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THE IMPACT OF SOLVENT COMPOSITION AND COPPER (Cu) ION DOPING ON DYE ANTHOCYANIN ON INCREASING DYE-SENSITIZED SOLAR CELL (DSSC) EFFICIENCY

Novi Dyah Puspitasari, Fahru Nurosyid*, Untung Riyadi, Sophia Dewi Nur Anisa, Kusumandari Kusumandari
Department of Physics, Faculty of Mathematics and Natural Sciences, Sebelas Maret University, Surakarta, Indonesia
*fahrunurosyid@staff.uns.ac.id

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ABSTRACT

The development of Dye Sensitized Solar Cells (DSSC) is increasing fast because fabrication costs are more affordable than silicon solar cells. In this study, anthocyanin pigments were used as a natural dye source. Anthocyanins are a group of flavonoids that can be extracted most proficiently in acidic conditions; therefore, variations in the composition of solvents and acids significantly impact anthocyanin yield. The anthocyanin pigments in this study were extracted from dragon fruit peels using a maceration method with variations in methanol composition and the addition of hydrochloric acid or citric acid (3/0; 3/0.5; 3/1). This study aims to improve the efficiency of DSSC by varying the solvent composition and adding Cu ion doping. The characterizations include measurement of absorbance, functional group, and efficiency using UV-Vis Spectrophotometer, Fourier Transform Infrared (FTIR), and current-voltage, respectively. The results show that anthocyanin dye with a composition of methanol/acid (3/0) and the addition of Cu ion produced the highest absorbance value and efficiency of 0.4102 $\Omega^{-1}m^{-1}$ and 0.016%, respectively.

Keywords: Anthocyanin; Efficiency; DSSC

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INTRODUCTION

Solar cells can transform solar energy into electrical energy. A dye-based third-generation solar cell device that acts as a photosensitizer is a dye-sensitized solar cell (DSSC). DSSC is less expensive than silicon solar cells, lighter, more flexible, and environmentally friendly [1-2]. Glass substrate (FTO or ITO), photoanode (TiO_2, SnO_2, or ZnO), electrolyte as a redox mediator, counter electrode (Pt or C), and dye as photosensitizer are the components of DSSC [3-5].

Dye or natural dyes are one of the essential components in increasing DSSC efficiency because dye acts as a photosensitizer, absorbing sunlight directly, producing photoelectrons, and exciting electrons to semiconductor materials [6-7]. The dyes used are classified into two types: synthetic dyes and natural dyes. Synthetic dyes of type N719 or ruthenium, which can produce DSSC efficiency of 10%-13% [89], are commonly used. Using ruthenium-based synthetic dyes has high stability and efficiency, but the price of synthetic dyes is very high, and the ruthenium dye synthesis process is complicated and unfriendly to the environment. An appropriate ruthenium substitute, namely natural dyes, is required to address this issue. Natural dye was chosen because of its durability. Natural dye was chosen because it is inexpensive, easy to manufacture, and environmentally friendly. However, the highest DSSC efficiency level obtained from natural dyes is deficient, namely 3% [10]. Anthocyanin pigments are natural dyes that can be used in place of ruthenium. Anthocyanin pigments absorb at the same wavelength range as ruthenium, which is 420 nm to 660 nm. Furthermore, anthocyanin pigments can be dissolved in water and have bonds that cause electrons to be excited, increasing DSSC efficiency [11]. The anthocyanins used in this study were extracted from dragon fruit peel because dragon fruit (Hylocereus undatus) is abundant in Indonesia, easy to obtain, and the extraction process is simple.

After removing organic compounds, anthocyanin dye modification can be done to increase the efficiency of DSSC; thus, selecting suitable solvents and extraction methods can affect the stability of DSSC. Because anthocyanin color stability and antioxidant activity are strongly influenced by pH and temperature factors, anthocyanins can be optimized by considering extraction conditions. Anthocyanins are a group of flavonoids that can be extracted most proficiently in acidic conditions. Acidic conditions in anthocyanin extraction decompose plant cell membranes, allowing anthocyanin pigments to dissolve and leave the cell while preventing flavonoid oxidation [12].

The acid must be added during the extraction process to optimize the anthocyanin pigment. The acids used in this study were citric acid and hydrochloric acid. Additionally, copper (Cu) ions can be added to increase the conductivity of anthocyanin dye. With the addition of Cu, the dye's electron transport can be maximized, facilitating the transfer of electrons from the valence band to the conduction band. As a result, this study concentrated on using methanol as a solvent and varying hydrochloric and citric acid concentrations. This study aims to improve the efficiency of DSSC based on dragon fruit peel that has been mixed with hydrochloric acid and citric acid in a methanol solvent, as well as to try to improve the conductivity of the dye with Cu ion doping on the TiO_2 semiconductor using the spin coating method.

METHOD

Dragon fruit peel extract is used to make anthocyanin dye. The dragon fruit skin is cut into small pieces and mashed to form a pulp. Twenty grams of dragon fruit peel were used in the anthocyanin extract, which was then dissolved in various ratios of methanol and citric acid (3:0; 3:0,5; 3:1). The mixture was then stirred for 2 hours at a speed of 300 rpm at a temperature of 40 ºC before being allowed to stand in a closed room for 24 hours. The dye was then filtered through Whatman filter paper no. 42. The preceding steps are repeated by adding another acid, hydrochloric acid. The anthocyanin dye was tested for UV-Vis absorption, IR spectrum with Fourier Transform Infra-Red (FTIR), and conductivity with the Two Point Probe method.

Cu doping was made by dissolving $CuSO_4.5H_2O$ with a concentration of 10^{-3} M into each variation of anthocyanin dye. The mixture was then stirred for 1 hour at 40 °C at a speed of 300 rpm. This mixture was then subjected to UV-Vis absorption, FTIR IR spectrum, and conductivity testing using the Two Point Probe method.

For making the photoanode, TiO_2 paste was dissolved in ethanol at a 1:2 g/ml ratio for 4 hours while stirring at 300 rpm. TiO_2 paste was deposited on a conductive glass of fluorine tin oxide (FTO). The conductive side of the FTO glass can be tested with a multimeter before scotch is applied to a 0.5x0.5 cm area. TiO_2 was deposited using the spin coating method at 1000 rpm for 60 seconds, followed by drying on a hotplate at 100 ºC for 15 minutes. The FTO glass was then annealed in a carbolite furnace for 10 minutes at 400 ºC. For 24 hours, the TiO_2 layer was immersed in a different anthocyanin dye solution.

The electrolyte solution was made by stirring for 30 minutes at 300 rpm a solution of potassium iodide (KI) and polyethylene glycol (PEG) in a ratio of (0.8:10) ml. After adding 1.2 grams of Iodine (I2) to the mixed solution, it was stirred at 300 rpm for 30 minutes.

Platinum (Pt) deposited on FTO glass was used as the counter electrode. Pt was deposited using a spin coating method at 1000 rpm for 60 seconds, then dried on a hotplate at 100 ºC for 15 minutes. The FTO glass was then annealed in a carbolite furnace for 10 minutes at 400 °C.

The DSSC configuration was used to combine the two active areas of the photoanode and counter electrode. The two electrodes were combined by applying a layer of thermoplastic sealant to the right and left of the electrode's non-active area, which was then heated. The electrolyte solution was injected into the DSSC arrangement, and the current-voltage was measured using a Keithley I-V meter. An essential quantity reflecting a solar cell’s total efficiency is the power conversion efficiency:

$$\eta = \frac{FF \; X \; I_{sc} \; x \; V_{oc}}{P_{in}} \; x \; 100\% \qquad (1)$$

V_{oc} is the open-circuit voltage that is in contrast with the Fermi level of TiO_2 and the redox potential of the electrolyte, and the incident-light power density is P_{in}. I_{sc} is the current width of the short circuit. FF is the fill factor that demonstrates the cell’s inherent quality.

$$FF = \frac{(I_{max} \; x \; V_{max})}{(I_{sc} \; x \; V_{oc})} \qquad (2)$$

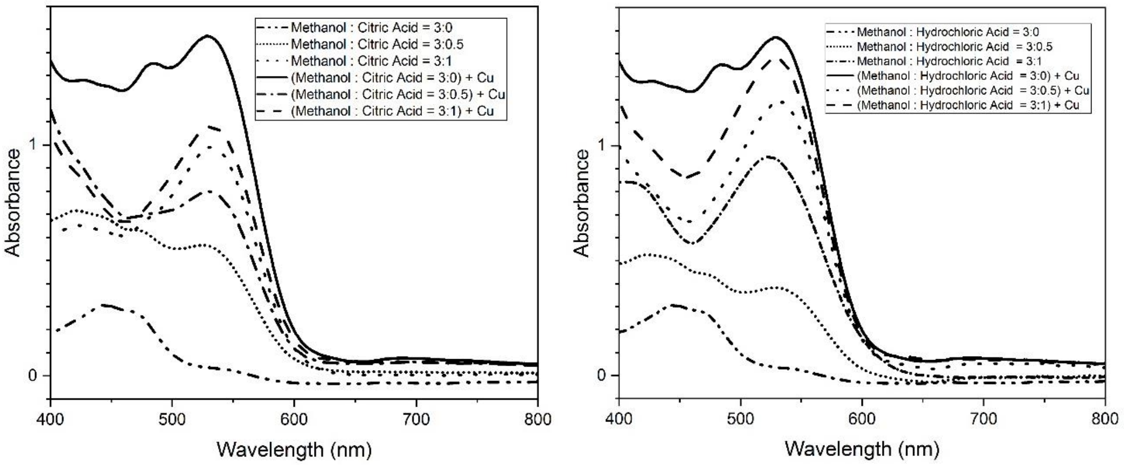
where V_{max} and I_{max} correspond to voltage (V) and current (I) values that maximize their product.

RESULTS AND DISCUSSION

Characteristics of optical properties of anthocyanin dye solution derived from dragon fruit peel extraction can be determined through UV-Vis testing. One of the essential components of DSSC is the dye anthocyanin, which absorbs at wavelengths ranging from 420 nm to 660 nm. This UV-Vis test was conducted to determine the absorption of anthocyanin dye from dragon fruit peel extraction with various acid compositions mixed in methanol. Cu doping was added to increase the absorbance and electrical conductivity of the dye solution.

Figure 1 depicts the presence of visible anthocyanins in the wavelength range of 450-600 nm, where the absorption includes the visible light region, allowing it to absorb sunlight and be used as a sensitizer in DSSC. The highest absorbance peak was obtained after extracting dragon fruit peel with methanol solvent and adding acid in a volume ratio of 3:0, followed by Cu doping, which showed a maximum absorbance value of 1.471 at a wavelength of 529 nm and an absorption width in the wavelength range of 463-583 nm. The absorbance value of the anthocyanin dye solution extracted with the addition of Cu doping was higher than the absorbance value of the anthocyanin dye solution extracted without the addition of Cu.

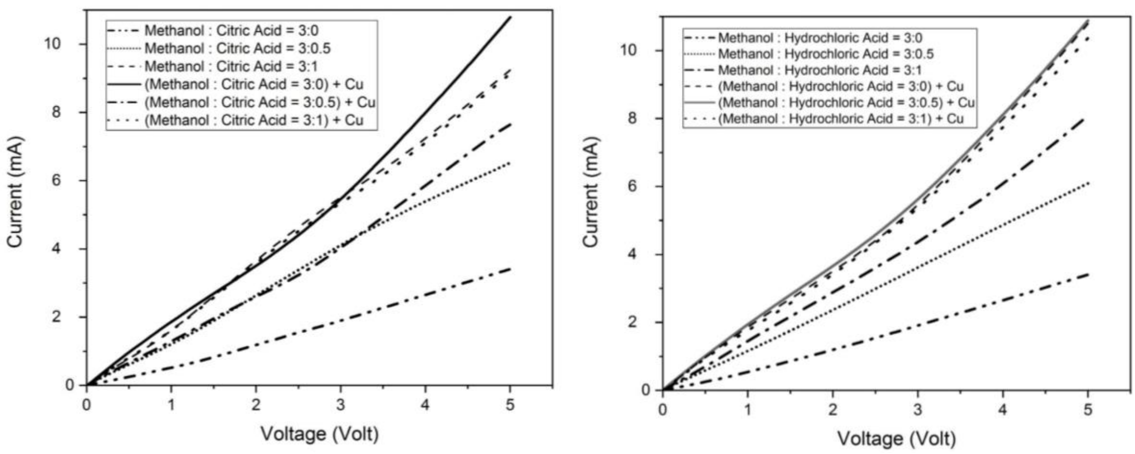
Cu doping in anthocyanin dye solution can increase light absorption, increasing the intensity of the absorbed light and producing free electrons that can fill the semiconductor's conduction band [13].



(a) (b)

Figure 1. The spectrum of dye absorption with variations in addition (a) citric acid and (b) hydrochloric acid

When the anthocyanin dye was mixed with acid in the ratios of 3:0.5 and 3:1, the amount of Cu added was reduced. This is because Cu has the highest value when added to a neutral or alkaline solution [14]. Anthocyanin dye extracted with methanol and added Cu had an acidic pH of 6. In contrast, anthocyanin dye added with acid and Cu had a pH of 5, indicating that a more acidic condition could affect the presence of Cu, resulting in a decrease in dye absorbance and conductivity.The two-point probe method was used to determine the conductivity of anthocyanin dye. The conductivity test results become one of the components that support the DSSC's performance. Electrical conductivity testing is performed to validate a dye solution's ability to conduct electric current. The ions contained in the solution carry the electric current [15].



(a) (b)

Figure 2. The conductivity of the dye solution with variations in the addition of (a) citric acid and (b) hydrochloric acid

The relationship between current and voltage from conductivity testing is typically linear, as illustrated in Figure 2, with the greater the current generated, the greater the voltage. The electrical conductivity of the dye solution with different methanol compositions and the addition of citric acid (3/0; 3/0.5; 3/1) is 0.1235 $\Omega^{-1}m^{-1}$; 0.2805 $\Omega^{-1}m^{-1}$; 0.3371 $\Omega^{-1}m^{-1}$, and when Cu is added, the conductivity value increases to 0.6922 $\Omega^{-1}m^{-1}$; 0.2809 $\Omega^{-1}m^{-1}$; 0.4086 $\Omega^{-1}m^{-1}$. Meanwhile, the electrical conductivity obtained by the dye solution with variations in the composition of methanol and the addition of hydrochloric acid (3/0; 3/0.5; 3/1) has a value of 0.1235 $\Omega^{-1}m^{-1}$; 0.2267 $\Omega^{-1}m^{-1}$; 0.2985 $\Omega^{-1}m^{-1}$and after added with Cu the conductivity value increased to 0.6922 $\Omega^{-1}m^{-1}$; 0.4102 $\Omega^{-1}m^{-1}$; 0.5108 $\Omega^{-1}m^{-1}$.

The highest conductivity value was obtained after extracting the dragon fruit peel with methanol solvent and adding acid in a 3:0 ratio, which was then combined with Cu doping. Anthocyanin dye solution containing Cu has higher conductivity value than that does not contain Cu. It is due to the formation of ionic compounds in the solution following the addition of Cu doping. Ionic compounds can conduct electricity because they are broken down into ions, and the ions are produced to aid in the DSSC's continuous electron transfer process.

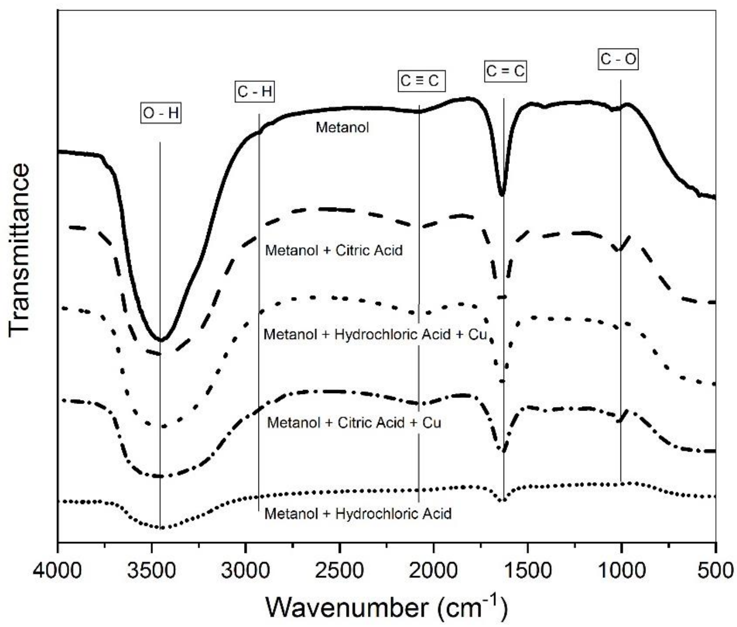
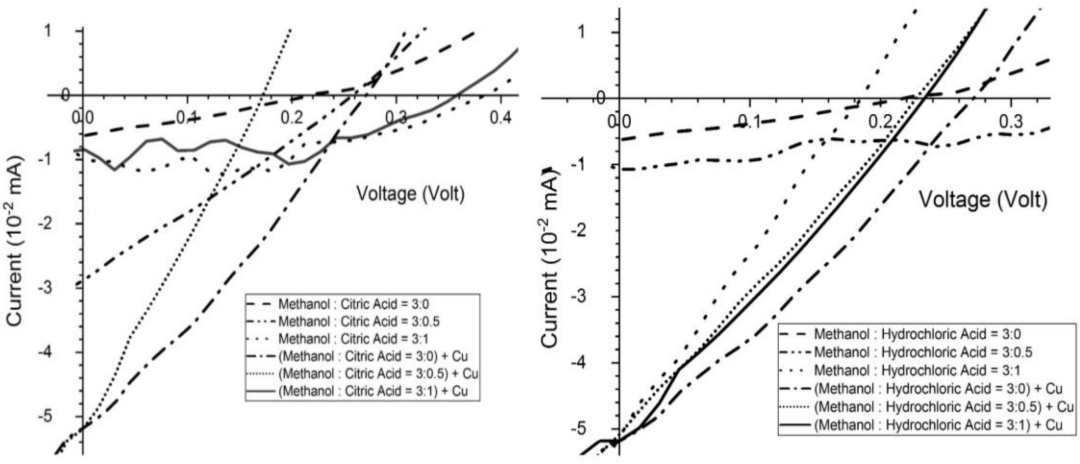


Figure 3. The FTIR spectrum of anthocyanin dye with citric acid and hydrochloric acid

FTIR was used to identify the chemical bonding groups in anthocyanin dye. Figure 3 depicts the spectrum obtained from the FTIR. Figure 3 shows that the anthocyanin dye solution has an O-H group in the 3400 cm^{-1} wave number range, a C-H group in the 2950 cm^{-1} wave number range, a C≡C group in the 2200 cm^{-1} wave number range, a C=C group in the 1600 cm^{-1} wave number range, and a C-O group in the 1300 cm^{-1} wave number range, with different intensities between anthocyanin dyes. When compared to the anthocyanin dye without doping, the transmittance intensity decreased. Because doping alters the molecular structure of anthocyanin, the molecular dipole moment changes, resulting in differences in transmittance intensity [16]. Figure 4 depicts the current and voltage measurements on the DSSC.



(a) (b)

Figure 4. I-V DSSC graph with variations in the addition of (a) citric acid and (b) hydrochloric acid

According to the I-V test, the efficiency value of DSSC with variations in methanol composition and the addition of citric acid (3/0; 3/0.5; 3/1) is 0.00162%; 0.007849%; 0.011748%, and when Cu is added, the efficiency value increases to 0.015926%; 0.009219%; 0.011827%. Meanwhile, the efficiency value of DSSC with different methanol compositions and the addition of hydrochloric acid (3/0; 3/0.5; 3/1) is 0.00162%; 0.005247%; 0.009585%, and when Cu is added, the efficiency value increases to 0.015926%; 0.012314%; 0.012912%. According to the efficiency values obtained, the efficiency of DSSC increases with the addition of acid in the extraction process. This is because the addition of acid can optimize the anthocyanin content of dragon fruit peel, increasing the absorbance peak and absorption width. Because of the formation of ionic compounds after the addition of Cu doping in the solution, where the ions produced will help the electron transfer process continuously in DSSC, the addition of Cu doping with the same concentration of 10^{-3} M can increase the efficiency of DSSC.

CONCLUSION

The use of acid in the extraction process, as well as the addition of Cu ion doping on anthocyanin dye, can improve efficiency. The value of DSSC efficiency with different methanol compositions and the addition of citric acid (3/0; 3/0.5; 3/1) is 0.00162%; 0.007849%; 0.011748%, and when Cu is added, the value increases to 0.015926%; 0.009219%; 0.011827%. Meanwhile, the efficiency value of DSSC with different methanol compositions and the addition of hydrochloric acid (3/0; 3/0.5; 3/1) is 0.00162%; 0.005247%; 0.009585%, and when Cu is added, the efficiency value increases to 0.015926%; 0.012314%; 0.012912%.

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