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The Analysis of *Caesalpinia Sappan* L. Wood as dye Sensitizer and TiO_2 Thickness Variation in Dye-Sensitized Solar Cells (DSSC)

A. Nasyori[1*], I. I. Panturengi[1*], Aisyah[2], H. S. Kusuma[3]

[1]*Department of Physics, Faculty Science and Technology, Alauddin Islamic State of Alauddin Makassar, 92113, Indonesia*

[2]*Department of Chemistry, Faculty Science and Technology, Alauddin Islamic State of Alauddin Makassar, 92113, Indonesia*

[3]*Department of Chemical Engineering, Faculty of Industrial Technology, Institut Teknologi Sepuluh Nopember, 60111, Indonesia*

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- ✓ Efficiency,
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achmad.nasyori1@gmail.com;
wadi.phys.dept@uin-alauddin.ac.id
Phone: +6285766247553

Abstract

Electrical energy is a paramount necessity, but source of used electrical energy is still a limited fossil fuel. One of the best solutions is solar cells. Dye Sensitized Solar Cell is the third generation of solar cells. The research aimed to obtain the highest absorption power of *Caesalpinia Sappan* L. wood by varying the maceration times and to get the highest efficiency value by varying the thickness of TiO_2 (titanium oxide) using a dye from *Caesalpinia Sappan* L. wood. The time of maceration applied in this research was 20 minutes, 24 hours and 48 hours. The TiO2 was material semiconductor wielded by applying a thickness of 11 μm, 15 μm and 20 μm. Spreading of the TiO_2 to ITO glass was done by technic of the doctor blade, which was continued by doing several testing such as UV-Vis spectrophotometr, FTIR spectroscopy, XRD, and SEM. UV-Vis spectrophotometry showed the highest absorption of *Caesalpinia Sappan* L. wood 2.883 at a wavelength of 444.5 nm at 24-hour immersion. The results of current and voltage measurements under sun illumination show the highest efficiency (η) 0.196629% with the current density Jsc = 0.196889 mA/cm^2 and the voltage Voc = 0.323 Volt and FF = 0.271467 according to the thickness of 15 μm. This research provides that the maceration of 24 hours is the best time in maceration having the best absorbent and the thickness of 15 μm is batter thickness with a higher of efficiency.

1. Introduction

Electrical energy is a paramount necessity for our life because its role supports all aspects of life. Generally, thousands of countries use fossil fuel to get electrical energy, which the longer and longer is limited, for instance, petroleum, natural gas, and coal [1]. Renewable energy is the best solution to minimize based electric energy from fossil fuel. Renewable energy has numerous superiorities like abundant resource and environmentally friendly, for example; wind energy, hydropower, biomass, bio-fuel, geothermal energy and solar cell [2]. The solar cell is one of the renewable energies possessing batter progress in the future. Dye-sensitized solar cells (DSSC) is the third generation of photovoltaics, which the first was developed by Michael Gratzel and Bria O'regan in 1991 in Switzerland. The benefit of DSSC is low-cost, easy fabrication and environmental friendly [3][4]. DSSC is commonly consisted of three important components like working electrodes, countering electrodes, and electrolytes [5].

In summary, the working principle of DSSC is based on a photoeletrochemical solar cell. The absorption will be done by dye, and then, the dye will adhere and spread on semiconductor, and then, wielding electrolytes renew dye. However, the value of current and voltage has not been stabil and the low-efficiency still becoming a challenge of the researcher. A lot of thing affect the value of efficiency just as the dye and the semiconductor material used.

First and foremost, dyes have a crucial role in permeating photons from the sun. The high and low absorption is depended on the absorbance value of the dye. In other words, if the absorbance value is large at the visible wavelength, the more photons will be absorbed. Generally, there are 2 types frequently used such as synthesis dyes like 719N (Ruthenium) [6][7] and natural dye, for instance, *Caesalpinia Sappan L.* [8], tamarillo [9], Cordyline fruticosa & hylocereus polyrhizus [10] and brown rice [11]. However, developing organic dye becomes attention because it has lots of benefits like abundant source and environmentally friendly. The several research reports of dye organic are extremely interesting like four different dyes (black rice, safflower, noni leaves and sappan wood) getting efficiency values of 0.00015%, 0.00007%, 0.058655% and 0.00165 [12], eight different dyes (aniline blue, eosin Y, carbolic fuchsin, alcian blue, methyl orange, fast green, crystal violet and bromophenol blue) efficiency values of 0.117%, 0.399%, 0.303%, 0.156%, 0.115%, 0.117% 0.249% and 0.12% [13], mango with efficiency 0.43% [14] and *Caesalpinia Sappan* L. with 1.1% efficiency[15]. This research focuses on organic dye from *Caesalpinia Sappan L.* because it is one of the most widely used coloring plants in Indonesia especially in South Sulawesi. The most structure of *Caesalpinia Sappan L.* is Brazilein [16]. It can be classified as carotenoid which can be applied in DSSC [10]. Furthemore, *Caesalpinia Sappan L.* shows promising efficiency report 1.1%.

Secondly and more importantly though, the semiconductor material is a place where the dye adheres and collects electron. Generally, there are 2 semiconductors frequently wielded such as ZnO (Zinc Oxide) and TiO_2 (Titanium Oxide) possessing small band-gap values. ZnO is one of the semiconductors that have a wide-bandgap of 3.37 eV and 3.3 eV (anatase) [17]. According to researchers was done by Po-Ching Kao et al. (2009) the effect of low temperature on particle ZnO is 50 ^{o}C which is the best temperature to obtain size particle and morphology in ZnO [18]. Report from Nuhad A. Al-Omair el al. (2014) using ZnO as a semiconductor obtained an efficiency value of 0.46% [19]. The energy band-gap on TiO_2 is 3.0 eV (rutile) and 3.2 eV (anatase) [20]. According to Yasuo C. HIBA el al. (2006) has done by using TiO_2 and succeeded in producing 11% efficiency [21]. TiO_2 has the many advantages of high photoactivity, good optical, easily accessible, photo-corrosion and non-toxic stability [22] and low bandgap values. The latest report in dye-sensitized solar cell showed the efficiency 8.8%, 10.7%, and 11.9% successively dye submodule, dye mini-module, and dye cell [23].

This work evaluated different times on the maceration process and the difference of thicknesses of TiO2 on the ITO glass. The research aims to analyze several submersion times on maceration with organic dye (*Caesalpinia Sappan* L.) and to analyze some thicknesses of TiO2 on ITO glass in improving the efficiency of DSSC.

2. Material and Methods

2.1. Material preparation.

ITO (Indium Tin Oxide) glass is used with specifications 7-9 ohms with an area of 20 × 20 × 7 mm from latech scientific supply (Singapore), TiO_2, *Caesalpinia Sappan* L. wood from Maros, South Sulawesi (Indonesia), 96% ethanol, KI (solid), I2 (fluid), candles, tissue and filter paper from Gowa, South Sulawesi (Indonesia).

2.2. Natural dye extraction

The sensitizer was created from *Caesalpinia Sappan* L. wood, Cutting the wood until the small size, and entering to blander resulted in a wood powder. The wood powder was weighed 50 grams and soaked in 96% ethanol for 20 minutes, 24 hours, and 48 hours on room temperature. Subsequently, it was filtered and inserted into the evaporator to acquire the original dye. Furthermore, the original dyes were measured by UV-Vis spectrophotometry with a ratio of 1: 10-100 ml (dye: ethanol) and a vulnerable wavelength of 300-800 nm. Then, which possesses the high-value absorbance was used for soaking work electrodes and tested FTIR spectrometer.

2.3. Fabrication of DSSC

The component in working electrode is ITO glass, TiO_2, and ethanol 96%. To Clean the ITO glass with 96% ethanol for 8 minutes used an ultrasonic cleaner and created a 1.5 × 1.5 cm mold with variations in the thickness of 11 μm, 15 μm and 20 μm. To mix TiO_2 and ethanol 96% into the mortar to grind and X-ray Diffraction testing as identification & analysis of TiO_2 size. The pasta of TiO_2 was smeared to surface of ITO glass by the method of the doctor blade. Furthermore, heating the working electrode used a hotplate for 1 hour at a temperature of 0-300 ^oC. Soaking the working electrode uses original dye for 15 hours and test Scanning Electron Microscopy for identification & analysis of the morphology of the working electrode. Counter electrode arranged ITO glass, candles, and 96% ethanol. Cleaning the ITO glass with 96% ethanol for 8 minutes using an ultrasonic cleaner. Burn the ITO glass on the resistance using a candle for acquiring the carbon. The electrolyte was made by dissolving 3 grams of KI into 5 ml of I2 solution and intermixed with input in an ultrasonic cleaner for 8 minutes.

2.4. Incorporation of DSSC

Work & counter of electrodes and electrolytes combined like a Figure 1 the test was carried out under sun illumination at 10:00 to 11:00 WITA with lux meter (Lx 1330B-Lux 200k) as input power calculation. It illustrates the work system of DSSC.

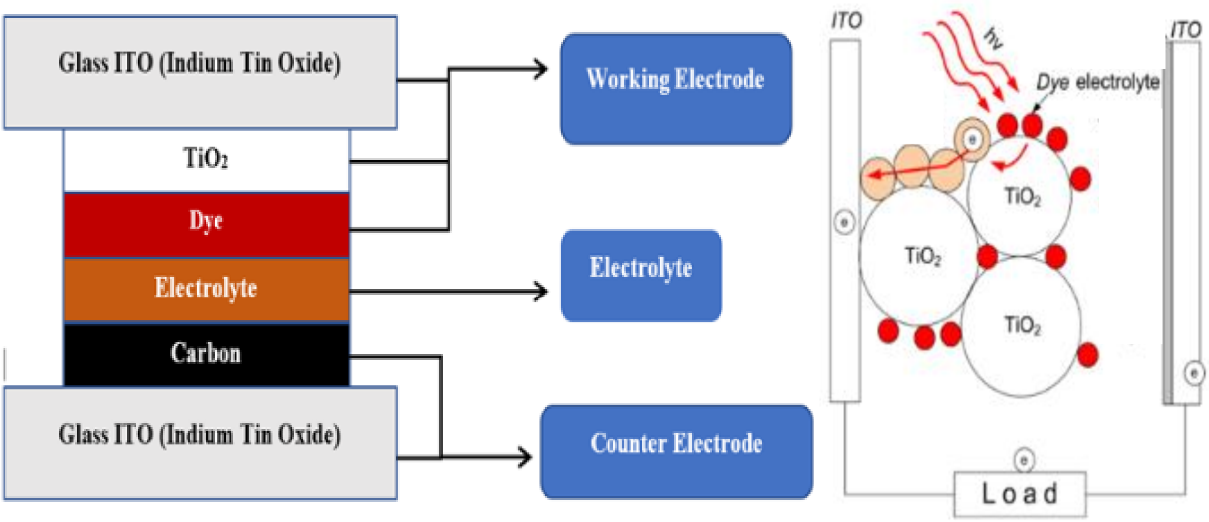

Figure 1: Sandwich and working system of DSSC

3. Results and discussion

The result of UV-Vis spectrophotometry (Figure.2) shows the absorbance value and wavelength of the sample *Caesalpinia Sappan* L. What uses several variations of maceration 20 minutes, 24 hours, and 48 hours to obtain the highest absorption. The results explained in the 20 minutes having two peaks at wavelengths of 693.5 and 444.5 nm with absorptions of 0.008 and 1.663. 24-hours had three peaks with wavelengths of 703.5, 667 and 444.5 in the absorbance rate of 0.029, 0.034 and 2.83. 48-hour immersion obtained one peak with a wavelength of 706 and an absorbance value of 0.009. The highest absorption rate is 2.83 having a wavelength of 444.5nm at 24-hour immersion. According to Landuma et al. (2015) wielded 3 hours macerations and used several weights 30 grams, 40 grams, and 50 grams on *Caesalpinia Sappan* L. obtained UV-Vis results at a wavelength of 328-515 nm and got 0.04108% [8]. Ananth et al. (2009) used dyes from *Caesalpinia Sappan* L. that obtained wavelengths 349 nm, 658 nm and acquired 1.1% [17]. In another word, efficiency is extremely influenced by macerations times. In this work, we reported that using various time macerations such as 20 minutes, 24 hours and 48 hours resulted in brazilein structure which includes a carotenoid category, one of the structures can be applied in DSSC [10], with characteristic reddish dye. Then, the obtained highest absorption value was used in the immersion of work electrode and tested with FTIR spectroscopy.

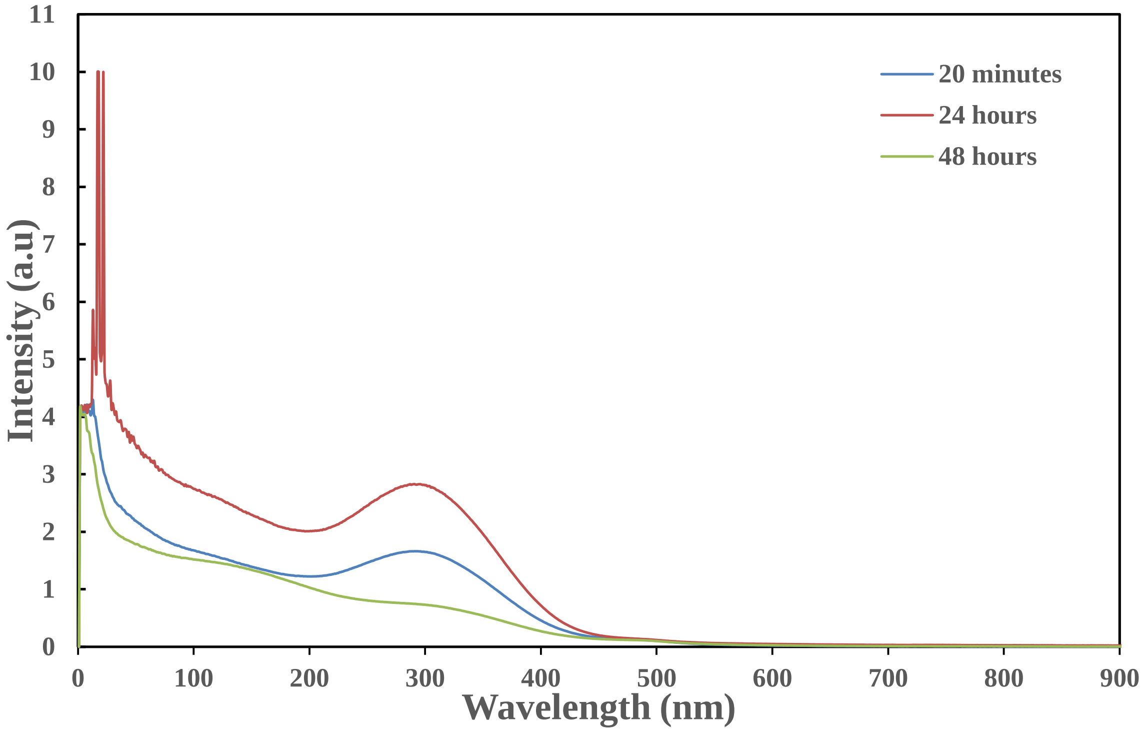

Figure 2: The absorption spectra of *Caesalpinia Sappan L.*

The wood of *Caesalpinia Sappan* L. with 24-hour immersion was wielded as a sensitized because it has a high absorption power at the visible wavelength. The result absorption is 2.81 at wavelength 444.5 nm (Figure 2) which means that the Brazilein assembles at wavelength 444.5 nm. The subsequent analysis used FTIR as the discovered classification in *Caesalpinia Sappan* L. (Figure 3). Figure 3 shows the wavelength and transmittance values of *Caesalpinia Sappan* L. wood. Table 1 shows the types of bonds obtained by O-H, C = O, C = C alkene, C-O and C-N at wavelengths 3448.66, 1707.1, 612.54; 961.46, 1200-1100, and 1430.04 cm^{-1}.

Table 1: The result of FTIR analysis

Sample	Wavenumbers (cm^{-1})	Type of bond
The Wood of *Caesalpinia Sappan L.* (24 hour)	3448.66 1707.1 612.54;961.46 1200-1100 1430.04	O-H C=O C=C alkane C-O C-N

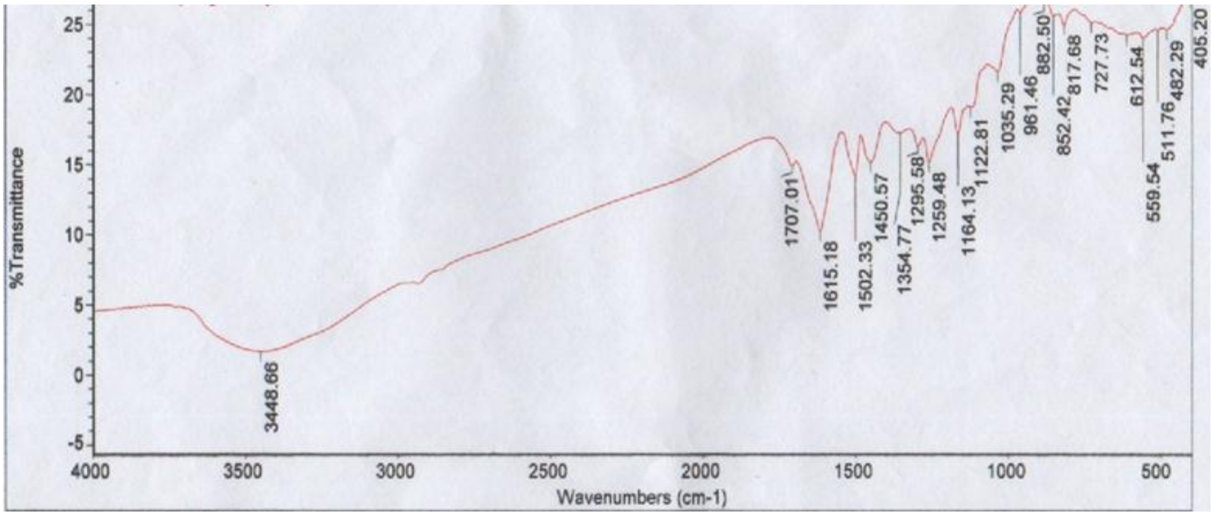

Figure 3: FTIR spectra of *Caesalpinia Sappan L.* 24-hour

X-ray Diffraction (XRD) was performed for phase analysis and particle size of TiO_2. The result obtained in Figure 4 showing that the used TiO_2 is in the anatase phase with a bandgap of 3.2 eV [20]. In addition, it shows the peaks with different points, namely at 2θ angles 25.3°, 37.8°, 48°, 55.1°, and 62.7° in the field 101, 004, 200, 202 and 204. Elfi et al. (2013) (use TiO_2 pure and TiO_2+ CU obtain the same results of anatase and peak phases (25°)) [24]. Next to find out the size of the particle size of the TiO_2 used solid is calculated by the following Scheerer equation:

$$Dn = \frac{k\,\lambda}{\beta\,\cos\theta} \qquad (1)$$

With k: the constant value of 0.89, λ: the wavelength of X-rays (Cu of 1.542 Å), θ: Bragg and β (angles): the half the peak of diffraction (rad). So that it can be seen in the following table.2.

Table 2: The size of TiO_2 (titanium oxide)

No	2-theta (deg)	K	Λ	β (rad)	Cos θ	D (nm)
1	25.353			0.181	12.677	0.59
2	37.852			0.17	18.926	0.42
3	48.085	0.89	1.5406	0.155	24.043	0.36
4	55.107			0.157	27.554	0.31
5	62.174			0.183	31.087	0.24

Diffraction of TiO_2 in Figure 4 represented that the phase TiO_2 which was applied in this research is anatase phase. Table 2 shows the size having by TiO_2 particles. By grinding TiO_2 with ethanol 96%, it successfully generated the size of TiO_2 to reach nanometer (nm) with the anatase phase. Using equation (1) succeeded in determining the size of TiO_2 at 0.59, 0.426, 0.36, 0.31 and 0.24 nm in Table 2. The obtained size is 0.59 nm. In other words, the smaller size of TiO_2 will absorb photons optimally because the smaller semiconductor size possesses huge surface area per-volume, and consequently, it can accommodate lots of dyes that will absorb numerous photons. Furthermore, the measurement has been done by SEM Joel type JSM-6510 LA to analyze the morphology of working electrode Figure 5. Figure 5 shows the results of the SEM test having been tested on the electrode-working surface. The working electrode was made with TiO_2 at sintering temperature from 0-350 °C for 1-hour. The results obtained are not homogeneous because there are differences in the size of TiO2, but the differences obtained are not significant because it is approximately 0.1-0.6 nm (Table 2). Figure 5A and Figure 5B illustrated the TiO_2 included in phase of anatase and coloring which adhere to TiO_2. Anatase is a phase that frequently is obtained on TiO_2 like according to Sahrul et al. (2013) used TiO2 as a semiconductor that it successfully created TiO_2 in the anatase and the size phase obtained by the nanometer [25]. Additionally, who was undertaken by Susanti et al. (2014) using TiO_2 by variation in burning temperature 550 ^oC, 650 ^oC and 750 ^oC for 60 & 120 minutes that the result reported the difference of temperature did not make a change in size [9].

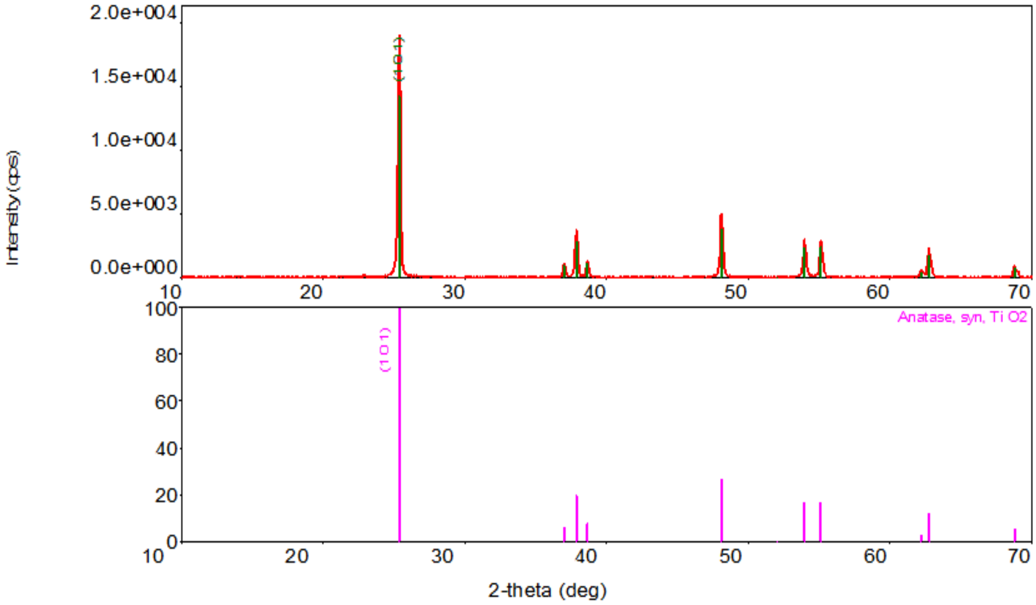

Figure 4: X-ray Diffraction of TiO2

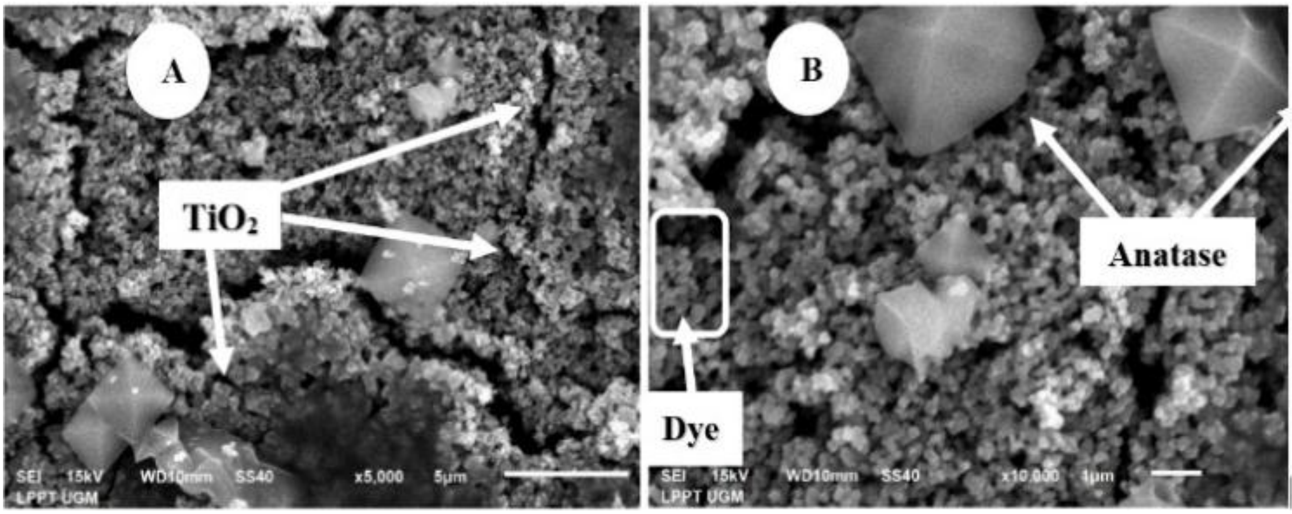

Figure 5. SEM morphologies of DSSC a. 5 µm and b. 1 µm

Measurement of current and voltage as fill factor analysis (FF) and efficiency value (ɳ) in DSSC was carried out at 10:00 to 11:00 WITA under sun illumination. The DSSC layer contains the working electrode, electrolyte and counter electrode. The working electrode was composed of TiO_2 with variations in the thickness of 11 µm, 15 µm, and 20 µm by sintering temperatures from 0-300 ^oC for 1 hour. After that, it was soaked *Caesalpinia Sappan L.* wood fluid (24 hours) for 15 hours in order that dye and semiconductor stick each other. Because the concept theoretically shows that the dye will work as absorbing photons, after that, the photons will bump electrons in semiconductors to occur electron transfer. While the carbon was made from burning ITO glass with wax. The result of current and voltage can be calculated by equations (2) and (3) [21] [26] :

$$FF = \frac{V_{max} J_{maks}}{V_{oc} J_{sc}} \quad (2)$$

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{I_0} \times 100\% \quad (3)$$

Where Jsc: highest current density (mA/cm^2); Jmax: maximum current density (mA/cm^2); Vmax: maximum voltage (V); Voc: the highest open-circuit voltage; FF: fill factor; Pout: output power (mW/cm^2); Pin: input power from the sun (lux conversion to mW/cm^2); η: Efficiency (%).

Table.3 Efficiency photovoltaics of DCCS Thickness

Thickness (μm)	Days	Jsc (mA)	Voc (V)	FF	Pin (mW/cm^2)	η (%)
11	H1	0.007111	0.259	0.486486	8.78	0.010205
	H2	0.062222	0.245	0.387172	8.78	0.067223
15	H1	0.084444	0.487	0.308138	8.78	0.144327
	H2	0.196889	0.323	0.271467	8.78	0.196629
20	H1	0.031111	0.217	0.367149	8.78	0.028231
	H2	0.060444	0.221	0.361688	8.78	0.055028

Table 3 shows the values obtained when it measures with thickness variations, namely: 11 μm, 15 μm and 20 μm. The thickness of 11 μm and 20 μm got the value of Jsc and Voc on the first day (0.007111 mA / cm^2: 0.259 V); (0.031111 mA/cm^2: 0.217 V) and the second day (0.062222 mA/cm^2: 0.245 V); (0.060444 mA / cm^2: 0.221 V) while the thickness of 15 μm had the value of Jsc and Voc greater more than before (0.084444 mA/cm^2: 0.487 V); (0.196889 mA/cm^2: 0.323 V). In other words, thickness greatly influences the value of the efficiency, like who was done according to Arman et al. (2015) to produce the higher efficiency of 7.5% the dye from N719 [6]. Additionally, who was reported by V. Baglio et al. (2011) by varying the thickness of TiO_2 6-14 μm produced the highest efficiency at a thickness of 10 μm of 1.44% the dye from N3 solution [27]. This research has calculated using equation 3, to obtain Jsc, Voc, and efficiency. The highest efficiency value in the study was 0.196629 % with FF values of 0.271467 at a thickness of 15 μm with organic dye from *Caesalpinia Sappan* L. in Table 3 Comparing to the research of Arman et al. (2015) and V. Baglio et al. (2011) uses some thicknesses of TiO_2 which produced good efficiency values but using the dye from non-organic.

The thickness of the semiconductor on the working electrode greatly influences the performance of the electron. The role semiconductor is to create the holes and to keep the electrons will be absorbed by the dye. In summary, the dye absorbs photons to crash electron, the free electrons are leaded by dyes with beginning HOMO (Highest Occupied Molecular Orbital) to LUMO (Lowest Unoccupied Molecular Orbital). After that, the electrons are inputted to the nano-semiconductor like TiO2, and consequently, ITO on glass surface accepts electron which will then occurs transferring energy. Then, the operation cycle occurs by helping I^- and I^{3-} [28]. Based on several research results, the thickness of the semiconductor was too thin, the number of holes will be formed more a little and an amount of electron will flow slightly and if the thickness of the semiconductor was too thick that it will affect the electrons like the electrons are difficult to move, and consequently, DSSC performance is not optimal [1, 2, 6, 7, 27]. So that, thickness accuracy is needed on a semiconductor to improve DSSC performance. The reported research used various thickness TiO_2 as a semiconductor and the organic dye of *Caesalpinia Sappan* L. that it has succeeded to improve the performance of DSSC which was better with a thickness of 15 μm and efficiency of 0.196629% (Table 3).

Conclusion

The effect of reducing the length of maceration on dye absorption has been carried out. Using dye from *Caesalpinia Sappan* L. wood and varying the immersion time of maceration namely; 20 minutes, 24 hours, and 48 hours resulted. The results of the UV-Vis test showed that with 24-hour immersion it succeeded in increasing the absorbency of *Caesalpinia Sappan* L. wood. The absorbance value was obtained at 2.83 with a wavelength of 444.5 nm (visible). In some literature, the content possessed by *Caesalpinia Sappan* L. wood is mostly Brazilin which is classified as a dye which can be applied in DSSC, namely flavonoids.

The effect of TiO2 thickness on the efficiency value has been analyzed. Using a thickness of 11 μm, 15 μm and 20 μm reported that the current and voltage measurements on under sun illumination showed that the thickness of 15 μm succeeded in increasing the performance of DSSC with Jsc & Voc of 0.621778 mA/cm^2: 0.528 V and FF & efficiency of 0.50393138 and 1.164458% while the thickness of 11 and 20 μm obtained smaller efficiency values of 0.041543 and 0.032468%.

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