sandwich structure where the top layer is the working electrode as the initial layer in receiving photons and the lower layer is the counter electrode and the middle is electrolyte to regenerate electron.

Dye criteria that can be used as a dye sensitizer is adsorption intensity at visible wavelengths, strong adsorption on the surface of the semiconductor, has the ability to inject electrons to the band conduction of the semiconductor, and has a group = O or -H to bind to the surface of TiO_2 which can increase the reaction rate of the electron transfer (Ludin, *et al*, 2014). Therefore, this study will utilize the potential of the natural dye that derived from extracts of krokot which are expected to fulfill the requirement as a natural sensitizer. Optical and electrical test are done in order to determine the compliance of the requirement and can be used in DSSC system.

Materials and Methods

Materials

Krokot, Indium Transparent Oxide (ITO), TiO_2 (degusa), KI, I2, polyethylene glycol, ethanol 96%, Polyvinyl alcohol (PVA), aquades, graphite pencil 8B and detergent

Methods

Sonikator, ultrasonic cleaner, hotplate, glassware, aluminium foil, paper clips, scothlite, screen proyektor (gasket) and cutter. spektrofotometer UV-Vis single beam, UV-Vis spekular reflektansi UV 1700 Pharmaspec, Fourier Transformation Infra-Red (FT-IR) Shimadzu and I-V meter Keithley 2400 Source Meter

Procedure

Krokot extraction (Portulaca oleracea L.)

Ten grams of krokot powder are macerated with 120 mL of 96% ethanol for 24 hours at 40°C, 50°C, 60°C and normally solution temperature. Then, it is filtered by using vacuum filtration and before it is used for further processing, it should be analyzed first using UV-Vis spectrophotometer in the wavelength range 400-700 nm.

Preparation of Working Electrode

TiO2 powder was weighed as much as 1.5 grams and then inserted into erlenmeyer and added with 3 mL of aquades. Then, it is stirred with a magnetite stirring spoon and sonicated with 20 kHz frequency for 2 hours. The next solution was then added with polyvinyl alcohol solution which previously has been made from 0.5 grams PVA added with 6 mL of aquades by heating at a temperature of 150oC until all of PVA are dissolved. The mixing is followed by stirring for 10 minutes until it is formed a homogeneous paste. Then, it is performed TiO2 paste deposition on surfaces glass of Transparent Indium Oxide (ITO) with Doctor Blanding technique. But before it, ITO should be washed with detergent and followed by aquades using ultrasonic cleaner for 10 minutes and rinsed with ethanol. Before TiO2 paste is dropped on ITO glass, the conductive part should be found and then each of it is given a scotchlite restraint and it is made a rectangular pattern by leaving a 1.8 x 1.3 cm room. Furthermore, in above of that fields, the TiO2 paste is distributed evenly with a glass rod and then dried in the air and the scotchlite is opened, then it is heated at 80 ° C for 1 hour.

Preparation of Elektrode TiO2/ dye

TiO2 film is inserted into the krokot extract, the container is covered with aluminum foil and then it is saved for 1, 8, 18 and 26 Hours. The film which has been soaked then removed and rinsed with ethanol to clean the edge of the layer. Then,it is dried at room temperature and analyzed by UV-Vis reflectance spectrometer and FT-IR. Gap energy calculation using the following equation:

$$R'\infty = \frac{R\infty\,(S\ \ \ )}{R\infty\,(S\ \ \ )} \quad (1)$$

$$F(R'\infty)\frac{(1-R'\infty)^2}{2R'\infty} \quad (2)$$

The calculation is performed on each sample by using the Kubelka Munk method in which the gap energy is obtained from the graph of hv (eV) vs. (F (R'∞) hv) 1/2 (Mikrajuddin & Khairurijal, 2010).

Preparation of the counter electrode

The graphite of a 8B pencil is spread into the surface of ITO on the conductive layer with the shading manner to average carbon layer. Then, it is heated at temperature of 300oC for 1 Hour.

Preparation of Electrolytes

Potassium iodide (KI) is weighed as much as 0.815 grams and then dissolved in 10 mL of polyethylene glycol (PEG) 400 and stirred until dissolved then added with 0.128 grams of I2 and stirred again until completely mixed. The finished Electrolyte solution then stored in the dark bottles and also sealed.

Fabrication of Dye-Sensitized Solar Cell (DSSC)

DSSC fabrication which is used is a sandwich construction with a composition such as: glass-ITO working electrode (TiO2 layer) that has been coated with dye-screen projector-counter electrode (carbon layer) – ITO glass. The use of screen proyector is intended to prevent the short on DSSC system. At the ends of the glass that does not stick together is spilled with the electrolyte solution and allowed to seep between the two layers after it is clamped with paperclip (binder clips) on two opposite sides are not coated.

Characterization of currents and Voltage DSSC

DSSC prototype was tested by measuring the I-V characteristic curve using a digital multimeter Keithley 2400, in the light of a xenon lamp at an intensity of 1000 W / m2.The result of the I-V characteristic curves test were then analyzed Voc, Isc, fill factor, and the efficiency of solar cells (Lee & Misook, 2010) by the equation:

$$F \ = \frac{V_{ma}\ .I_m}{V_o\ .I_s} \quad (3)$$

$$\eta = \frac{V_o\ (V).I_S\ (A).F}{P_{i}\ \left(\frac{W}{c\ \ 2}\right).A\,(c\ \ \ ^2)} \quad (4)$$

Results and Discussion

Characterization of Optical properties krokot dye at diffrerent temperature extract

The result of characterization of Krokot dye absorption spectrum in different extract temperature was showed at Figure 1.

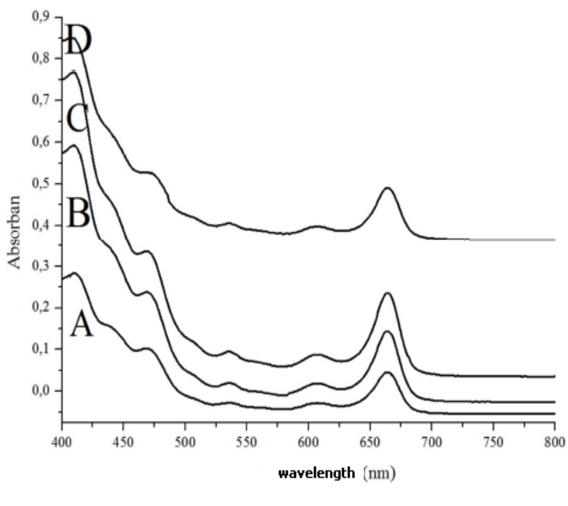

Figure 1. The graph of krokot dye (A) normally solution temperature extract (B) 40°C temperature extract (C) 50°C temperature extract (D) 60°C temperature extract.

Figure 1 shows the Krokot extract absorbs the blue spectrum (400-450 nm) and red (650-700 nm) with peak absorbance is absorbed at λ = 420.5 with a absorbance value of 2.678 Abs, λ = 536.5 with a absorbance value of 0.567 Abs, λ = 608 with a absorbance value of 0.473 Abs and λ = 665.5 with absorbance values of 1.753 Abs so that from the great absorbance at a wavelength of 420.5 nm and 665.5 nm can be known that the more dominant krokot extract contains the pigment chlorophyll. This is because the wavelength is included in the wavelength range of visible light. So that chlorophyll can be used as a dye in DSSC because it has characteristic to absorb the visible light that produced by sunlight.

Temperature extract was influence the absorbance intensity that in hight temperature was decrease the adsorbance intensity. It was indicated that the pigment chlorophyll decresed in dye with hight temperature extract. The pigment chlorophyll was convert into pheophytin pigment in heat treatment (putri et al 2013, gross, 1991).

Characterization of Thin Layer electronic properties TiO2-Dye

Figure. 2 shows the absorbance graphic of plot toward thin film wavelength of TiO2 that has been soaked in dye with variation of temperature extract.

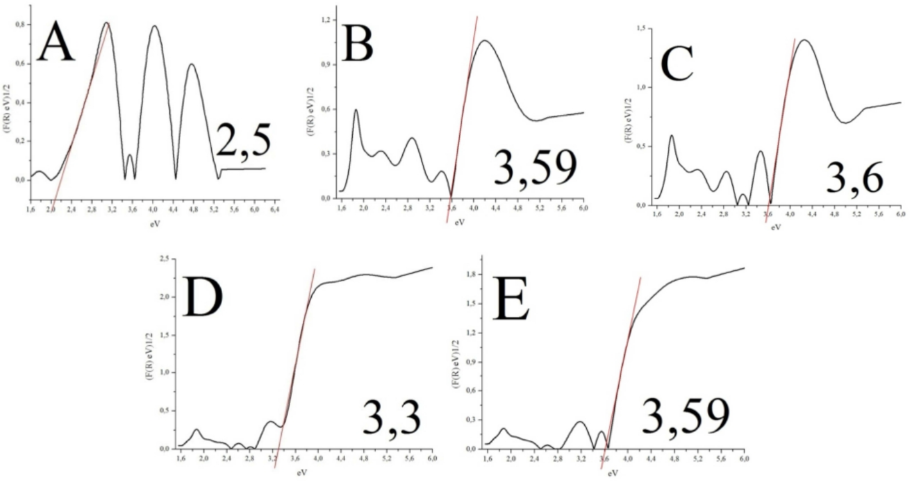

Figure 2. Energy gap (A) thin layer TiO2, (B) thin layer TiO2-dye solution temperature extract (C) thin layer TiO2-dye 40°C temperature extract (D) thin layer TiO2-dye 50°C temperature extract and (E) thin layer TiO2-dye 60°C temperature extract.

Absorbance is used to calculate the band gap energy (Eg) in the film of TiO2 and TiO2-dye film with temperature extract variation by tauc plot method. Figure. 2 shows that the form of the TiO2 band gap is 3.3 eV. This value fullfills the major requirements of semiconductor material that will be used as a DSSC where its band gap energy should more than 3.0 eV so that be able to absorb the energy of the photon in the most of the spectrum of sunlight.

At the variation temperature extract of film TiO2 immersion in the dye for 1 hour there was an Eg increasing. This is as expected that the higher temperature extract capable to increase Eg on TiO2 so that allowing the electrons injection of dye sensitized into the conduction band of nanoparticles TiO2 becomes easier because it takes a lower photon for excitation mechanism or in other words the deposited TiO2 has been more active in the area of low energy or visible light region.

Characterization with Fourier Transform Infra-Red (FT-IR)

Infrared absorption spectrum of a material has a distinctive pattern so that it possible to identify the material and also shows the existence of the major functional groups in the identified structure. The bond can be estimated if the IR spectra of TiO2-dye system shows the appearance of a significant new peak or functional groups shift if it is compared with the spectra of dye and spectra of TiO2film. Krokot extract used in this study contains carboxyl and carbonyl because in the analysis that uses UV-Vis is identified to contain chlorophyll so it is possible there is efficient sensitization through the formation of a bond between the dye and TiO2.

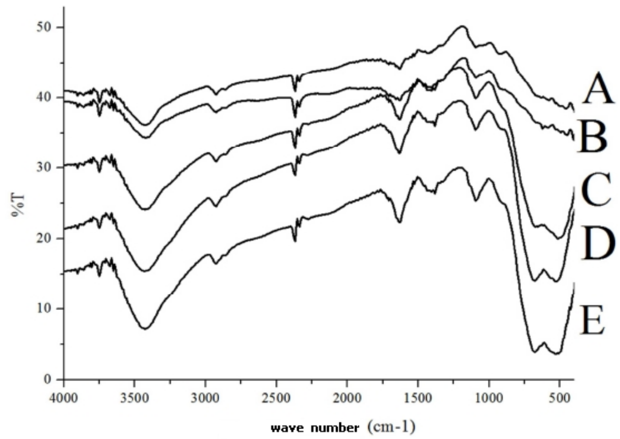

Figure 3. Infrared spectra (A) thin layer TiO2, (B) thin layer TiO2-dye solution temperature extract (C) thin layer TiO2-dye 40°C temperature extract (D) thin layer TiO2-dye 50°C temperature extract and (E) thin layer TiO2-dye 60°C temperature extract.

The results of FTIR analysis for TiO2 film, and TiO2-dye film of Krokot extract is shown in the Fig. 4 which shows the existence of the carbonyl absorption at wave number 1627.92 cm-1 and there is absorption at 3425.58 cm-1 region which is the absorption area of hydroxyl groups. Carbonyl and hydroxyl group that is owned by krokot extract that can bind to the group of Ti (IV) on TiO2.

From FTIR analysis is not seen the significant difference from treatment with variation of temperature extract. It is only seen the carbonyl absorption shift of in TiO2 film is at a wavelength of 1635.64 cm-1 shifted to a wave number 1627.92 cm-1. This shift occurs when a film of TiO2 is coated with krokot extract.

Current and Voltage Measurement Systems Solar Cells

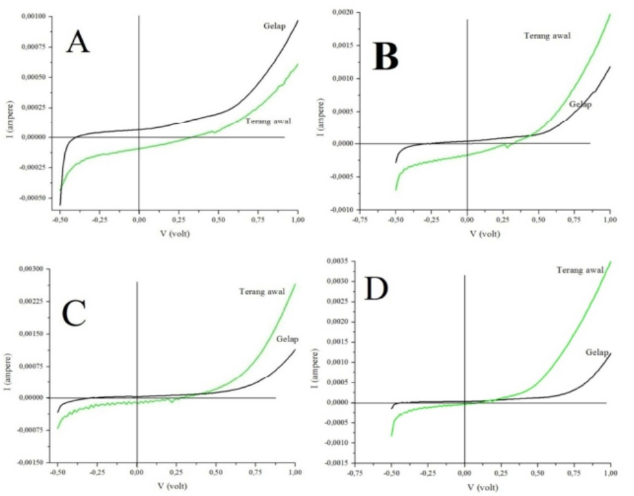

Figure 4. IV meter grafic (A) thin layer TiO2-dye solution temperature extract (B) thin layer TiO2-dye 40°C temperature extract (C) thin layer TiO2-dye 50°C temperature extract and (D) thin layer TiO2-dye 60°C temperature extract

In Table. 1 the efficiency obtained by determining the amount of voltage and the maximum current shown in the fig. 5. From that figure, it can be seen that the current legible shows the dye on TiO2 layers undergo the electron transfer from the excited state of the dye to the conduction band of TiO2. The highest efficiency found in a layer of TiO2-dye with a 40°C temperature extract with an efficiency of 2.63 x 10-3%.

Table. 1. The parameters of solar cells.

Ekstrak krokot	Isc (μ)	Voc (mV)	FF	η(%)
Ekstrak krokot A	0.092	0.32	24.4565217x10^{-2}	1.44x10^{-3}
Ekstrak krokot B	0.165	0.31	25.7576x10^{-2}	2.635x10^{-3}
Ekstrak krokot C	0.08	0.135	29.1667x10^{-2}	6.3x10^{-4}
Ekstrak krokot D	0.034	0.09	34.3137x10^{-2}	2.1x10^{-4}

In this study, the little DSSC efficiency which is produced can be caused by the performance of the natural dye used is still low due to the effect of the extract used still contains a lot of pigment with the long structure R which lead steric hindrance of the pigment to the surface band structure so as to prevent oxidation of TiO2 molecules bind with TiO2 in effective to cause the transfer of electrons from the conduction band to the dye molecule is reduced.

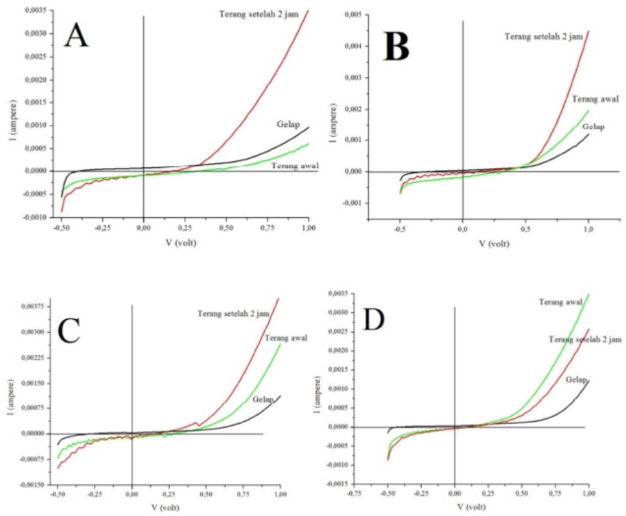

Figure 5. IV meter grafic after 2 hours irradiated (A) thin layer TiO2-dye solution temperature extract (B) thin layer TiO2-dye 40°C temperature extract (C) thin layer TiO2-dye 50°C temperature extract and (D) thin layer TiO2-dye 60°C temperature extract.

Table. 2. The parameters of solar cells after irradiated.

Ekstrak krokot	Isc (μ)	Voc (mV)	FF	η%	Δ η(%)
Ekstrak krokot A	0.092	0.32	24.4565217 x 10^{-2}	1.44 x 10^{-3}	40.27778
	0.09	0.17	28.104575 x 10^{-2}	8.6 x 10^{-4}	
Ekstrak krokot B	0.165	0.31	25.7576 x 10^{-2}	2.635 x 10^{-3}	86.33776
	0.045	0.1	0.4	3.6 x 10^{-4}	
Ekstrak krokot C	0.08	0.135	29.1667 x 10^{-2}	6.3 x 10^{-4}	-11.1111
	0.135	0.145	17.8799 x 10^{-2}	7 x 10^{-4}	
Ekstrak krokot D	0.034	0.09	34.3137 x 10^{-2}	2.1 x 10^{-4}	16
	0.035	0.092	27.3913 x 10^{-2}	1.76 x 10^{-4}	

Conclusion

The result of the UV-Vis shows that the absorption of wave-length from chlorophyll pigment. For the UV-Vis solid system, there are the highest band gap in 50°C extract temperature. The functional group analysed by FT-IR, there are shiften-carbonil and hydroxyl group after they are sensitized. From the current and voltage test with I-V meter is resulted that on the 50°C extract temperature produces the highest efficiency of reaches which is 2.63 x 10-3 %.

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Department of Chemistry, Faculty of Science and Technology UIN Sunan Kalijaga Yogyakarta.

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