Utilization of Urang-Aring (*Eclipta prostrata* L.) Leaf as Natural Pigments for Sensitizers TiO_2 Based Dye-Sensitized Solar Cells

Noor Hindryawati[a], Irfan Ashari Hiyahara, M. Syaiful Arief, and Yunistira Yunistira

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Mulawarman University, Jalan Barong Tongkok No.4, Samarinda 75123, Indonesia

[a] Corresponding author: hindryawati@gmail.com

Abstract. Sensitizers for TiO_2 based dye-sensitized solar cells (DSSC) were extracted from the leaves of Urang-aring (*Eclipta prostrata* L.). The purpose of this study is to determine the maximum efficiency value of DSSC utilizing a dye derived from Urang-aring leaf extract. Sample preparation and extraction, material characterization, DSSC assembly, and current and voltage testing were all part of the study process. The DSSC was prepared with three different weights of TiO_2 paste: 0.0045 g, 0.0085 g, and 0.0135 g. The doctor blade approach was used to apply TiO_2 paste on Indium Tin Oxide (ITO) glass. With an absorbance value of 0.015, which was assumed to represent the wavelength of the flavonoid luteolin-7-O-glycoside complex, the dyes showed absorption throughout a broad range of the visible region of the solar spectrum (400-700 nm) and appreciable adsorption onto the semiconductor (TiO_2) surface. According to the Scanning Electron Microscopy results, the surface morphology of TiO_2 was spherical and agglomerated. The highest current and voltage were tested using the sunlight source at 11.00 a.m., yielding 5.45×10^{-4}A and 14.715 V, respectively, with a DSSC maximum efficiency rating of 1.

INTRODUCTION

Electricity is a primary necessity that must be satisfied in the current period, such as the use of lights, household appliances, mobile phones, and so on, and its use is increasing over time. Because the majority of electrical energy comes from fossils such as coal, oil, natural gas, and others, which is non-renewable energy, additional options for generating electrical energy are required. Solar cells are a well-known renewable technology. Solar cells generate electricity by absorbing the sun's energy. Today, the sun is the largest source of thermal energy; the sun's energy is 3.1024 joules each year, which is equivalent to 2.1017 W [1]. Solar cells work as a technique for obtaining electrical energy, converting sunlight energy to electrical energy.

Dye-sensitized solar cells (DSSC) are a type of solar cell. The method of DSSC is converting solar energy into electric power with the help of dyes that can increase the sensitivity of solar cells. The advantages of DSSC are easy to use, low cost, and environmentally friendly [2]. However, the efficiency and performance of DSSC are still relatively low, so DSSC technology needs to be developed to get better efficiency and performance values.

The DSSC structure is usually in the form of a sandwich-like layered structure consisting of 3 main arrangements, namely the working electrode, the reference electrode (counter electrode), and electrolyte solution. The working electrode is glass transparent conductive oxide (TCO) coated with semiconductors like TiO_2, ZnO, SnO_2, Nb_2O_5, and sensitized dye. There are many methods such as doctor blade, screen printing, electro position, spin coating, tape casting, dip coating, liquid phase deposition (LPD), organic metal chemical vapor deposition (MOCVD) Mix-solvent-thermal method [3]. In the working principle of DSSC, the current is generated from the electrons generated from the dye due to the photons that are emitted sunlight. Then the electrons will flow to the TiO_2 conduction band, which will then flow to the reference electrode or carbon electrode. The triiodide from the

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electrolyte will trap outer electrons with the support of carbon as a catalyst. The excited electrons will re-enter the cell and react to the dye oxidized with the electrolyte. Electrolytes provide replacement electrons for dye undergo oxidation. So it will return to the initial equation [2].

The performance of the DSSC is influenced by a number of parameters, including the dye used, the electrolyte solution used, the amount of TiO_2 utilized, and the DSSC's storage duration. The quantity of TiO_2 utilized is one of the most important parameters in DSSC performance. The more TiO_2 applied, the more dye is absorbed, requiring more compounds to absorb light, and the higher the DSSC efficiency attained [4]. Another factor that affects the performance of the DSSC is the storage time of the DSSC. This happens because the longer the storage of the DSSC, the lower the efficiency of the DSSC that is obtained [5]. Based on these descriptions, this research aims to develop a DSSC using dye from Urang-aring leaf extract (*Eclipta prostrata* L.) and a semiconductor TiO_2, based on the influence of weight TiO_2 and DSSC storage period. This plant is easy to obtain because of the spread spacious and easy to breed. In addition, the content of bioactive compounds Urang-aring plants, among others the flavonoid group, based on identification by chromatography, showed flavonoid compounds, namely luteolin-7-O-glycoside, which has potential as a dye [6]. As for the innovations carried out in this study, namely the use of dye from Urang-aring leaf extract because Urang-aring leaves have not been widely developed as a dye, the weight variation added in this study is also an innovation in increasing the efficiency value in DSSC.

MATERIAL AND METHOD

Equipment

The instruments used in this research were Scanning Electron Microscope (SEM-EDX JEOL JSM-6510LA), UV-Vis Spectrophotometer, Fourier Transformed Infrared (FTIR) Bruker brand with type Alpha II. The other tools were multimeter, lux meter, analytical balance, furnace, measuring flasks, beakers, mortar and pestle, rotary evaporator, crucibles, electric stoves, test tubes, spray bottle, spatula, stir bar, dark container, small bowl, tongs, scotch tape, Erlenmeyer pumpkin, connecting cable, dropper.

Materials

The materials used in this study included ITO (Indium Tin Oxide) glass, TiO_2, Urang-aring leaves (*Eclipta prostrata* L.) from the village of Rawa Makmur Palaran Samarinda, East Kalimantan, electrolyte solutions of Iodine and Potassium Iodide (I-/KI), Ethanol (96% Alcohol), PEG 4000, chloroform, HCl, Mg, H_2SO_4, Dragendroff's reagent, Liebermann Burchard reagent (mixture of glacial acetic acid solution with H_2SO_4 solution), $FeCl_3$, HCl, NaOH solution and 8B pencil.

Methods

The Extraction of Urang-aring Leaf

A total of 600 g of Urang-aring leaves (*Eclipta prostrata L.)* was washed clean. The leaf was then dried in aerated with no direct sunlight for five days. A total of 300 mL of 96% ethanol was added to the container, continued with macerated for five days at room temperature in a dark room that was not exposed to sunlight, and then filtered using filter paper. The obtained filtrate was concentrated using a rotary evaporator to get a thick extract and took 3 g of thick extract of Urang-aring leaves to dissolve with 96% ethanol solvent as much as 10 mL to be used as a dye.

Phytochemical Test

According to [7] Alkaloid Test, the ethanolic extract of Urang-aring leaves (*Eclipta prostrata* L.) was dissolved using the appropriate solvent. After adding 1 mL of the extract solution and five drops of 2N H_2SO_4, the solution was shaken and set aside for a while before adding three drops of Dragendroff's reagent a mixture of $Bi(NO_3)_3.5H_2O$

in concentrated nitric acid and KI solution to the test tube and observing it. The orange to red-brown precipitate generation is a positive test for alkaloids.

Flavonoid Test the ethanolic extract of Urang-aring leaves (*Eclipta prostrata* L.) was dissolved with a suitable solvent. 1 mL of the extract solution was added with 2 mg of Mg powder and three drops of $HCl_{(P)}$. A positive test for flavonoids was the formation of a yellow, orange or red color.

The crude ethanol extract of Urang-aring leaves (*Eclipta prostrata* L.) dissolved in ethanol was used to conduct the steroid/triterpenoid test. With the reagent Liebermann Burchard, a total of 1 mL of extract solution was added (mixture of glacial acetic acid solution with H_2SO_4). A positive steroid test will be blue or green, whereas a positive triterpenoids test would be purple or red.

The phenolic test ethanolic extract of Urang-aring leaves (*Eclipta prostrata* L.) was dissolved using a suitable solvent. A total of 1 ml of the extract solution was added with three drops of 1% $FeCl_3$ solution. A positive phenolic test was the formation of a strong purple, green, black, red, or blue color.

In the Saponin Test, the crude ethanol extract of Urang-aring leaves (*Eclipta prostrata* L.) was dissolved using a suitable solvent. As much as 1 mL of the extract solution was added with hot water and then shaken vigorously; if foam appears, the solution is added with one drop of $HCl_{(p)}$. The positive test for saponins is foam with a height of 1-3 cm, which is stable for 15 minutes.

In the Quinon Test, crude extract of Urang-aring leaves (*Eclipta prostrata* L.) was dissolved using a suitable solvent. A total of 1 ml of the extract solution was added with five drops of 5% NaOH solution and observed, then the solution was added with five drops of 2N HCl solution and observed. Positive test for quinone that is back to the initial color.

Coating of TiO_2 on the ITO (Working Electrode) glass

A total of 1.5 g of PVA (Polyvinyl Alcohol) powder was put into 13.5 mL of distilled water. It was then stirred using a magnetic stirrer for 30 minutes at 60˚C. As much as 0.5 g of TiO_2 powder was put into a mortar, and 15 drops of PVA solution were added and then crushed to form a paste. After that, the paste was deposited on the ITO glass by the method doctor blades. The conductivity of ITO glass (2 × 2 cm) was measured to determine the active side. TiO_2 (2 × 1.5 cm) was applied above the surface of the conductive glass that formed the area. Then put tape on the side of the ITO glass as a barrier. The paste was deposited and flattened using a spatula. After that, the layer was allowed to stand for 10 minutes and then calcined using the furnace for 30 minutes at 450 °C. The TiO_2 layer made was soaked in Urang-aring leaf extract in a petri dish for 24 hours in a dark room. Then the glass was lifted using tweezers. The side of the glass was cleaned using tissue and cotton bud. The morphology of the TiO_2 thin layer was characterized using Scanning Electron Microscopy (SEM) [8].

Preparation of Comparison Electrodes

ITO glass was scratched using carbon from an 8B pencil with an area of 2 cm x 1.5 cm [9].

Preparation of electrolyte solution

A total of 3 g of Potassium Iodide is mixed into 5 mL of Iodine and stirred using a magnetic stirrer for 30 minutes. Then the gelling compound was prepared, namely, PEG (Polyethylene glycol) 4000 as much as 6 g is dissolved in 6 mL of chloroform; the solution is then mixed in the liquid electrolyte and stirred using a magnetic stirrer for an hour at a temperature of 60 °C so that PEG 4000 quickly dissolves into the solution. The electrolyte solution is stored in a closed container to avoid evaporation [10].

Preparation of Sandwich DSSC

The working electrode (TiO_2) was sandwiched between the carbon electrodes in a layer-like arrangement. To reinforce the two electrodes, the two sides of the glass were fastened together using a paperclip. The clamped DSSC was opened on one side. The glass then clamped back after two drops of electrolyte solution dripped on the sidelines of the working and carbon electrodes. Then repeat the process on the opposite side.

DSSC Current and Voltage Testing

The DSSC test was conducted by measuring current and voltage with a multimeter (Heles UX-78) while using sunlight as a light source for 1 hour at 11.00-12.00 PM and under bright sunlight illumination. The test was performed with resistance variations of (0, 20, 27, 40, 54, 68, 74, 88, 95, 108) K. The intensity of sunshine was then measured with a Lux meter. Furthermore, measurements were obtained every day for six days in the same way as before to determine the ability of DSSC. The DSSC efficiency value was then calculated with the following equation [11]:

$$P_{in} = I_r \times A \tag{1}$$

$$P_{out} = I_{max} \times V_{max} \tag{2}$$

$$\%Efficiency = \frac{P_{out}}{P_{in}} \times 100\% \tag{3}$$

Where I_r is sun intensity (W/cm^2), A is ITO glass cross-sectional area (cm^2), P_{in} is Sunlight Power (W), P_{out} is Measurement Data on DSSC (W), I_{max} is maximum current (A), V_{max} is maximum voltage (V).

RESULTS AND DISCUSSION

Characteristics of Urang-Aring (*Eclipta prostrata* L.) Leaf extract

In this study, phytochemical tests were carried out on Urang-aring leaves samples to determine the content of secondary metabolites in Urang-aring leaves. Phytochemical tests were carried out using a qualitative color test method using specific reagents from these secondary metabolites. The results of the phytochemical test of Urang-aring leaf extract can be seen in Table 1.

TABLE 1. Phytochemical Test of Urang-aring Leaf Extract (*Eclipta prostrata* L.).

Compounds Group	Test results
Alkaloids	+
Flavonoids	+
Phenolic	+
Steroids	+
Triterpenoids	+
Saponins	-
Quinone	-

Note: (+) = indicates positive containing secondary metabolites
(-) = indicates negative contains secondary metabolites

The results of phytochemical screening of the ethanol extract of Urang-aring leaves obtained in this study indicate that alkaloids, flavonoids, phenolics, steroids, and triterpenoids can be attracted in ethanol solvents. The content of bioactive compounds in Urang-aring plants such as flavonoid compounds, tannins, phenolic compounds, alkaloids, coumarin derivatives, thiophene, polyacetylene, and triterpene glycosides qualify as natural dyes [12]. The results of this phytochemical test show that the compounds contained in urang-aring leaves can meet the requirements as natural dyes so that they can be used as dyes in DSSC, where dye is also a factor that can increase the efficiency value due to the contribution of photon binding by dye from sunlight so that more is obtained. More electrons to improve the performance of DSSC in generating electric current.

In this study, the solution dye made from Urang-aring leaf extract has excellent light absorption ability in the range of Visible wavelength 650-700 nm. The results of UV-Vis spectrophotometry analysis of Urang-aring leaf extract can be seen in Fig 1.

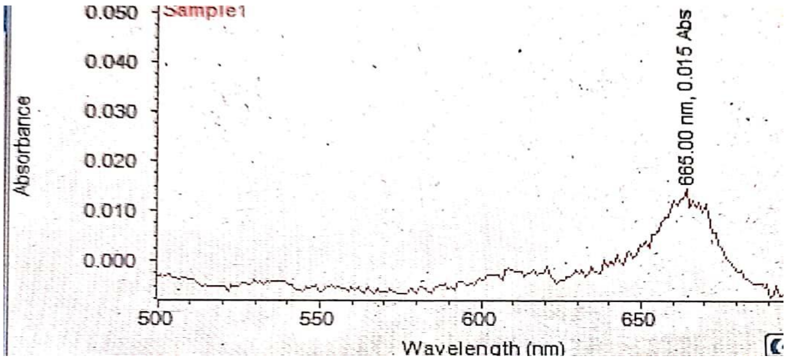

FIGURE 1. UV-Vis Spectrophotometry Analysis of Urang-aring Leaf Extract

Figure 1 showed that the ethanolic extract of Urang-aring leaves was 600-700 nm with a maximum wavelength of 665.00 nm with an absorbance value of 0.015; this indicates that the dye can absorb light visible is in the sun. According to [13], the wavelength of 650-700 nm with a maximum wavelength of 670 nm is a compound luteolin-7-O-glycoside Flavonoids are dyes that can absorb sunlight.

The Fourier Transformed Infrared (FTIR) aims to determine the functional groups in Urang-aring leaf extract in the wavenumber range of 4000-600 cm^{-1}. The results of the FTIR analysis are shown in Fig. 2.

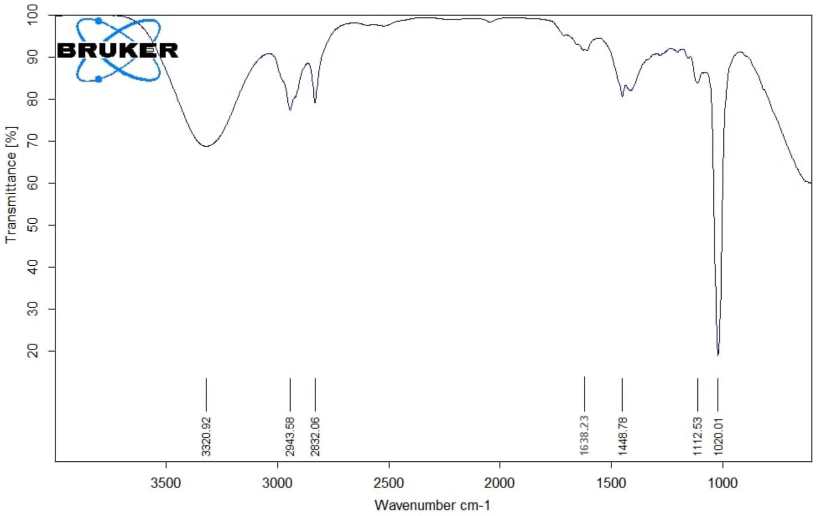

FIGURE 2. FTIR spectrum of Urang-aring Leaf Extract

Based on Fig. 2 showed the presence of absorption extends to the wavenumber 3320.92 cm$^{-1,}$ which is a typical wavenumber of hydrogen bonds between the –OH group and other –OH groups and is strengthened by the sharp absorption at a wavenumber of 1020.01 cm$^{-1,}$ which is the wavenumber absorption of the –CO group glycoside. There is absorption at a wavenumber of 1638.23 cm$^{-1,}$ which is the wavenumber of the unsaturated C=O group and is supported by the absorption at the wavenumber of 1448.78 cm^{-1} which is the wavenumber of C=C aromatics. There is a sharp absorption at the wave number 2943.58 cm$^{-1,}$ which is the wavenumber of saturated hydrocarbons and is supported by the absorption at wavenumber 1112.53, which is the wavenumber of the CO group stretching. The presence of –OH, C=O, C=C aromatic groups, CO glycoside, and CO in saturated hydrocarbons are thought to be functional groups belonging to luteolin-7-O-glycoside [14]. Based on the results in Fig. 1 and 2, it can be assumed as a luteolin-7-O-glycoside compound that can be used as a dye to manufacture DSSC.

Scanning Electron Microscope (SEM) Image of TiO_2

The SEM aims to see surface phenomena in the form of images morphology of TiO_2 after calcination. Based on Fig. 3, the surface morphology of the TiO2 is shaped like spherical, and there are many agglomerations. According to [15], this is because in the process of TiO_2 paste preparation using a binder in the form of a gel made of PVA solution. The amount of agglomeration depends on the composition of the binder used. In the picture, it can be seen that the spherical particle where this particle functions in the adsorption of molecules dye into the electrode layer, the contained on the surface of the layer also affect the effectiveness of adsorption of dye molecules into the surface and also facilitates the spread of the electrolyte solution on the working electrode of the cell system [15].

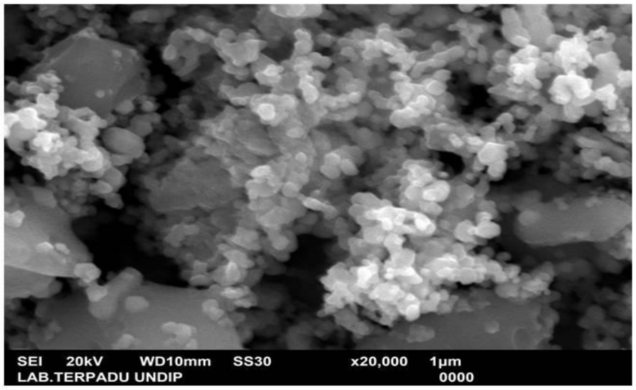

FIGURE 3. TiO_2 surface morphology of TiO_2 at 20,000x magnification.

Current Test and Efficiency Value

The maximum current and voltage values of each DSSC with variations in pasta weight were 0.0045 g, 0.0085 g, and 0.0135 g were shown in Fig 4.

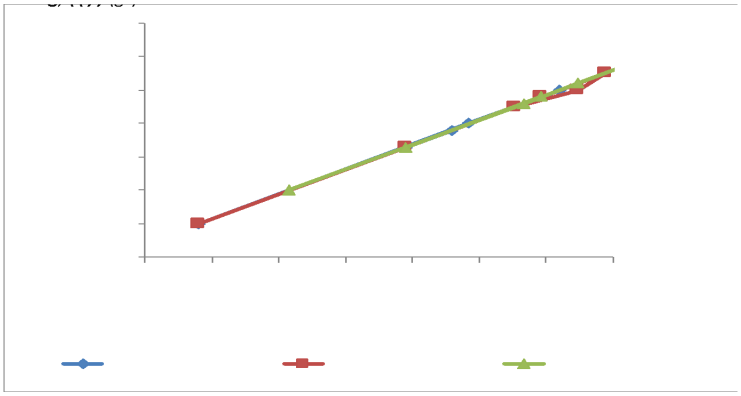

FIGURE 4. DSSC Current and Voltage Graph with TiO_2 Weight Variation

Based on Fig. 4, it can be seen that from the three current and voltage results, there is no significant difference in current and voltage values which is under Ohm's law which states that the greater the current, the greater the potential difference with a constant resistance value. The results of the current and voltage relationship curves can be used to find the efficiency value of DSSC.

The DSSC efficiency value is measured using a multimeter which functions to measure current (I) and voltage (V), lux meters to measure the intensity of sunlight. Result value efficiency of DSSC using various weights of TiO_2

can be seen in Fig. 5. The determination of the efficiency value is also carried out for six days to see the performance of DSSC.

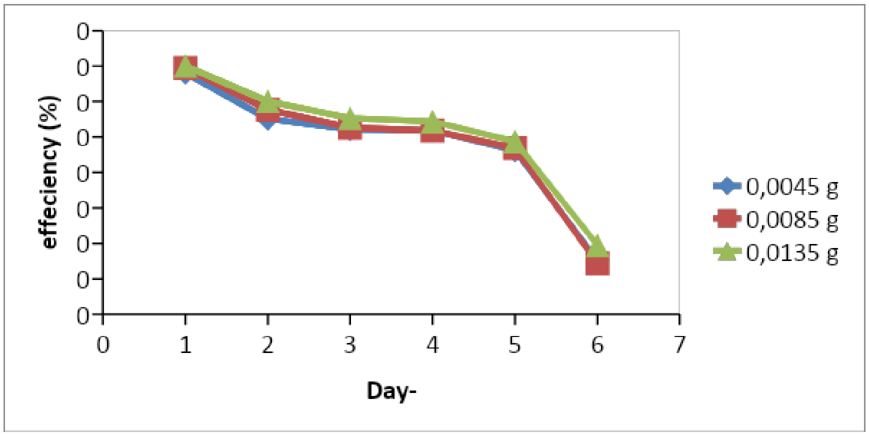

FIGURE 5. Various storage time with DSSC efficiency

Based on Fig. 5, the efficiency value obtained by DSSC by weight of TiO_2 0.0135g has a higher efficiency value compared to DSSC thickness one and with a weight of 0.0085 g, where the highest efficiency value is obtained on the first day of $1.401x10^{-4}$%. This efficiency is classified as higher than the research conducted by [16], which uses dye from rosella flower extract with an efficiency of $0.712x10^{-4}$%. However, DSSC decreased until the sixth day with an efficiency value of $0.391x10^{-4}$ %. This can be caused by the electrolyte solution used, namely Iodine, which is easily oxidized by air, and the oxidation process becomes faster due to the presence of heat. Another factor that is quite influential in the low efficiency of solar cells is the damage to the solar cell dye, which is less stable. So that after being stored for six days, the DSSC decreased ineffectiveness to generate electric current.

Fig. 5 showed the efficiency value obtained by DSCC, TiO_2 0.0135 g. It was higher than DSCC thickness 1 with a 0.00085 g. The highest efficiency value was obtained on the first day, $1.401x10^{-4}$%. This efficiency was considered higher than the research conducted by [16], which used dye from rosella flower extract with an efficiency of $0.712x10^{-4}$%. However, DSSC decreased until the sixth day with an efficiency value of $0.391x10^{-4}$%. It occurred because the electrolyte solution called Iodine was easily oxidized by air. The heat also causes the oxidation process to become faster. The other factor causing the low efficiency of solar cells was the damage of the less stable solar cell dye. After being stored for six days, the DSCC effectiveness decreased to generate electric current.

Based on the results of the efficiency values of the three samples, it can be seen that the DSSC with the highest weight is 0.0135 g has better efficiency for converting solar energy into electrical energy. According to [17], the weight of the paste will affect the efficiency of the DSSC, where a lot of paste will increase the number of dyes that can be absorbed. The more dye and incoming light are on, the more electron current is generated, and the cell's performance improves directly. The thickness of the paste layer affects the results produced by TiO_2. A thick paste layer allows fewer electrons to flow into the conductive glass layer. This is because the electron recapture by oxidized dye [18]. In addition, according to [19], the non-uniform layer thickness also affects the inhibition of the electron ejection process so that the resulting voltage output is less than optimal.

CONCLUSION

Phytochemical test results and UV-Vis spectrophotometer proved that Urang-aring leaf extract contains luteolin-7-O-glycoside compounds to be used as a sensitized dye in DSSC. FTIR results show that dye Urang-aring leaves have a –OH group and a carbonyl group which can bond to the surface of the TiO2. Dye-Sensitized Solar Cell has been successfully made with a weight of 0.0135 g TiO_2 paste resulting in a maximum efficiency of $1.401x10^{-4}$%, which lasted for six days and decreased until an efficiency of 0.391x10-4% was obtained. On the contrary, the too heavy paste will inhibit the entry of photons into the electrode. The longer the storage of DSSC, the lower the efficiency of DSSC is.

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