The Effect of ZnO and TiO$_2$ with Natural Dye of Broccoli (*Brassia oleracea var. italica*) on Dye-Sensitized Solar Cell (DSSC)

C Cari$^1$, Deny Kurniawan$^1$ and Agus Supriyanto$^1$

$^1$Physics Department Post Graduate Program Sebelas Maret University, Jl. Ir. Sutami 36A Kentingan Jebres Surakarta 57126, Indonesia

Email: cari@staff.uns.ac.id and kurniawan.deny93@gmail.com

Abstract. Zinc oxide having the chemical formula ZnO, while titanium dioxide is titanium oxide having the chemical formula TiO$_2$. Zinc oxide and titanium dioxide are inorganic compounds. Zno and TiO$_2$ are often used for Dye-Sensitized Solar Cell (DSSC). This research was conducted by mixing ZnO and TiO$_2$ as photoanodes. The mixture of ZnO and TiO$_2$ is made by mixing ZnO and TiO$_2$ with a ratio of 1:1, 1:2, 1:3 then dissolved in ethanol. The natural dye used is broccoli extract (*Brassia oleracea var. italica*). Fabrication is carried out using FTO glass with a work area of 1cm x 1cm. The efficiency results obtained by nanocomposite ZnO/TiO$_2$ (1:1) with an efficiency ($\eta$) of 0.07180%, nanocomposite ZnO/TiO$_2$ (1:2) with an efficiency ($\eta$) of 0.1555% nanocomposite ZnO/TiO$_2$ (1:3) with an efficiency ($\eta$) of 0.1713%. When compared to the efficiency using ZnO/TiO$_2$ (1:1) with TiO$_2$, the efficiency increased by 0.002%. At ZnO/TiO$_2$ (1:2) the efficiency increased by 0.0886%. Whereas at ZnO/TiO$_2$ (1:3) the efficiency increased by 0.1023%.

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...
TiO₂ 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 TiO₂ which has characteristics as an indirect band gap semiconductor [11,12].

In this study, ZnO was made using the ZnO synthesis process with the sol-gel method. Solution A precursor zinc nitrate tetrahydrate 5.23 gram (Zn(NO₃)₂·4H₂O) into 100 ml distilled water. Solution B polyethylene glycol (PEG) 3 grams in 50 ml of water. Solution B is added 0.15 mol NH₄OH 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. Methods

2.1. Nanocomposite ZnO/TiO₂ manufacture
The process of making nanocomposite ZnO/TiO₂ is done by mixing ZnO and TiO₂ then dissolving it in ethanol. Preparation of nanocomposite ZnO/TiO₂ using a ratio of 1 gram of ZnO mixed with 1 gram of TiO₂ was dissolved into 4 ml of ethanol. Then stirred using a stirrer for 1 hour. Next, make nanocomposite ZnO/TiO₂ with 1 gram of ZnO and 2 grams of TiO₂ dissolved in 4 ml ethanol. Finally, make nanocomposite ZnO/TiO₂ with 1 gram of ZnO and 3 grams of TiO₂ dissolved in 4 ml ethanol.

2.2. Dye Extraction
The dye used was chlorophyll from broccoli (Brassia oleracea var. italica) extract Figure 1. 20 grams of broccoli (Brassia oleracea var. Italicca) mixed with 80 ml of ethanol then stirred for 2 hours. Then stored for 24 hours and filtered to remove sediment.

![Figure 1. Broccoli (Brassia oleracea var. italica)](image_url)

2.3. DSSC Fabrication
DSSC electrodes are made using the spin coating method. The preparation of the nanocomposite ZnO/TiO₂ was carried out by dissolving it with ethanol. The nanocomposite ZnO/TiO₂ (1:1, 1:2, 1:3) was dropped on the FTO glass working area and flattened using a spin coating. Then heated to 450 °C
for 30 minutes. Then allowed to stand at room temperature for the cooling process. After cooling, the working electrode layer was immersed in the dye for 24 hours. The DSSC counter electrode was made by heating the FTO glass at 250 °C which was dropped by 3 drops of platinum for 2 minutes.

After that, the counter electrode was reheated to a temperature of 450 °C for 30 minutes. Then allowed to stand at room temperature for the cooling process. Preparation of electrolytes using PEG 20 ml, KI 0.8 grams, I₂ 0.127 grams, stirring for 1 hour. After compiling a series of DSSC such as sandwich form (FTO, nanocomposite ZnO/TiO₂, dye, electrolyte, platinum, FTO) then clamp from both sides. For DSSC characterization using Keithley 2602A.

3. Result and Discussion

3.1. Absorbance

Dye derived from chlorophyll colouring agents used are broccoli (Brassia oleracea var. Italica). Absorbance measurement is done by taking a dye solution mixed with ethanol. Then use a UV-Visible Lambda 25 spectrophotometer with a wavelength of 300-800 nm. The test results can be seen in Figure 2. In the chlorophyll extract broccoli first peak absorbance value is located at a wavelength of 434 nm and second peak is at a wavelength of 664 nm. Dye absorbance occurs at visible wavelengths.

![Figure 2. Absorption spectrum broccoli (Brassia oleracea var. italic)](image)

3.2. Characterization I-V

Voltage-current (I-V) characterization was performed using Keithley 2602A with illumination beam radiation of 1000 W/m². The results of characterization can be seen in Figure 3. Dscc which has the greatest efficiency is found in the nanocomposite Zno/TiO₂ (1:3) Figure 3 (c) because it has the largest area in four quadrants compared to nanocomposite Zno/TiO₂ (1:1) and nanocomposites Zno/TiO₂ (1:2). In Figure 3 (a) it can be seen that the area formed between Vₘₐₓ and Iₘₐₓ in quadrant 4 is equal to efficiency. Figure 3 (b) shows the area formed from Vₘₐₓ and Iₘₐₓ. The greater the Vₘₐₓ and Iₘₐₓ values,
the greater the efficiency value. This shows that with the addition of TiO₂, the efficiency will increase. The results of the efficiency of selecting ZnO/TiO₂ nanocomposites can be seen in table 1.

In nanocomposite ZnO/TiO₂ (1:2) there was a significant increase in efficiency of nanocomposite ZnO/TiO₂ (1:1). Then for nanocomposite ZnO/TiO₂ (1:3) an increase in efficiency of nanocomposite ZnO/TiO₂ (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 ($\eta = 2.163\%$) [14]. However, when compared with the results of the study using TiO₂ with broccoli dye, the efficiency obtained was quite large from the results of the study (Cari et al) which only resulted in efficiency ($\eta = 0.069\%$) [15].

When compared to the efficiency using ZnO/TiO₂ (1:1) with TiO₂, the efficiency increased by 0.002%. At ZnO/TiO₂ (1:2) the efficiency increased by 0.0886%. Whereas at ZnO/TiO₂ (1:3) the efficiency increased by 0.1023%. The use of ZnO is expected to be able to inhibit the recombination process of TiO₂ photocatalysts, so that it can increase the photocatalyst activity of TiO₂.

**Table 1. DSSC efficiency with Dye-sensitizer broccoli (Brassia oleracea var. italica)**

| Materials Comparison | $I_{max}$ (mA) | $V_{max}$ (mV) | $I_{sc}$ (mA) | $V_{oc}$ (mV) | $\eta$ (%) |
|----------------------|----------------|----------------|---------------|---------------|------------|
| Nanocomposite ZnO/TiO₂ (1:1) | 0.00021 | 0.22740 | 0.00169 | 0.33338 | 0.07180 |
| Nanocomposite ZnO/TiO₂ (1:2) | 0.00036 | 0.42432 | 0.00140 | 0.50010 | 0.15557 |
| Nanocomposite ZnO/TiO₂ (1:3) | 0.00043 | 0.39402 | 0.00185 | 0.54555 | 0.17136 |

(a)
4. Conclusion
The process of making nanocomposite ZnO/TiO$_2$ is done by mixing ZnO and TiO$_2$ then dissolving it in ethanol. Preparation of nanocomposite ZnO/TiO$_2$ using a ratio (1:1), (1:2) and (1:3) was dissolved.
into 4 ml of ethanol. Dye used was chlorophyll from broccoli (Brassia oleracea var. italic) extract. From the I-V measurements the efficiency of nanocomposite ZnO/TiO\textsubscript{2} (1:1) with an efficiency ($\eta$) of 0.0718\%, nanocomposite ZnO/TiO\textsubscript{2} (1:2) with an efficiency ($\eta$) of 0.1555\%, nanocomposite ZnO/TiO\textsubscript{2} (1:3) with an efficiency ($\eta$) of 0.1713\%. Significant changes in efficiency occur between nanocomposite ZnO/TiO\textsubscript{2} (1:1) with nanocomposite ZnO/TiO\textsubscript{2} (1:2). Then for nanocomposite ZnO/TiO\textsubscript{2} (1:3) an increase in efficiency of nanocomposite ZnO/TiO\textsubscript{2} (1:2) but not significant. The difference in efficiency results due to the effect of adding TiO\textsubscript{2} mass.

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6. References
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