

Influence of Dye Adsorption Time on TiO₂ Dye-Sensitized Solar Cells with Krokot Extract (*Portulaca oleracea* L.) as A Natural Sensitizer

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ABSTRACT

Dye sensitized solar cells (DSSC) photoelectrodes were fabricated using titanium oxide (TiO₂) and sensitized with the krokot extract dye. This study investigated the effect of dye adsorption time to an efficiency of the solar cells. The fabrication cells immersed with krokot extract dye for 1, 8, and 26 hours. The photochemical performance of the DSSC showed that the open circuit voltage (V_{oc}) were 0.33, 0.036 and 0.27 V with short photocurrent density (I_{sc}) 8.00×10^{-5} , 6.80×10^{-7} and 3.10×10^{-4} . The photo-to-electric conversion efficiency of the DSSC reached $4.63 \times 10^{-3} \%$ for 26 hours adsorption time.

Keywords: dye sensitized solar cells (DSSC), krokot extract dye, titanium oxide

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 [1]. 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 [2]. This mechanism shows the optical absorption and charge separation processes through the association of a sensitizer as a light absorber with a nano crystal semiconductor that has a wide band gap [3].

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 tri-iodide ion (I^-/I_3^-) carbon layer as the catalyst, porous TiO₂ nano crystal as photo anode, and a dye photosensitizer [2]. 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 TiO₂ which can increase the reaction rate of the electron transfer [4]. Krokot extract contained some compounds such as oxalic acid, caffeine, maleic acid, alkaloid,

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coumarin, flavonoid, cardiac glycoside, anthraquinone, glycoside, alanine, catechol, saponin, and tannin [5]. Flavonoid composed of kaempferol, apigenin, myricetin, quercetin, and luteolin [6,7].

Another fabrication factor is the dye adsorption time, which determines the quantity and the nature of the adsorbed dye molecules. The dye adsorption time should be sufficiently long, so that the interfacial surface of the oxide film is completely covered with a monolayer of dye molecules. In fabricating TiO_2 -based photoanodes, the length of the dye adsorption time is determined. This is because TiO_2 is insensitive to prolonged sensitization times because of its higher chemical stability [8-10]. Ideally the oxide surface should be covered with a monolayer of dye molecules to achieve efficient electron injection. When dye molecules undergo aggregation, electron injection becomes less efficient, and overall conversion efficiency declines. For TiO_2 -based cells, it is essential to optimize the dye adsorption time to minimize the formation of dye aggregates and the damage to TiO_2 surfaces. Because the dye molecules must penetrate the mesoporous oxide film before they attach to the interfacial surface, the optimal dye adsorption time likely depends on the thickness of the TiO_2 film. Thus, this study investigates the dye adsorption time was important. Although these factors have been reported the influences of dye concentration adsorption time on DSSC performance [11,12]. Therefore, this study 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. To further understand the effect of dye adsorption time was used to investigate the electron transport characteristics of the fabricated cells. This study shows the correlation between efficiency and dye loading as a function of the dye adsorption time.

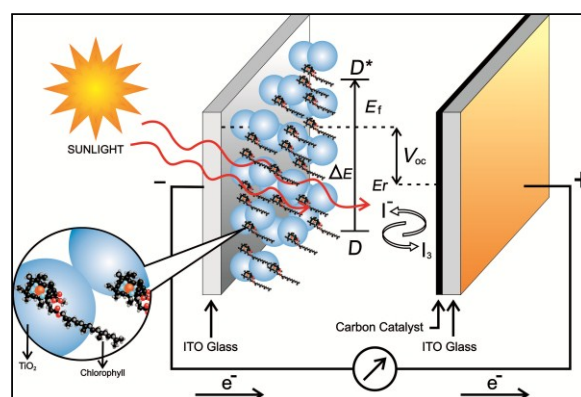


Figure 1. DSSC with krokot extract dye sceme

EXPERIMENT

Chemicals and instrumentation

Chemicals used for research are krokot (*Portulaca oleracea* L.), Indium Transparent Oxide (ITO), TiO_2 (degusa), KI, I_2 , polyethylene glycol, ethanol 96%, Polyvinyl alcohol (PVA), aquadest, graphite pencil 8B and detergent.

Instrumentation applied for research are ultrasonic cleaner, hotplate, glassware, aluminium foil, paper clips, scotchlite, UV-Vis spectrophotometers single beam, UV-Vis specular reflectance, Fourier transform infrared spectroscopy (FT-IR) Shimadzu and I-V meter Keithley 2400.

Preparation of krokot (*Portulaca oleracea* L) extract

Ten grams of krokot powder are macerated with 120 mL of 96% ethanol for 24 hours. 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 g and then inserted into an erlenmeyer and added with 3.0 mL of aquadest. 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 g PVA added with 6.0 mL of aquadest by heating at temperature of 150°C until all of PVA were dissolved. The mixing is followed by stirring for 10 minutes until homogeneous. Then, it is performed TiO₂ paste deposition on surfaces glass of ITO with Doctor Blanding technique. But before it, ITO should be washed with detergent and followed by aquadest 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 was given a double tape restraint and it was made a rectangular pattern by leaving a 1.8 by 1.3 cm room. Furthermore, in above of that field, the TiO₂ paste was distributed evenly with a glass rod and then dried in the air and the scotchlite was opened, then it is heated at 80 °C for 1 hour.

Preparation TiO₂/dye electrode

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 was dried at room temperature and analyzed by UV-Vis reflectance spectrometer and FT-IR.

Preparation of the counter electrode

The graphite pasted into the surface of ITO on the conductive layer with the shading manner to average carbon layer. Then, it is heated at temperature of 300 °C for 1 hour.

Preparation of electrolytes

Potassium iodide (KI) is weighed as much as 0.815 g and then dissolved in 10 mL of polyethylene glycol (PEG) 400 and stirred until dissolved. Then it was added with 0.128 g of I₂ and stirred again until completely mixed. The finished electrolyte solution was stored in the dark bottle and also well sealed.

Fabrication of Dye-Sensitized Solar Cell (DSSC)

DSSC fabrication which was and wich construction consist of glass-ITO working electrode (TiO₂ layer) that has been coated with dye-screen projector-counter electrode (carbon layer)-ITO glass. The use of screen 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 combine between the two layers after it is clamped with paper clip on two opposite sides are not coated.

Characterization of currents and voltage of DSSC

DSSC prototype was tested by measuring the I-V characteristic curve using a digital multimeter Keithley2400, in the light of a xenon lamp at an intensity of 1000 W/m^2 . The result of the I-V characteristic curves test were then analyzed V_{oc} , I_{sc} , fill factor, and the efficiency of solar cells [6] by the equation:

$$FF = \frac{V_{max} \cdot I_{max}}{V_{oc} \cdot I_{sc}} \quad (1)$$

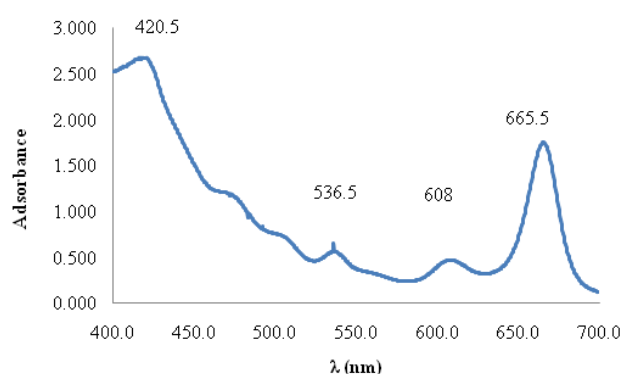
$$\eta = \frac{V_{oc}(V) \cdot I_{sc}(A) \cdot FF}{P_{in} \left(\frac{W}{cm^2} \right) \cdot A (cm^2)} \quad (2)$$

RESULT AND DISCUSSION

Characterization the optical properties of krokot extract

Figure 2 demonstrates the UV-VIS absorption spectra of extract krokot dye. It was found that the absorption peak is about 420.5, 536.5, 608 and 665.5 nm. The absorption maximum peaks are 420.5 and 665.5 nm suggest to chlorophyll adsorption. So that chlorophyll can be used as a dye in DSSC because it has characteristic to absorb the visible light that produced by sunlight.

Figure 2. (right)
Absorption
spectra of extract
krokot dye
(right)



Characterization of electronic properties TiO_2 -dye

Figure 3 shows the absorption spectrum of TiO_2 film sensitized by different dye adsorption time. It aims to find out that the longer the adsorption time so there are more dye that are absorbed on the surface of TiO_2 so that there are more electrons will be generated. From the figure it can be seen that the TiO_2 has a high absorption in the ultraviolet light region and the low absorption in the region of visible light. The addition of the dye serves as a sensitizer to increase the absorption area of the semiconductor. It is seen that the addition of the dye will enhance the ability of TiO_2 electrode layer to absorb the visible region.

In the TiO_2 sample testing, the maximum absorbance at a wavelength of 326 nm and then increased to 332 nm when is done immersion in the dye for 1 hour. There was a decreasing became 331 nm after 8 hours immersion and 315 nm after 18 hours immersion and increased back to 337 nm after 26 hours immersion. The increasing of wavelength irregularities are due to the number of molecules in the dye that can cause steric effects then cause the interaction of the dye with a film of TiO_2 not optimal.

Absorbance is used to calculate the band gap energy (E_g) in the film of TiO_2 and TiO_2 -dye film with different adsorption time by Tauc plot method. Figure 4 shows the form of the TiO_2 band gap is 3.3 eV. This value reach 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.

Figure 3 (Right) The graph of absorbance to wavelength (A) thin layer TiO₂, (B) thin layer TiO₂-dye 1 hour, (C) thin layer TiO₂-dye 8 hour, (D) thin layer TiO₂-dye 18 hour, and (E) thin layer TiO₂-dye 26 hour

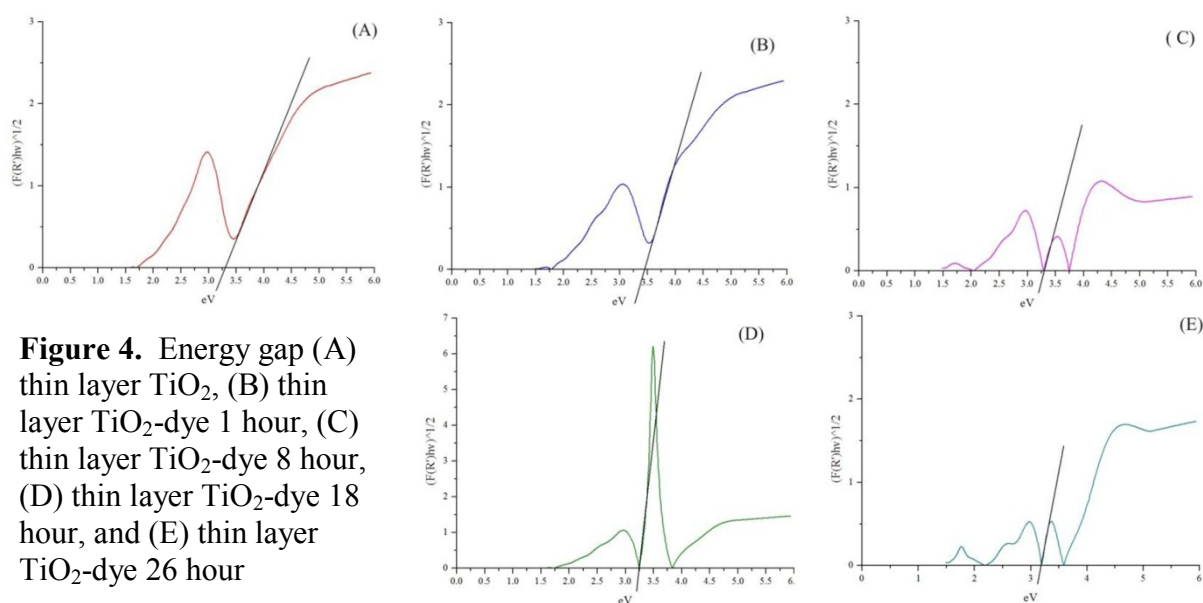
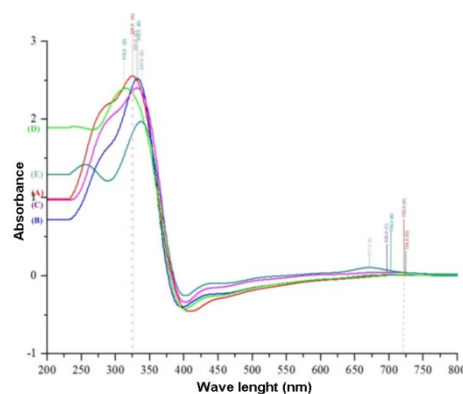


Figure 4 shows the band gap energy (E_g) of TiO₂ with different dye adsorption time. TiO₂ with an hour adsorption time was 3.45 eV. Meanwhile band gap energy (E_g) for 8, 18 and 26 hours adsorption time indicates a consecutive decreasing to 3.30, 3.25, and 3.10 eV. This is as expected that the longer of the TiO₂ film immersion in dye capable to decrease E_g 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 FT-IR spectrophotometer

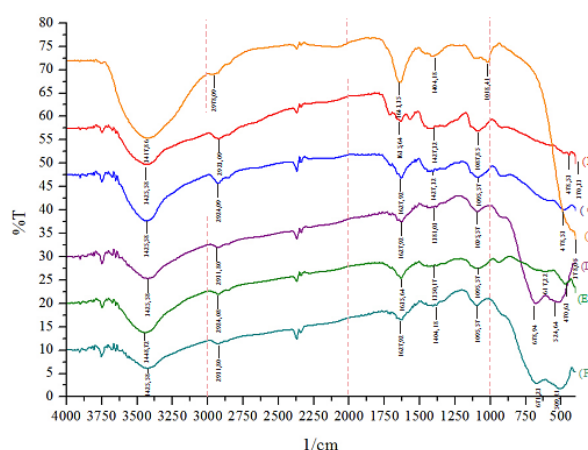
Infrared absorption spectrum of a material has a distinctive pattern to identify the material and also shows the existence of the major functional groups in the identified structure. The FTIR spectra of TiO₂-dye system shows the appearance of a significant new peak or functional groups shift if it is compared with the spectra of dye and spectra of TiO₂ film. Krokot extract contains carboxyl and carbonyl groups of chlorophyll that possible to form a chemical bond with TiO₂.

The results of FTIR analysis for TiO₂ film and TiO₂-dye film of krokot extract is shown in the Figure 5. This shows the existence of the carbonyl absorption at wave number

1627.92 cm^{-1} and absorption at 3425.58 cm^{-1} region is the absorption area for hydroxyl groups. Carbonyl and hydroxyl groups that is owned by krokot extract can bind to the group of Ti(IV) on TiO_2 .

The FTIR spectra resulted (Figure 5) indicates no significant difference from treatment with variation of immersion. It is only seen the carbonyl absorption shift of in TiO_2 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 TiO_2 is coated with krokot extract and relatively constant for the time variation of 1, 8, and 26 hours and does not change for 18 hours. This shows that krokot extract does not bind yet optimally with a TiO_2 film or the possibly interaction occur as physical interaction.

Figure 5 (right). The infrared spectra of (A) krokot extract, (B) thin layer of TiO_2 , (C) thin layer of TiO_2 -dye 1 hour, (D) thin layer TiO_2 -dye 8 hour, (E) thin layer TiO_2 -dye 18 hour, and (F) thin layer TiO_2 -dye 26 hour



Current and voltage measurement systems solar cells

The manufactured of DSSC consists of the working-electrode, counter electrode and the electrolyte. The arranging is made from sandwich system which is then tested using the I-V meter Keithley 2400 for current characteristics and the voltage at the DSSC. The presence of irradiation by the light source to the sample surface will increase the electron-hole pairs. Electron-hole pairs will be separated by an electric field which is then contributes to the increased flow. When the voltage at the maximum position, then, there is no current flowing and so it is called as voltage open circuit (V_{oc}). Instead voltage is zero when the flow/current is occurred in the short-circuit (I_{sc}).

In Table 1 was summarized the efficiency obtained by determining the amount of voltage and the maximum current shown in the Figure 5. From that figure, it can be seen that the current legible shows the dye on TiO_2 layers undergo the electron transfer from the excited state of the dye to the conduction band of TiO_2 . The highest efficiency found in a layer of TiO_2 -dye with an absorption time of 26 hours with an efficiency of $4.63 \times 10^{-3}\%$.

The current value, which is very small, indicates the presence of the cell electrolyte leakage due to construction of DSSC which are not meeting between the working electrode and the counter electrode. Possibly because it is only clamped with paper clipper and the carbon which serves as a catalyst redox reaction is not functioning optimally. As the result the redox reaction in the electrolyte is not running perfectly. It causes the exchange of electrons from the redox reaction cannot counter balance with the generation of electrons from the dye sensitization so that the overall value of the current-flowing becomes small and influence the efficiency of solar cells tested.

Table 1. The parameters of solar cells

Characterization I-V	Thin layer TiO ₂	Thin layer TiO ₂ -dye 1 hour	Thin layer TiO ₂ -dye 8 hour	Thin layer TiO ₂ -dye 26 hour
V _{max} (V)	0.027	0.175	0.02	0.12
I _{max} (A)	1.00 x 10 ⁻⁵	4.50 x 10 ⁻⁶	6.80 x 10 ⁻⁷	1.60 x 10 ⁻⁴
P _{max} (W)	2.70 x 10 ⁻⁷	7.87 x 10 ⁻⁶	1.36 x 10 ⁻⁸	1.92 x 10 ⁻⁵
I _{sc} (A)	1.60 x 10 ⁻⁵	8.00 x 10 ⁻⁵	6.80 x 10 ⁻⁷	3.10 x 10 ⁻⁴
V _{oc} (V)	0.08	0.33	0.036	0.27
Fill Factor	0.2109	0.2982	0.5555	0.2293
efficiency (%)	6.52 x 10 ⁻⁵	1.90 x 10 ⁻³	3.28 x 10 ⁻⁶	4.63 x 10 ⁻³

In this study, the small DSSC efficiency was afforded possibly because the performance of natural dye extracted from kerkot plant still contains a lot of pigment with long alkyl groups. This group that normally with consist of long alkyl group provided the steric hindrance effect to the surface band and this also affected on the oxidation of TiO₂ molecules to bind with TiO₂. Due to this limitation then the transfer of electrons from the conduction band to the dye molecule is reduced.

CONCLUSION

The result shows that the absorbance spectrum of the kerkot extract dye is stretched in the range of visible light to the maximum absorbance peak at a wavelength of 420.5 nm and 665.5 nm. It summarized the presence of chlorophyll. There is a decrease of the energy gap of TiO₂ film which is sensitized with kerkot extract with the variation of dye adsorption time of 3.3 eV for TiO₂ film to 3.10 eV after 26 hours adsorption time. The results of TiO₂ film and after sensitized by kerkot extract with different adsorption time show no significant shift in functional group and also there is an increasing of efficiency of 6.52x10⁻⁵% for TiO₂ film, 1.90x10⁻³% for an hour adsorption time to 4.63 x 10⁻³% for 26 hours.

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