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Comparison of Nanocomposite ZnO/TiO$_2$ Composition Dye-Sensitized Solar Cell (DSSC) with Natural Dye Leaves of Green Mustard (*Brassica rapa*)

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Abstract. ZnO and TiO$_2$ are semiconductor materials used to make DSSC. In this research Dye-Sensitized Solar Cell (DSSC) manufacturing by mixing ZnO and TiO$_2$ materials. ZnO is made by synthesis using the sol-gel method with a mixture of zinc tetrahydrate ($Zn(NO_3)_2.4H_2O$), ammonium hydroxide (NH_4OH) and polyethylene glycol (PEG). In this research, the dye used was extracted leaves of green mustard (*Brassica rapa*) and nanocomposite ZnO/TiO$_2$ with ratio (1:1, 1:2, 1:3). Fabrication using FTO glass with a work area of 1cm x 1cm obtained the results of the efficiency of nanocomposite ZnO/TiO$_2$ (1:1) with an efficiency (η) of 0.0755%, nanocomposite ZnO/TiO$_2$ (1:2) with an efficiency (η) of 0.1935%, nanocomposite ZnO/TiO$_2$ (1:3) with an efficiency (η) of 0.2098%.

1. Introduction

Dye-Sensitized Solar Cell (DSSC) is a type of photoelectrochemical solar cell that consists of a field of work containing dyes. DSSC consists of semiconductor electrodes, counter electrodes, and electrolytes that contain redox pairs (I^-/ I_3^-). When DSSC is illuminated by sunlight, the dye molecules on the surface of the semiconductor conduction band absorb light. The absorption of light by the dye molecules is followed by the electron injection of the dye in the semiconductor conduction band and subsequent transfer to transparent oxides. Finally, electrons flow through an external circuit [1-4].

DSSC have been widely investigated as a promising alternative to conventional photovoltaic devices due to their low fabrication cost, nontoxicity and promising conversion efficiency [5-7]. Due to its low fabrication cost, permanence, environmental compatibility, and simple fabrication process, interest in its application to low power devices such as small electronic devices and photoelectrochromic windows has grown considerably [8,9]. In a DSSC system, the interaction between the dye and the semiconductor oxide particles determines the process of converting light energy into electrical energy.

It is known that with the increasingly small size of a material to the nanometer scale, the ratio between the surfaces to volume (surface to volume ratio) will be even greater and the opportunity for interaction with the surrounding environment will be higher [10]. The most frequently used material in DSSC is TiO$_2$ nanoparticles. However, currently zinc oxide (ZnO) is considered as an alternative to TiO$_2$ because of some of the advantages it has, including the position of the valence band which is right under the conduction band (direct band gap) so that it is possible faster excitation of electrons during the absorption of DSSC photon energy under sunlight exposure compared to TiO_2 which has characteristics as an indirect band gap semiconductor [11,12].

2. Methods

2.1. Synthesis ZnO

ZnO nanorod synthesis process with the sol-gel method. Solution A precursor zinc nitrate tetrahydrate 5.23 gram ($Zn(NO_3)_2.4H_2O$) into 100 ml distilled water. Solution B polyethylene glycol (PEG) 3 gram in 50 ml of water. Solution B is added 0.15 mol NH_4OH this addition is carried out until the mixture solution reaches pH ~ 10.5, the stirring process is accelerated accompanied by heating of the mixed solution to a temperature of 75 °C for 2 hours to obtain a pale white precipitate. The precipitate is completely formed at the 2nd hour and then filtered and rinsed using ethanol and aquadest 3 times. The ZnO nanorod white powder is then dried in an oven at 60 °C for a minimum of 12 hours [13].

2.2. Dye Extraction

The dye used is chlorophyll from leaves of green mustard (*Brassica rapa*) extract showed Figure 1. 20 gram leaves of green mustard (*Brassica rapa*) mixed with 80 ml of ethanol and stirred for 2 hours. Then stored for 24 hours and then filtered to remove sediment.

Figure 1. Leaves of green mustard (*Brassica rapa*)

2.3. DSSC Fabrication

Electrodes are made using the spin coating method. Making nanocomposite ZnO/TiO_2 by dissolving with ethanol. Nanocomposite ZnO/TiO_2 (1:1, 1:2, 1:3) is dripped in the work area of the FTO glass then flattened using spin coating. Then it is heated to 450 ^oC for 30 minutes. Then allowed to stand at room temperature for the cooling process. After a cold layer of the working electrode is then soaked in dye for 24 hours. Making counter electrodes by heating the FTO glass with a temperature of 250 ^oC which is dropped by platinum as much as 3 drops is allowed for up to 2 minutes.

After that, the counter electrode is heated again to 450 ^oC for 30 minutes. Then allowed to stand at room temperature for the cooling process. Electrolyte manufacturing using PEG 20 ml, KI 0.8 gram, I_2 0.127 gram is stirred for 1 hour. After arranging the DSSC circuit such as a sandwich shape (FTO, nanocomposite Zno/TiO_2, Dye, electrolyte, platinum, FTO) then pinch from the second side. For DSSC characterization using *Keithley 2602A*.

3. Result and Discussion

3.1. Absorbance

Dye derived from chlorophyll colouring agents used are leaves of green mustard. Absorbance measurement is done by taking a dye solution mixed with ethanol. Then use a *UV-Visible Lambda 25 spectrophotometer* with a wavelength of 200-800 nm. The test results can be seen in Figure 2. In the chlorophyll extract leaves of green mustard first peak absorbance value is located at a wavelength of 476 nm and second peak is at a wavelength of 611 nm. Dye absorbance occurs at visible wavelengths.

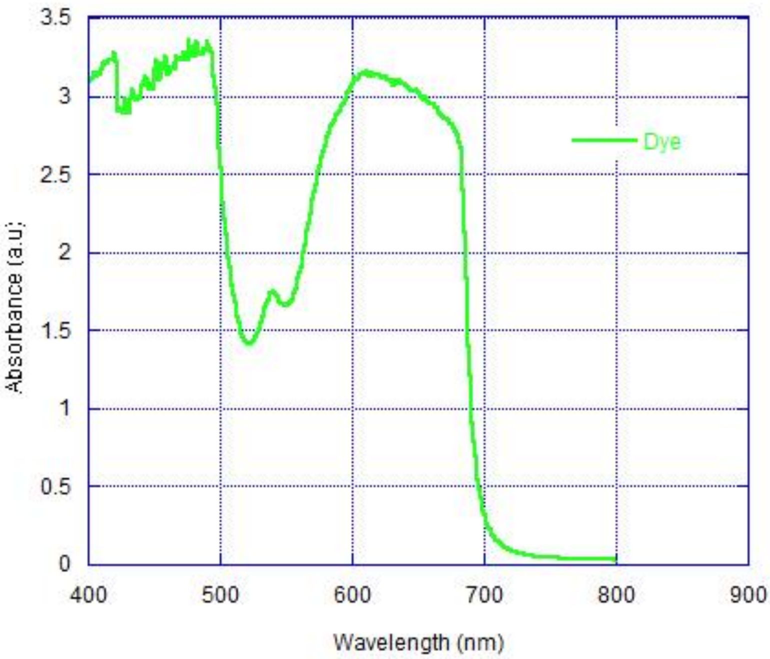


Figure 2. Absorption spectrum leaves of green mustard

3.2. Characterization I-V

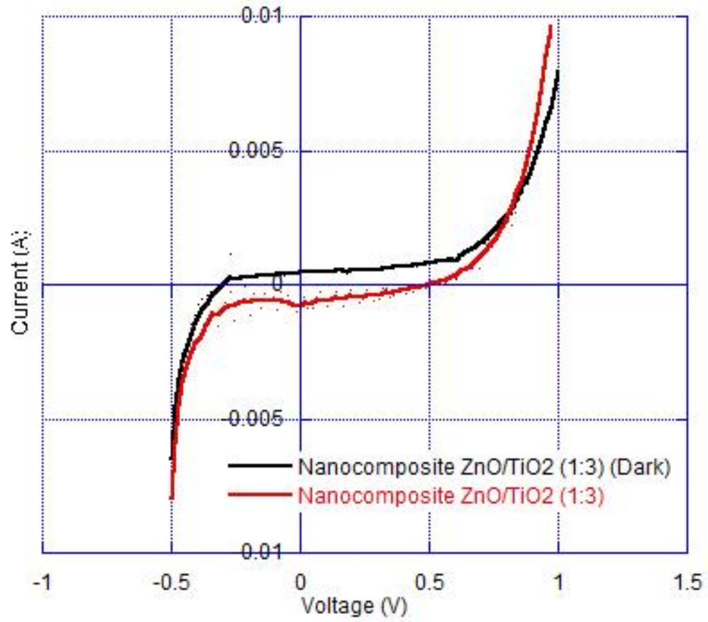
Voltage-current (*I-V*) characterization was carried out using *Keithley 2602A* with 1000 W/m^2 illuminated light beam radiation. The results of the characterization can be seen in Figure 3.

The greatest efficiency is found in nanocomposite ZnO/TiO_2 (1:3) figure 3(a) because it has the largest area in four quadrants compared to nanocomposite ZnO/TiO_2 (1:1) and nanocomposite ZnO/TiO_2 (1:2). From Figure 3(a) it can be seen that the area formed between V_{max} and I_{max} in quadrant 4 is equal to efficiency. Figure 3(b) shows the area formed from V_{max} and I_{max}. The greater the value of V_{max} and I_{max}, the greater the value of efficiency. This shows by adding TiO_2, the efficiency is increasing. The results of the selection efficiency of nanocomposite ZnO/TiO_2 can be seen in table 1.

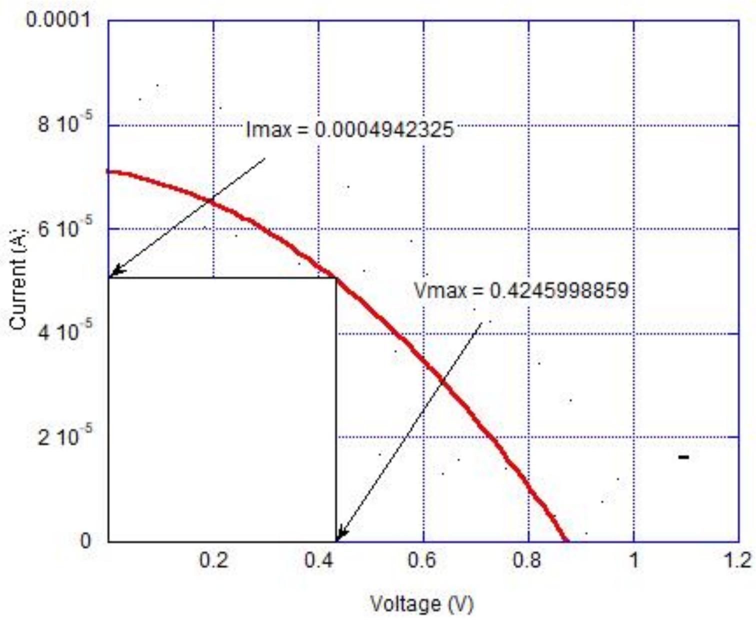
Table 1. DSSC efficiency with Dye-sensitizer leaves of green mustard (*Brassica rapa*)

Materials Comparison	I_{max} (mA)	V_{max} (mV)	I_{sc} (mA)	V_{oc} (mV)	η (%)
Nanocomposite Zno/TiO_2 (1:1)	0.00023	0.22751	0.00111	0.33337	0.07559
Nanocomposite Zno/TiO_2 (1:2)	0,00039	0.48521	0.00184	0.54591	0.19352
Nanocomposite Zno/TiO_2 (1:3)	0.00049	0.42459	0.00131	0.50041	0.20985

In nanocomposite ZnO/TiO_2 (1:2) there was a significant increase in efficiency of nanocomposite ZnO/TiO_2 (1:1). Then for nanocomposite ZnO/TiO_2 (1:3) an increase in efficiency of nanocomposite ZnO/TiO_2 (1:2) but not significant. The efficiency produced in this study is still too small compared to the results of the study (Chao et al) with the same material but with different methods that produce efficiency (η = 2.163%) [14].



(a)



(b)

Figure 3. (a) Nanocomposite ZnO/TiO_2 (1:3), (b) Area of Nanocomposite ZnO/TiO_2 (1:3)

4. Conclusion

The making of ZnO is carried out by means of synthesis using the sol-gel method. Synthesis was carried out by means of precursor $Zn(NH_3)_2.4H_2O$ and a mixture of PEG and NH_4OH. From the I-V measurements the efficiency of nanocomposite ZnO/TiO_2 (1:1) with an efficiency (η) of 0.07559%, nanocomposite ZnO/TiO_2 (1:2) with an efficiency (η) of 0.19352%, nanocomposite ZnO/TiO_2 (1:3) with an efficiency (η) of 0.20985%. Significant changes in efficiency occur between nanocomposite ZnO/TiO_2 (1:1) with nanocomposite ZnO/TiO_2 (1:2). Then for nanocomposite ZnO/TiO_2 (1:3) an increase in efficiency of nanocomposite ZnO/TiO_2 (1:2) but not significant. The difference in efficiency results due to the effect of adding TiO_2 mass.

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