



The Correlation Between Dye Absorption and Illumination Wavelengths on DSSC Performance

Manuntun Manurung^a, I Putu Tedy Indrayana^b, Fiar Tri Santika^b, Hery Suyanto^{b,*}

^a Department of Chemistry, Faculty of Mathematics and Natural Sciences, Udayana University, Bali, Indonesia

^b Department of Physics, Faculty of Mathematics and Natural Sciences, Udayana University, Bali, Indonesia

* Corresponding author: hery@unud.ac.id

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Abstract

This study examines the effect of the wavelength of light illuminated on DSSC on the absorption wavelength and gap dye energy. The dye used was sea lettuce anthocyanin from Sanur Beach, Bali. As much as 20 grams of dried sea lettuce powder was dissolved in 80 mL of 96% ethanol and 6% HCl. After 24 hours of immersion, it was filtered with Whatman 41 paper. The filtrate was characterized using a UV-Vis-NIR spectrophotometer and obtained anthocyanin dye absorption wavelengths of 272.5 nm, 417 nm, and 653.5 nm. The gap energy was calculated using the Tauc Plot method, and the result was 2.826 eV. The dye was used to make DSSC using the sandwich method, and then it was illuminated with white, red, and purple LEDs. The peak wavelengths of the LEDs were 439.67 nm and 550.29 nm for white, 629.04 nm for red, and 425.38 nm for purple. The irradiation intensity of each LED was varied to 1000 lux, 2000 lux, and 3000 lux. Illumination using purple LEDs produced maximum current and highest efficiency compared to white and red at 1.33 mA, 1.57 mA, and 1.83 mA for 1000 lux, 2000 lux, and 3000 lux, respectively. The efficiency was 0.0039 for 1000 lux. The purple color has a wavelength close to and intersects with the absorption wavelength of the dye and has an energy (2.918 eV) greater than the gap energy of the dye.

1. Introduction

Human dependence on electricity may result in the depletion and decrease of fossil fuel sources. One of the efforts to overcome the limitations of fossil fuels is the development of affordable, environmentally friendly, and endless renewable energy sources, such as using solar energy converted directly into electrical energy through a solar cell system. One type of widely studied solar cell that uses plants is the dye-sensitized solar cell (DSSC). Since the development of DSSC in 1991 [1], many researchers have conducted research to improve DSSC performance. One method of enhancing DSSC efficiency is by lowering the energy gap of the dye, thus resulting in a greater amount of sunlight absorption. Therefore, many researchers have attempted to accomplish this in numerous ways, such as by extracting chlorophyll from diverse plants in various methods [2, 3, 4, 5] and using anthocyanins as dyes [6, 7, 8]. In addition, several studies

have used various methods, such as mixing between anthocyanins and chlorophyll [9, 10], adding silver nanoparticles (AgNPs) both before TiO₂ is coated onto a conducting glass substrate (FTO/AgNPs/TiO₂) and after (FTO/TiO₂/AgNPs) and also mixed into TiO₂ in making photoanode electrodes [11, 12], and mixing chlorophyll extract with nanoparticles [13]. These studies only pay attention to the optimum absorption conditions based on the calculation of the gap energy of the dye material, which has not taken into account how the gap dye energy is after being combined with the DSSC constituent material or after being coated on the TiO₂ semiconductor material at the anode (working electrode). According to Junger *et al.* [14], the dye's adsorption wavelength shifted towards the red (bathochromic) wavelength after being coated onto the TiO₂ semiconductor, thus requiring an adjustment in the wavelength of the light illuminating onto the DSSC.

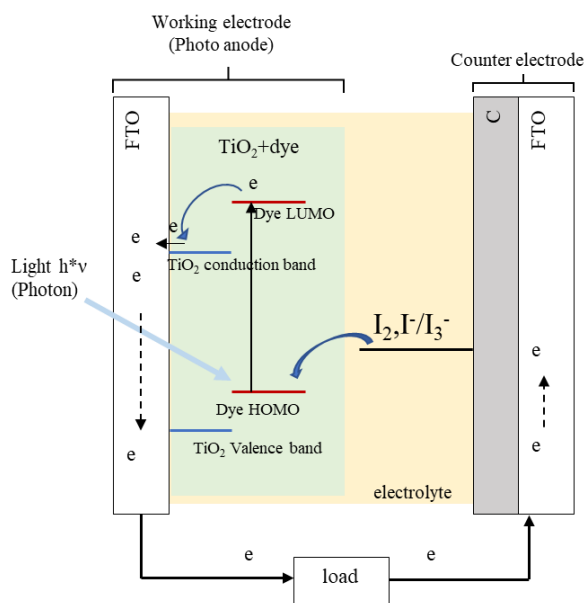


Figure 1. DSSC mechanism of action

The working principle of DSSC is shown in Figure 1, starting from the dye molecule (sensitizer) absorbing photons with a wavelength corresponding to the energy gap difference between the lowest unoccupied and highest occupied molecular orbitals (LUMO and HOMO). The electrons in the HOMO that absorb these photons then move to the LUMO (excited state), which is then injected into the conduction band (CB) of the TiO_2 semiconductor. Through the diffusion process, these electrons flow to the glass substrate conducting layer, FTO (anode). Furthermore, the electrons flow past the external load towards the cathode (comparison electrode, counter electrode) and produce a current that returns to the DSSC after recombining with the acceptor in the electrolyte [15].

Based on the description of the relevant research results and the workings of DSSC, the performance of DSSC increases when there is a match between the wavelength of the incident light and the absorption wavelength of the dye molecule. This paper discusses the suitability of the wavelength of light illuminated on a DSSC to the absorption wavelength and energy gap of the dye and its effect on the efficiency of the DSSC. The wavelengths of light used come from white, red, and purple LEDs and dye from sea lettuce anthocyanin molecules obtained from Bali's Sanur Beach.

2. Materials and Methods

2.1. Materials

The materials used include anthocyanin (sea lettuce from Sanur Beach Bali), 6% HCl, 96% ethanol (analytical grade) (Merck), potassium iodide (analytical grade) (Merck), iodine solution (I_2), TiO_2 powder, graphite, conducting glass substrate (FTO) 2 cm x 2 cm, distilled water, and wire clamp.

2.2. Preparation of Anthocyanin Extract

In this study, the sensitizer used was sea lettuce anthocyanin dye originating from Sanur Beach, Bali. Sea lettuce samples were washed, cut into pieces, then dried

for seven days in a room without sunlight. The dried samples were mashed using a blender until they turned into a fine powder, then extracted by maceration technique. This method is preferred because it uses straightforward procedures and tools and a natural extraction process to prevent the active ingredients in heat-resistant materials from decomposing [16, 17]. Twenty grams of sea lettuce sample powder was macerated in a solvent mixture of 80 mL of 96% ethanol [18], previously added with 6% HCl [19], for 24 hours. An extract was obtained, known as an anthocyanin extract sample which is green in color.

The extracted sample was filtered using the Whatman filter paper number 41. Then its absorbance was characterized with a UV-Vis-NIR spectrophotometer (Shimadzu/UV-1800) at a 200–800 nm wavelength range. According to Saha *et al.* [20], the typical absorption of anthocyanins is not only in the UV region with a wavelength of 260–280 nm and the visible region at a wavelength of 490–550 nm but also in the region of a wavelength of 400–450 nm indicates the presence of anthocyanins. Samples resulting from characterization using a UV-Vis-NIR spectrophotometer were analyzed to determine the absorption of anthocyanins in the sample and the energy gap using the Tauc plot method [13, 21, 22].

2.3. Electrode Preparation

The electrode is a component that plays a major role in DSSC. There are two types of electrodes in DSSC: anode or photoanode (working electrode) and cathode (comparison electrode, counter electrode). The working and reference electrodes used fluorine-doped tin oxide (FTO) glass as a base material to form transparent conductive oxide (TCO) glass.

The working electrode consisted of a translucent conducting glass (TCO) coated with TiO_2 , a wide energy gap semiconductor material (3.2 eV), and a layer of dye molecules adsorbed by TiO_2 . A total of 3.5 grams of TiO_2 powder was dissolved in 15 mL of ethanol (analytical grade) and stirred for 30 minutes with a magnetic stirrer to form a TiO_2 paste. Then, the conductive part of the TCO glass (2 cm x 2 cm) was bounded by a tape of 0.5 cm x 2 cm in size and 50 μm in thickness; therefore, the area of the TCO glass to be coated with TiO_2 was (2 x 1.5) cm^2 . The TiO_2 paste was dripped onto the TCO glass on the conductive part, which was then carried out by slip casting using a mortar until the thickness of the TiO_2 was the same as the thickness of the tape (50 μm). The thickness of TiO_2 was maintained in this study. The other electrode was the cathode, a conducting glass substrate (FTO) carbon-coated.

2.4. DSSC Circuit Production

The main components of DSSC were the photoanode (working electrode), cathode (comparison electrode), and electrolyte [15]. After TiO_2 was coated on TCO and immersed in sea lettuce dye, a working electrode was formed, which was then combined with a reference electrode by the sandwich method and filled with electrolyte (tri-iodide and iodide redox couple) [9, 15].

Furthermore, the two electrodes were connected through an external load of 45.8 Ω, as shown in Figure 2.

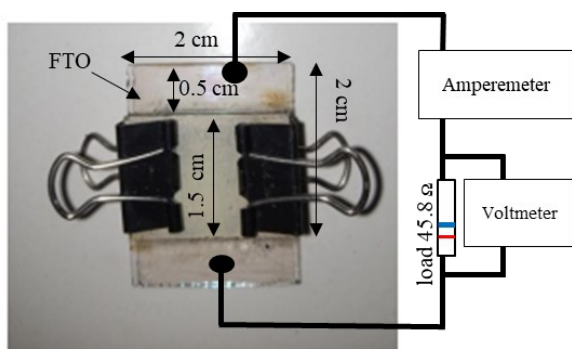


Figure 2. DSSC using the sandwich method

2.5. Efficiency Calculation

The DSSC was illuminated with white, red, and purple LEDs with varying intensities of 1000 lux, 2000 lux, and 3000 lux to determine its performance. The efficiency values were calculated after the current and voltage values were obtained. Efficiency is the ratio of the output power of the DSSC to the input power of the LED multiplied by 100%. The output power is the product of the current and the voltage generated from the ammeter and voltmeter. Meanwhile, the input power was the product of the intensity of the LED with the effective area of the DSSC (2 cm x 1.5 cm) illuminated by the LED.

3. Results and Discussion

Before analyzing the suitability between the wavelength of the photon illuminated on the DSSC and the absorption wavelength of the sea lettuce dye, it is first necessary to characterize the absorption wavelength and energy gap of the sea lettuce dye. The results can be presented in Figures 3 and 4.

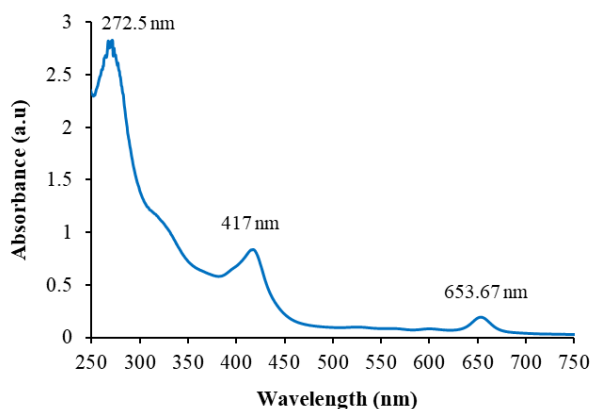


Figure 3. Absorbance spectra of sea lettuce dye with ethanol-HCl solvent

Figure 3 shows the absorbance spectra of the wavelength function of the extracts of sea lettuce analyzed with a UV-Vis-NIR spectrometer. The graph shows three absorbance peaks from the sea lettuce extraction at wavelengths of 272.5 nm, 417 nm, and 653.5 nm. Furthermore, from the results of this absorbance, the energy gap was determined using the Tauc plot method [22]. It was only taken in the visible light wavelength range (400–700 nm), resulting in

2.826 eV, as shown in Figure 4. The selection of this wavelength range is based on the study by Juhász junger *et al.* [23], who reported that UV wavelengths do not affect DSSC efficiency. Furthermore, this sea lettuce dye was used to produce DSSC by the sandwich method, which combines working electrodes, reference electrodes, and electrolytes [15, 24], as shown in Figure 2.

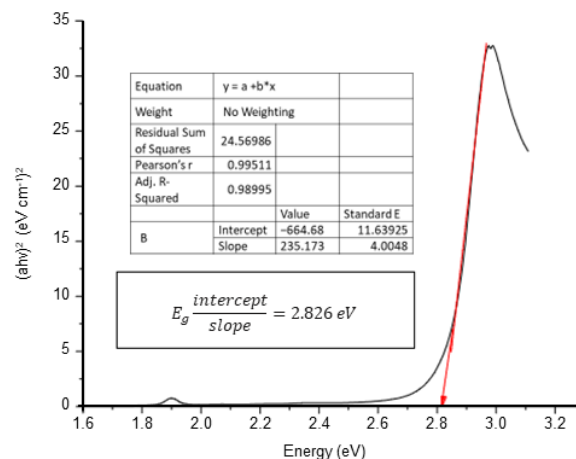


Figure 4. Graph of energy gap (E_g) of sea lettuce dye

It can be seen in Figure 4 that the conducting glass is an FTO (conducting glass substrate) with a size of 2 cm × 2 cm, but the effective area of TiO₂-coated DSSC and carbon catalyst and dye molecules is 1.5 cm × 2 cm, and the effective area of DSSC is 3 cm². Then DSSC (3 cm²) was illuminated by LED with three intensity variations of 1000 lux, 2000 lux, and 3000 lux. Based on the standard value for the effectiveness of an LED which is 90 lm/watt, each intensity is equivalent to 0.033 watts, 0.067 watts, and 0.1 watts. Three LED light colors, white, red, and purple, were used for DSSC illumination with the wavelength spectra of each color, as shown in Figure 5.

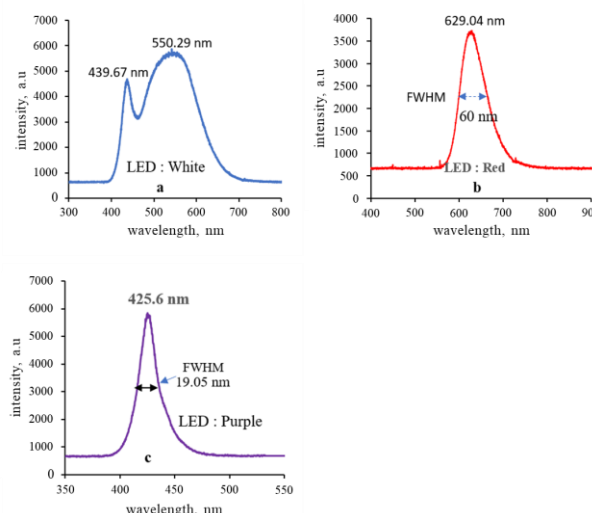


Figure 5. LED spectra a) white, b) red, c) purple

Figure 5 shows the white, red, and purple LED spectra (visible light) with their respective wavelength regions of 400–700 nm (with peaks at 439.67 nm and 550.29 nm), 629.04 nm, and 425.38 nm. The current and voltage flowing in the DSSC circuit were measured to determine the performance of the DSSC due to the influence of the

illuminated LED wavelength. The results of the measurements can be seen in Figure 6.

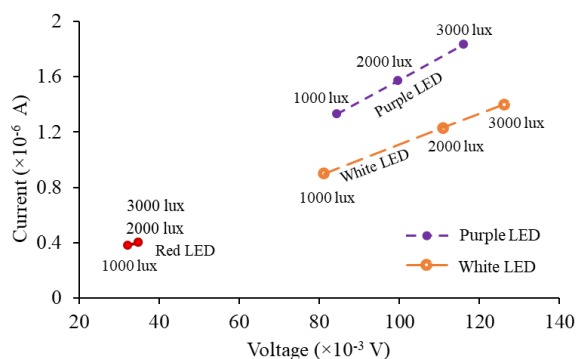


Figure 6. Graph of current-voltage (I-V) of DSSC with an external resistance of 45.8 Ω

Figure 6 shows the relationship between the maximum voltage and maximum current of the DSSC flowing through an external resistance load of 45.8 Ω, which is illuminated with white, red, and purple LED lights with varying intensities of 1000 lux, 2000 lux, and 3000 lux.

Based on the data in Figure 6, when the DSSC is illuminated with a purple LED, the flowing current is greatest compared to the other two LED colors. This is because the purple color has a peak wavelength of 425.38 nm which can still be absorbed by sea lettuce dye in the absorption wavelength region of 417 nm or, to be precise, in the absorption wavelength range from 404.72 nm to 446.50 nm (the shaded part) with a peak wavelength of 418.7 nm as shown in Figure 7. This can be explained based on Tables 1 and 2 by paying attention to the full width at half maximum (FWHM) value, which means that the two spectra have a mid-spectral width of 27.31 nm for dye spectra at a wavelength of 417 nm and 19.05 nm for LED purple color at a wavelength of 425.38 nm. As a result, the two spectra overlap where the absorption area is limited by the two spectra in the absorption wavelength range from 404.72 nm to 446.50 nm (shaded area) with a peak wavelength of 418.7 nm as shown in Figure 7.

In addition, the purple wavelength has an energy of 2.918 eV [25] which is larger than the energy gap of sea lettuce dye (2.826 eV). Therefore, the electrons in the HOMO orbital that are released after absorbing this purple wavelength energy can move to the LUMO orbital [15] by using an energy difference of 0.092 eV (i.e., the purple LED energy minus the gap dye energy, which is 2.918 eV - 2.826 eV = 0.092 eV) and then generates a current. This can be proven also by increasing the intensity. If the intensity of the illuminated purple LED is increased to 1000 lux (0.033 W) to 2000 lux (0.067 W) and 3000 lux (0.1 W), then the current also increases from 1.33 mA, 1.57 mA, and 1.83 mA, respectively, as shown in Figure 6. This can be explained by the fact that, as the intensity increases, the number of purple light photons illuminated also increases [25], resulting in more electrons absorbing photons and releasing them in the HOMO orbitals. Consequently, the number of electrons moving into the LUMO orbitals increases as well and causes the current to

increase. This kind of phenomenon is identical to the process of the photoelectric effect [25].

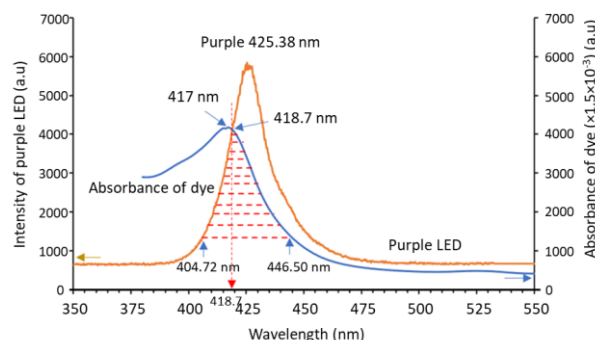


Figure 7. Spectra of purple LED light and sea lettuce dye

Table 1. Wavelength, FWHM, and energy of white, red, and purple LED lights

Color /LED	Peak Wavelength (nm)	FWHM (nm)	Energy (eV) [25]
White	439.67	65	2.825
	550.29	156	2.257
Red	629.04	60	1.974
Purple	425.67	19.05	2.918

Table 2. The wavelength, FWHM, and gap dye energy of sea lettuce

Dye sea lettuce	Peak wavelength (nm)	FWHM (nm)	The energy gap of dye (eV)
Peak 1	272.5	-	
Peak 2	417	27.31	2.826
Peak 3	653.67	23.50	

The same thing happens to the white LED, which has two wave peaks at 439.67 nm and 550.29 nm. In this case, the one that plays a role in the operation or absorption by DSSC is at a wavelength of 439.67 nm because it is still closer to the dye wavelength (417 nm) than the 550.29 nm wavelength to the dye absorption wavelength of 653.67 nm. Although the wavelength for the peak of 439.67 nm is quite far from the absorption wavelength of sea lettuce anthocyanin dye (417 nm), there are still wavelengths absorbed by the dye after it is placed in the range of 400.19 nm to 462 nm (shaded area) with overlap at 427 nm as in Figure 8, so that white LED light can also release some of the electrons in the HOMO orbitals.

In addition, the white LED light at a wavelength of 439.67 nm has an energy of 2.825 eV (Table 1), which is nearly identical to the energy of the sea lettuce gap dye (2.826 eV), allowing the released electrons to travel to the LUMO orbitals and generate currents in the outer circuit, as shown in Figure 6. For the same reason as the purple LED light, when the intensity of the white light is increased from 1000 lux to 2000 lux and 3000 lux, the resulting current also increases from 0.9 mA to 1.23 mA and 1.4 mA, respectively.

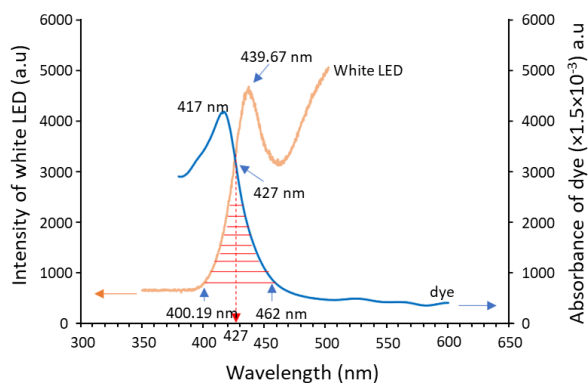


Figure 8. White LED spectra and sea lettuce dye spectra at a wavelength of 417 nm

Based on the research of Junger *et al.* [14] and Juhász junger *et al.* [23], the absorption peak of the dye shifts towards a longer wavelength (bathochromic shift) when the dye molecule is coated on TiO₂. This shift is caused by the anthocyanin dye, which is adsorbed/coated on the surface of TiO₂, which facilitates the transfer of electrons through the long conjugate double bond so that the energy drops and causes a shift to a longer wavelength. Thus, the absorption wavelength peak of the anthocyanin molecule (417 nm) is shifted to the right, increasing the overlap with the peak wavelength of purple and white LED light (Figures 7 and 8). Consequently, more electrons absorb the energy from these colors, then excited from the HOMO orbitals to LUMO, thus generating a current.

On the other hand, when a red LED light illuminates the DSSC, the current flowing in the DSSC is very little even though the energy or color wavelength is entirely absorbed by the anthocyanin dye molecule as shown in Figure 9 (part of the shaded area). This is because the energy of the red color of 1.974 eV (Table 1) is lower than the gap energy of the sea lettuce dye (2.826 eV), so theoretically, the released electrons cannot move to the LUMO orbital, but in reality, there is a current of 0.38 μA. Furthermore, the intensity is varied to determine the current phenomenon. There is a very small current change from 0.38 μA to 0.4 μA when the intensity is changed from 1000 lux to 2000 lux. However, there is no increase in current flowing when the intensity is increased from 2000 lux to 3000 lux, as shown in Figure 6. This type of current is called dark current, which does not depend on the light illuminated in DSSC.

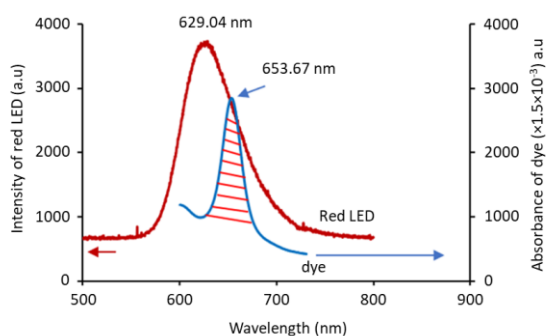


Figure 9. Red LED spectra (629.04 nm) and sea lettuce dye spectra at a wavelength of 653.57 nm

Efficiency was calculated to further determine the DSSC's characteristics as a function of the absorbed light wavelength. DSSC efficiency (η) is the ratio between the output and incident light power on the DSSC. Based on the measured current-voltage data in Figure 6, the efficiency for an intensity of 1000 lux is obtained, as shown in Figure 10.

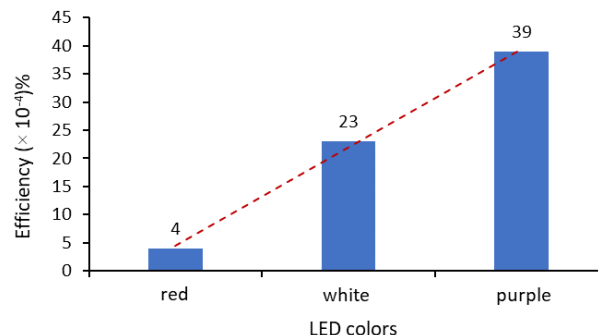


Figure 10. DSSC efficiency graph with white, red, and purple LED light sources with an outer resistance of 45.8 Ω for an illumination intensity of 1000 lux

It can be seen in Figure 10 that the efficiency increases with increasing light energy illuminated to the DSSC. This is because the higher the energy of the illuminated light, the more electrons are released from the HOMO orbital and move to the LUMO orbital, resulting in a greater current which consequently increases the output power or efficiency.

4. Conclusion

Based on the research data, there is a correlation between the wavelength of light illuminated on the DSSC and the absorption wavelength of the dye on the DSSC. In the DSSC process, the dye only absorbs the wavelength of light that matches the absorption wavelength and will produce a current if the absorbed light energy has the smallest energy equal to the energy gap.

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