Synthesis of TiO₂/ZnO-Anthocyanin Hybrid Material for Dye Sensitized Solar Cell (DSSC)

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Abstract. Hybrid materials are composed of materials that have broad spectra absorption and can be added to other materials that improve their spectrum absorption. The characteristics of hybrid materials are the same characteristics as their constituent materials. When hybrid materials were added to organic compounds which combined with semiconductors, they can be used as photovoltaic applications. One of the most widely hybrid material research developments is its use as the solar cell. This research focused on TiO₂/ZnO hybrid materials synthesis combined with anthocyanin as a pigment to determine the characteristics of the hybrid material obtained. In this research is to find the extent to which method applied that determines the success of the targeted hybrid materials formation. In the synthesis process for various ratios, TiO₂ and ZnO have been formed a composite material which shown by diffractogram of characteristic peaks of TiO₂ and ZnO and vibrations of Zn-O-Ti detected in FTIR spectra. Testing hybrid materials by using FTIR showed a C=O vibration of anthocyanin in material hybrid TiO₂/ZnO-anthocyanin, than quality testing of hybrid materials was carried out using the DR UV-Vis instrument and was proved by enhancement of band gap energy between 3.2 to 3.3 eV

Key words — Anthocyanin, TiO₂, ZnO, Hybrid material, DSSC.

1. Introduction

As technology develops, new materials are also found including thin layers, thin silicon, organic photovoltaic cells, double linking, and organic-inorganic hybrids [1]. Each material has advantages, such as in organic-inorganic hybrids, which are cheaper and easier to synthesize. Hybrid materials are also composed of semiconductors which have broad absorption spectra and can be added with other materials which improve the absorption spectrum [2]. Organic compounds combined with semiconductors can be used as photovoltaic applications. This hybrid material has the same properties as its constituent material [3].

One of the developments in hybrid material that has been widely studied is its use as a solar cell. These solar cells become alternative energy sources that can be used besides biomass, geothermal, hydropower, marine, wind and solar [4]. The application of hybrid material as a forerunner to solar cells has the advantage of environmentally friendly properties [5]. Solar cells or known as Dye Sensitized Solar Cells (DSSC) consist of semiconductor components, sensitizers, electrolytes, electrodes, and conduction glass [6]. Several techniques and compositions of hybrid
materials have been investigated because they are possible to replace petroleum-based energy, have lower operational costs, and have a wide enough light absorption [4]. An important component in DSSC is semiconductors, because semiconductors also play a role in absorbing dyes that aim to make DSSC more efficient [7]. Common semiconductors for use are TiO$_2$, ZnO, and NiO which have advantages and disadvantages. The use of TiO$_2$ in DSSC has advantages in efficient light absorption. ZnO material has the advantage of slower charge recombination whereas for NiO it has advantages in fast hole injection. Then the TiO$_2$ material has the disadvantage of a fast reverse electron transfer rate, whereas for ZnO it has a shortage of clumping and ZnO instability and then for NiO has the disadvantages of rapid recombination and low dye regeneration [8]. Alwan and Ali (2015) have conducted a composite modification study between TiO$_2$ and ZnO to improve the performance of DSSC. The results of the study found that TiO$_2$ / ZnO composites had an efficiency value of 2.29%, while for TiO$_2$ and ZnO were 1.32% and 2% [9].

Another factor influencing DSSC performance in addition to semiconductors is the sensitizer. Sensitizer has a role as a light absorber to be converted into electrical energy ([10–12]). In this case the source that is often used as a sensitizer is pigment. Pigments are organic compounds that have double or conjugated bonds. When a pigment interacts at a certain wavelength, it can produce a color that is a particular reflection of light [13]. At present, many studies in the DSSC field are applying pigments as sensitizers. This selection is based on cheaper, easily available, and sustainable prices [14].

One of the pigments that can be used as a sensitizer is anthocyanin. Anthocyanins can be obtained from various natural sources such as rosella flowers. Roselle flowers have various active compounds including organic acids, hydroxycitric acids, hibiscus acids, anthocyanins, flavonoids and polysaccharides [15]. The anthocyanin compounds in rosella flowers are the most important pigment from vascular plants, are harmless and what makes them interesting is that they are soluble in water media [16]. Anthocyanin extract is one of the most successful natural sensitizers for solar cells, because this organic dye produces photon to high current conversion results and is easy to obtain and inexpensive [7]. Anthocyanin can be a potential sensitizer, because it has a spectrum of light from red to blue. Anthocyanins also have carbonyl and hydroxyl groups so they can bind to the surface of TiO$_2$ [17].

DSSC compiler component material needs to be considered for the purpose of obtaining the highest or maximum efficiency through modification of composites and appropriate color sources as sensitizers. This research is focused on making hybrid material consisting of TiO$_2$, ZnO, and anthocyanin pigments obtained from rosella flowers. Preliminary studies are needed to determine the nature or characteristics of the hybrid material obtained. The extent to which the methods applied determines the successful formation of the targeted hybrid material. If this research is successful it will be directed to further research in which the hybrid material obtained can be applied as DSSC. The composition of hybrid material in the form of TiO$_2$, ZnO, and anthocyanin was chosen by considering the following factors, namely that previous researchers have developed composites in the form of TiO$_2$ / ZnO composites made from TiO2 and ZnO alone with various types of pigments such as carotenoids, betalain, flavonoid or chlorophyll groups. Including anthocyanin. Research on TiO$_2$ / ZnO composites through the incorporation of anthocyanin pigments has never been done before. In addition, the superior properties of the TiO$_2$ material combined with ZnO are expected to have a synergistic effect when the two substances are combined. The choice of anthocyanin is considered because this pigment has a short wavelength so that it can produce high energy [18].

2. Materials and Methods

2.1 Materials and Chemicals

The materials and chemicals used in this study have a purity degree of pro analysis and include, among others: ZnO (merck), TiO$_2$(merck), HNO$_3$(merck), ethanol 96%(sigma-aldrich), KI(merck),
I$_2$(sigma-aldrich), and ethylene glycol(sigma-aldrich). Anthocyanin pigments obtained from rosella flowers on the market were extracted using distilled water (under optimal operational conditions: temperature of 40 °C, frequency of 24 kHz, time of 5 minutes, and ratio of 1:25).

2.2 Synthesis TiO$_2$/ZnO Composites

In making TiO$_2$/ZnO composites using TiO$_2$ and ZnO ratios in several comparisons, namely the ratio of 75:25, 50:50, and 25:75 with a total mixture of 1 g. Then the two compounds were mixed and ground with a mortar pounder for 20 minutes. Paste making begins with preparing 15 mL of distilled water in a beaker added to 1 drop of HNO$_3$ (69%) solution in distilled water. The solution that has been made is taken 2 mL and mixed with 6.5 mL 96% ethanol. The solution is mixed with a mixture that has been made and put in a 100 mL beaker until a stable suspension is formed. In the subsequent pasta making, TiO$_2$ and ZnO ingredients were weighed as much as 1 gram then mixed with the existing solution as in the manufacture of the mixed paste.

Then the conductive side is checked and identified by measuring the value of the resistance that occurs using a multimeter. After checking is complete, the outer side of the FTO glass (Fluorine doped tin oxide) is closed by using insulation and on top of the FTO glass dripped a paste that is flattened using a glass spatula to make a composite. In the final stage, the insulation is removed and then heated at 300° C for 30 minutes.

2.3 Synthesis hybrid materials

In the manufacture of hybrid material is carried out through a stage where the composite that has been affixed to FTO glass is immersed in an anthocyanin solution for a certain time. In this process, the anthocyanin will be impregnated attached to the composite and a hybrid material is formed. After the immersion time has been reached, the FTO glass is removed and allowed to dry. Composite immersion in anthocyanin solutions carried out for 1, 3, 4, 6, 9, 12, and 24 hours intended to find out how much anthocyanin is attached to the composite.

2.4 Application of hybrid materials for DSSC

DSSC is composed of several components that form like a sandwich by having a comparison electrode and a working electrode. Comparative electrodes are made by first making a composite from a combination of TiO$_2$ and ZnO or just a semiconductor then affixed to the FTO glass. After affixing the FTO glass with the existing composite soaked with anthocyanin solution to make a hybrid material that will be used for the preparation of DSSC, while for comparison electrodes made by means of FTO glass burned to attach carbon to the glass. When everything is ready, a new DSSC is arranged and the gap between the comparison electrode and the work is given an electrolyte that is used for regeneration. After the DSSC has been prepared, irradiation is performed using an incandescent lamp and UV lamp to determine the voltage generated by the DSSC. In incandescent lamps an intensity of 209 lux is used while for UV lamps 366 nm uses an intensity of 27 lux.

3. Results and Discussion

3.1 Synthesis of TiO$_2$/ZnO Composites

The TiO$_2$/ZnO composites used in this study were made by mixing ZnO and TiO$_2$ at a ratio of 75:25, 50:50, and 25:75. Composites are made by mixing TiO$_2$ and ZnO at a predetermined ratio and milled with a mortar pounder to form a composite. The purpose of the difference comparison is to determine the effect of the ratio on the DSSC capabilities produced. ZnO and TiO2 materials used first need to be characterized in advance using XRD, FTIR, and DR UV equipment. XRD to get data about the crystalline phase in the sample, determine the lattice parameters and determine the crystal size. The sample was analyzed using the diffraction method in the angle range between 5° to 95°. The results of the characterization using XRD equipment are shown in Figure 1. For ZnO obtained characteristic peaks at an angle of 2θ of 31.76°; 34.41°; 36.24°; 47.52°; and 56.57° which is a diffraction pattern...
(100), (002), (101), (012), (110) and the results are in accordance with the COD (Crystallography Open Database) reference 9004178. In addition, TiO$_2$ has different characteristic peaks with ZnO, where at TiO$_2$ has characteristic peaks at an angle of 2θ of 25.29°; 36.93°; 37.78°; 38.55°; and 48.02° which is a diffraction pattern (011), (013), (004), (112), (020) of TiO$_2$ and the results have also fulfilled the COD (Crystallography Open Database) reference requirements of 9015929.

![Figure 1 Diffractogram of (1) TiO$_2$ and (2) ZnO](image)

Through analysis using MATCH software, the crystal form is known and can be seen in Table 1 and Figure 2 where the crystalline forms formed on TiO$_2$ and ZnO are tetragonal and hexagonal.

**Table 1 Characteristics of crystals from TiO$_2$ and ZnO**

| Data   | TiO$_2$ | ZnO |
|--------|---------|-----|
| a (Å)  | 3.7845  | 3.2494 |
| b (Å)  | 3.7845  | 3.2494 |
| c (Å)  | 9.5143  | 5.2038 |
| Crystal system | Tetragonal | Heksagonal |
| Density (g/cm$^3$) | 3.894 | 5.681 |

The synthesized composite was continued in the analysis process using XRD to study the phase composition that occurred. Each composition of different ratio has a different phase. In Figure 3 it is known that the characteristic peaks of TiO$_2$ and ZnO are arranged in each composite and have different phases according to Table 2. When ZnO and TiO$_2$ are made into composites with a ratio of 25:75, then a merging of characteristic peaks will occur both from ZnO and TiO$_2$. The results obtained are a combination of characteristic peaks at an angle of 2θ of 25.29°; 36.93°; 37.78°; 38.55°; and 48.02° which is the characteristic peaks of TiO$_2$ with 75.4% phase. While the characteristic peaks at an angle of 2θ amounted to 31.76°; 34.41°; 36.24°; 47.52°; and 56.57° are the characteristic peaks of ZnO with a phase of 24.6%.

When using the ZnO and TiO$_2$ ratio of 75:25, it was found that the characteristic peak at an angle of 2θ 25.44°; 37.90°; 38.72°; 48.17° and 54.03° which is the characteristic peak of TiO$_2$ with 22% phase using the COD reference 1530151, while for ZnO it is at an angle of 2θ at 31.90°; 34.56°; 36.24°; 47.52°; and 56.72° using the COD 901162 reference with a ZnO phase of 78%. When using TiO$_2$ and ZnO composites with a ratio of 50:50, the characteristic peaks at an angle of 2θ were 25.30°; 36.94°; 37.79°; 38.57° and 48.02° are the characteristic peak of TiO$_2$ with 49.8% phase using COD 9009086. While the characteristic peak of ZnO at 2θ angle is 31.76°; 34.41°; 36.24°; 47.52° and
56.57° with 50.2% phase using COD 2300450. The intensity obtained is influenced by the number of ratios of a compound such as when on TiO\textsubscript{2} and ZnO composites with a ratio of 75:25 then the peak characteristic of TiO\textsubscript{2} will be more prominent than with the characteristic peak of ZnO, and also vice versa the greater the ZnO ratio, the intensity of the characteristic peak of ZnO will be even greater. In addition, the characteristic peaks in sharp diffractogram patterns and having symmetrical Gauss peaks indicate that TiO\textsubscript{2} and ZnO particles in composite samples have high crystallinity.

| Table 2 Composite phase TiO\textsubscript{2}/ZnO |
|-----------------|-----------------|-----------------|
| TiO\textsubscript{2}: ZnO | Rasio | Rasio | Rasio |
| 75:25 | 50:50 | 25:75 |
| TiO\textsubscript{2} (%) | 75.4 | 49.8 | 22 |
| ZnO (%) | 24.6 | 50.2 | 78 |

Figure 3 TiO\textsubscript{2} / ZnO composite diffractogram with a ratio of (1) 75:25 (2) 50:50 and (3) 25:75

Figure 4 FTIR spectra of (1) TiO\textsubscript{2}, (2) ZnO (3) TiO\textsubscript{2}/ZnO 75:25 (4) TiO\textsubscript{2}/ZnO 50:50 and (5) TiO\textsubscript{2}/ZnO 25:75

To strengthen the analysis also carried out characterization using FTIR to find out the functional groups in the sample. In FTIR, there are two methods that are often used, namely KBr and ATR. The method used in this study is to use KBr with wave numbers ranging from 400 to 4000 cm\textsuperscript{-1}. The spectra results obtained from FTIR in Figure 4 show that TiO\textsubscript{2} has symmetrical stretching vibrations from Ti-O-Ti and O-Ti-O vibrations at wavelengths of 507.3 and 673.18 cm\textsuperscript{-1} because TiO\textsubscript{2} has spectra at wave number 400 up to 800 cm\textsuperscript{-1} [19]. The O-H function group is found in wave number 3425.69 cm\textsuperscript{-1}. Then in ZnO found Zn-O stretching vibration groups at wavelengths 437.86 and 488.01 cm\textsuperscript{-1} which are the transverse optical modes of ZnO namely the phonon TO (Transverse Optical) frequency and the LO (Longitudinal Optical) phonon [20]. O-H function groups are found in wave number 3433.41 cm\textsuperscript{-1}. Based on the wave numbers obtained through FTIR analysis it can be concluded that there has been a composite formation between TiO\textsubscript{2} and ZnO.

Based on the FTIR results in Table 3, the TiO\textsubscript{2} / ZnO composite with a ratio of 75:25 ratio can be proven that the composite made has formed with the Zn-O-Ti bond found at wave number 399.28 cm\textsuperscript{-1} due to a shift in the wave number. At wave numbers 505.37 and 677.04 cm\textsuperscript{-1} are stretching vibration groups of Ti-O-Ti and O-Ti-O. Then there is the O-H stretching vibration group at wave number 3433.41 cm\textsuperscript{-1} which is a group of water adsorbed on the surface. In the TiO\textsubscript{2} / ZnO composite with a ratio of 50:50 or 25:75, the composite was formed due to the shift in wave numbers to 423.78 and 435.83 cm\textsuperscript{-1}, which indicates that the Zn-O-Ti bond was formed. TiO\textsubscript{2} / ZnO composites with a ratio of
50:50 have a wave number of 441.14 cm\(^{-1}\) indicating a Zn-O functional group, 674 cm\(^{-1}\) indicating an O-Ti-O functional group, and 3443.76 cm\(^{-1}\) indicating a group OH function. Then for the TiO\(_2\)/ZnO composite with a ratio of 50:50 it has a wave number of 674 cm\(^{-1}\) which shows O-Ti-O functional groups, and 3443.76 cm\(^{-1}\) which shows O-H functional groups.

Composite testing in the form of another characterization is by applying a UV-Vis DR device that aims to find out the difference in band gap energy of a material. Wavelengths used range from 200 to 800 nm to measure the material or sample used. In this test, when a material has a short wavelength, the gap energy of the band gap is greater, and vice versa when the wavelength is greater, the gap energy of the band gap is smaller. Band gap energy is the gap energy between the valence band full of electrons and the conduction band having holes. Differences in band gap energy that are too small will cause electron jumps from the valence band to the conduction band so that recombination can occur, while differences in band gap energy that are too large can inhibit electron jumps from the valence band to the conduction band so that the flow of electrons will be inhibited. The difference in bandgap energy can be calculated using the Kubalka-munk equation related to energy as in Figure 5.

Table 3 FTIR of TiO\(_2\), ZnO and TiO\(_2\)/ZnO

| Material       | Wave number (cm\(^{-1}\)) | Group function |
|----------------|---------------------------|----------------|
| TiO\(_2\)      | 507.3, 673.18             | (Ti-O-Ti), (O-Ti-O) |
|                | 3425.69, 437.86, 488.01   | (O-H), (Zn-O), (Zn-O) |
| ZnO            | 3433.41                   | (O-H)          |
| TiO\(_2\)/ZnO (75:25) | 399.28, 505.37, 677.04   | (Zn-O-Ti), (Ti-O-Ti), (O-Ti-O) |
|                | 3433.41                   | (O-H)          |
| TiO\(_2\)/ZnO (50:50) | 441.14, 674             | (Zn-O), (O-Ti-O) |
|                | 3443.76                   | (O-H)          |
| TiO\(_2\)/ZnO (25:75) | 435.83, 674         | (Zn-O-Ti), (O-Ti-O) |

The difference in bandgap energy can be obtained from the results of a straight line intersection on a curve that intersects the x-axis. TiO\(_2\) has a gap gap energy of 3.31 eV while for ZnO it is 3.22 eV, but there is a change in the gap gap energy when the two compounds are made as composites. TiO\(_2\) and ZnO with a ratio of 75:25 have a band gap energy difference of 3.15 eV, while for TiO\(_2\) and ZnO with a ratio of 50:50 have a band gap energy difference of 3.19 eV. The biggest difference in band gap energy is TiO\(_2\) and ZnO composites with a ratio of 25:75 of 3.2 eV, each composite ratio will produce different band gap energy in Table 4. The obtained spectrum not only shows that there is an interaction between TiO\(_2\) and ZnO, but can also show that composites have wider spectra so they can absorb visible light. When TiO\(_2\) and ZnO are made as composites, they can cause changes in electronic transportation by shifting the wavelength position and thus causing changes in band gap energy. Composites have a small band gap energy can be caused, because it has a valence band of ZnO and a conduction band of TiO\(_2\) which is lower than ZnO then the excited electrons will move to the ZnO conduction band so that the band gap energy obtained is smaller.
Figure 5 UV-Vis spectra of (a) TiO$_2$ and ZnO, (b) TiO$_2$/ZnO composites

### 3.2 Synthesis of material hybride

In the hybrid material manufacturing process is carried out through the stages where the composite that has been affixed to FTO glass is immersed in anthocyanin solution for 1, 3, 4, 6, 9, 12, and 24 hours which is intended to find out how much anthocyanin is impregnated on the composite. In Figure 6 shows that the longer soaking the anthocyanin bound to the composite material will be more and more equilibrium occurs when immersion for about 6 hours. When immersed there is a bond between the pigment chromophore from anthocyanin with Ti$^{4+}$ from TiO$_2$ and Zn$^{2+}$ from ZnO, where an OH$^-$ ion from Ti$^{4+}$ and OH$^-$ from Zn$^{2+}$ binds to an H$^+$ ion from the anthocyanin pigment to form a H$_2$O molecule [21].

Figure 7. shows an example of absorption spectra of the effect of binding time for hybrid TiO$_2$/ZnO-anthocyanin material with TiO$_2$:ZnO composites at a ratio of TiO$_2$:ZnO 25:75 with variations of immersion time 1 - 24 hours. In order to know the formation of hybrid material that has been formed, an analysis was carried out using FTIR. Based on FTIR results in Table 3 and Figure 8 show that anthocyanin has O-H functional groups at 3446.91 cm$^{-1}$, C = O stretching vibrations at 1631.83 cm$^{-1}$, and C-O-C ester stretching vibrations at 1093.67 cm$^{-1}$. Then for hybrid material seen from the spectra of TiO$_2$, ZnO, and TiO$_2$/ZnO composites with various ratios that have been administered with anthocyanin, shows that the material obtained using TiO$_2$ has a wave number of 1629.9 cm$^{-1}$, ZnO has a wave number of 1618, 33 cm$^{-1}$, composite TiO$_2$/ZnO 75:25 ratio has wave number 1626.05 cm$^{-1}$, ratio 50:50 has wave number 1623.29 cm$^{-1}$ and ratio 25:75 has wave number 1633.41 cm$^{-1}$ shows that the wave number obtained is a stretching vibration C = O from anthocyanin. This shows that in the hybrid material made there is already anthocyanin.
When the composite or semiconductor is charged with anthocyanin into a hybrid material, there is an increase in the gap energy of the band, so that the electron jump from the valence band to the conduction band will be hampered resulting in impeded electron flow. The hybrid material of TiO$_2$ will increase to 3.33 eV and ZnO to 3.25 eV, while for composites TiO$_2$ and ZnO with a ratio of 75:25 to 3.2 eV then for the ratio of 50:50 and 25:75 increased to 3.21 eV and 3.22 eV. Increased bandgap energy can be caused by anthocyanin which has a large bandgap energy so that it affects the composite and increases the bandgap energy from hybrid material.

**Figure 6.** Effect of binding time on TiO$_2$ / ZnO composites

**Figure 7.** Absorption spectra of the effect of binding time for hybrid TiO$_2$/ZnO-anthocyanin at a ratio of TiO$_2$: ZnO 25:75

**Figure 8.** FTIR spectra of (1) anthocyanin and hybrid material (2) TiO$_2$-anthocyanin (3) ZnO-anthocyanin (4) TiO$_2$ / ZnO-anthocyanin (75:25) (5) TiO$_2$ / ZnO-anthocyanin (50:50 ) and (6) TiO$_2$ / ZnO-anthocyanin (25:75).
3.2 Application of Hybrid Materials for DSSC

DSSC is composed of several components that form like a sandwich by having a comparison electrode and a working electrode. Comparative electrodes are made by first making a composite of a combination of TiO$_2$ and ZnO or only a semiconductor then affixed to the FTO glass. After affixing the FTO glass with the existing composite soaked with anthocyanin solution to make a hybrid material that will be used for the preparation of DSSC, while for comparison electrodes made by means of FTO glass burned to attach carbon to the glass. When everything is ready, a new DSSC is arranged and the gap between the comparison electrode and the work is given an electrolyte which is used for regeneration.

The electron produced is the excitation process of the dyes due to obtaining a specific wavelength in the visible light region, after which it will be injected into the semiconductor conduction band. Electrons can move easily because of the bond between the dyestuff and the semiconductor used, but if there is a bond between the dyestuff and the semiconductor it will be difficult for the electron to be injected into the semiconductor. In addition, electrons also cannot move, due to contact between the working electrode and the comparative electrode due to the electrolyte solution not being distributed evenly.

After DSSC has been compiled, irradiation is carried out using incandescent lamps and UV lamps to determine the voltage generated by DSSC. In incandescent lamps an intensity of 209 lux is used while for UV lamps 366 nm uses an intensity of 27 lux. Based on Table 4, in incandescent and UV lamps, ZnO has the highest voltage of 81 and 341 mV while for the highest voltage using TiO$_2$ / ZnO 25:75 composites of 19 and 284 mV, and the lowest voltage of 0 mV and 15 mV when using TiO$_2$ / ZnO composites with a ratio of 75:25. UV lamps can produce more energy because UV lamps have a small wavelength so they have more energy than incandescent lamps that have waves in the absorption of visible light.

| Material       | Incandescent Lamps (mV) | UV Lamps (mV) |
|----------------|-------------------------|--------------|
| ZnO            | 81                      | 341          |
| TiO$_2$        | 23                      | 101          |
| TiO$_2$:ZnO 25:75 | 19                     | 284          |
| TiO$_2$:ZnO 50:50 | 5                      | 40           |
| TiO$_2$:ZnO 75:25 | 0                      | 15           |

DSSC characterization using the Keithley IV meter aims to measure the efficiency or voltage and current produced with a light intensity of 20 W / m$^2$ as shown in Figure 9. Based on Table 9, ZnO has the highest efficiency with an efficiency of 0.0168% while for the highest efficiency by using TiO$_2$ / ZnO composite 25:75 with an efficiency of 0.0135%, and the lowest efficiency with an efficiency value of 0.0036% when using a TiO$_2$ / ZnO composite with a ratio of 50:50. TiO$_2$ / ZnO composites have the highest efficiency because they have a fill factor or can absorb more dye than others.
Figure 9. curve I-V meters

Although TiO\textsubscript{2} / ZnO composites at a ratio of 25:75 also have a high fill factor, recombination is easily seen from the low Jsc results due to the accumulation of ZnO interference which makes deeper pores in the film so that it can produce direct contact between FTO and electrolytes. In addition, low efficiency can be caused by the morphology of the uneven composite so that the resulting efficiency is not too high and a long immersion time can cause semiconductors or composites can not stick perfectly to the glass, thereby reducing the efficiency of DSSC.

The efficiency of solar cell conversion can be calculated from the short circuit current output and the open circuit voltage, with formula (1):  
\[ \eta = \left( \frac{J_{sc} \times V_{oc} \times FF}{Pin} \right) \times 100\% \]  

Symbol \( \eta \) refers to efficiency, Jsc as short-circuit current density, and Voc as Open circuit voltage. Ratio of maximum power from solar cells to open circuit voltage products and short circuit current density is described as FF and Pin as The intensity used in the test.

| DSSC          | Jsc (mA) | Jsc (mA/cm\textsuperscript{2}) | Voc (V) | Fill Factor | Efisiensi (%) |
|---------------|----------|---------------------------------|---------|-------------|---------------|
| TiO\textsubscript{2} | 0.0694   | 0.0193                          | 0.433   | 0.483       | 0.0147        |
| TiO\textsubscript{2}:ZnO 25:75 | 0.0263   | 0.0073                          | 0.5     | 1.016       | 0.0135        |
| TiO\textsubscript{2}:ZnO 50:50 | 0.0338   | 0.0094                          | 0.23    | 0.463       | 0.0036        |
| TiO\textsubscript{2}:ZnO 75:25 | 0.0443   | 0.0123                          | 0.342   | 0.364       | 0.0056        |
| ZnO           | 0.0568   | 0.0158                          | 0.475   | 0.615       | 0.0168        |

These results indicate that the difference is very small due to the tool used only 20 W / m\textsuperscript{2}, whereas for standard measurements using an intensity of 100 W / m\textsuperscript{2} because the intensity produces optimum energy for excitation. The use of low intensity can cause the measurement of efficiency produced to be incorrect or inaccurate.

4. CONCLUSION

The synthesis process has been carried out at various ratios of TiO\textsubscript{2} and ZnO. The diffractogram of the composite shows the characteristic peaks of TiO\textsubscript{2} and ZnO and the FTIR spectra shows the vibrations of Zn-O-Ti. This proves that the composite was successfully synthesized. Then the quality testing of
hybrid material was carried out using the DR UV-Vis instrument and it was proven that there was an increase in band gap energy between 3.2 to 3.33 eV, compared to TiO$_2$ / ZnO composites which had band gap energy of 3.15-3.2 eV, TiO$_2$ which has a band gap energy of 3.31 eV, and ZnO which has a band gap energy of 3.22 eV.

References
[1] Abdulrazzaq O A, Saini V, Bourdo S, Dervishi E and Biris A S 2013 Part. Sci. Technol. 31 427
[2] Liras M, Barawi M and De La Peña O’Shea V A 2019 Chem. Soc. Rev. 48 5454
[3] Wright M and Uddin A 2012 Sol. Energy Mater. Sol. Cells 107 87
[4] Ellabban O, Abu-Rub H and Blaabjerg F 2014 Renew. Sustain. Energy Rev. 39 748
[5] Kothari R, Tyagi V V. and Pathak A 2010 Renew. Sustain. Energy Rev. 14 3164
[6] Gong J, Liang J and Sumathy K 2012 Renew. Sustain. Energy Rev. 16 5848
[7] Suhaimi S, Shahimin M M, Alahmed Z A, Chyský J and Reshak A H 2015 Int. J. Electrochem. Sci. 10 2859
[8] Ooyama Y and Harima Y 2012 ChemPhysChem 13 4032
[9] Ali D B A F H 2017 Int. J. Sci. Res. 6 1609
[10] Sathyajothi S, Jayavel R and Dhanemozhi A C 2017 Mater. Today Proc. 4 668
[11] Zhou H, Wu L, Gao Y and Ma T 2011 J. Photochem. Photobiol. A Chem. 219 188
[12] Lee C P, Li C T and Ho K C 2017 Mater. Today 20 267
[13] Mulders K J M, Lamers P P, Martens D E and Wijffels R H 2014 J. Phycol. 50 229
[14] Hug H, Bader M, Mair P and Glatzel T 2014 Appl. Energy 115 216
[15] Da-Costa-Rocha I, Bonnlaender B, Sievers H, Pischel I and Heinrich M 2014 Food Chem. 165 424
[16] Castañeda-Ovando A, Pacheco-Hernández M de L, Páez-Hernández M E, Rodríguez J A and Galán-Vidal C A 2009 Food Chem. 113 859
[17] Hao S, Wu J, Huang Y and Lin J 2006 Sol. Energy 80 209
[18] Calogero G, Yum J H, Sinopoli A, Di Marco G, Grätzel M and Nazeeruddin M K 2012 Sol. Energy 86 1563
[19] Mahalingam T, Selvakumar C, Ranjith Kumar E and Venkatachalam T 2017 Phys. Lett. Sect. A Gen. At. Solid State Phys. 381 1815
[20] Anžlovar A, Crnjak Orel Z, Kogej K and Žigon M 2012 J. Nanomater. 2012
[21] Narayan M R 2012 Renew. Sustain. Energy Rev. 16 208