Dye Sensitized Solar Cells (DSSC) Performance Reviewed from the Composition of Titanium Dioxide (TiO2)/ Zinc Oxide (ZnO)

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Abstract. This research aims to examine the influence of the composition of TiO2 and ZnO as the working electrode on the efficiency of DSSC. The working electrode is prepared by depositing TiO2 and ZnO pastes on top of the FTO glass using the doctor blade method. The samples were then heated in an oven at a temperature of 250 °C for 4 hours. In this study, three TiO2 / ZnO compositions were prepared and assembled into DSSC components with red spinach dye. SEM image shows that the composition of TiO2 / ZnO (0:2) produces the best surface morphology that is indicated by the number and aggregate uniform pores. This is consistent with the results of testing the electrical properties of the sample. The solar cell with the working electrode composed of TiO2 / ZnO (0:2) yields an efficiency of 0.0515%, higher than the composition (2:0) and (1:1) which respectively yields 0.0044% and 0.0015%.

1. Introduction
Dye Sensitized Solar Cell is a potential solar cell generation for future application. It is because DSSC does not require highly purified materials so that it can lower the production process. In addition, the process of light absorption and electrical charge separation occurs in a separate process [1,2] The dye molecule acts as a light absorber, while the charge separation is accelerated by an organic semiconductor molecule with a wide energy gap [3]. The use of semiconductors with wide energy gaps will widen the absorption spectrum so that it will multiply the electrons flowing from the conduction band to the valence band [4]. One of the most widely used semiconductor materials as electrodes in DSSC is TiO2. This material has a strong oxidizing power, good stability against photo corrosion and chemical corrosion, and has a nanopore structure that can absorb the dye molecule in large quantities. TiO2 has a wide energy gap of 3.2 - 3.8 eV and is photo catalyst. The other semiconductor ZnO has a similar energy gap to TiO2. Although ZnO stability is lower than TiO2, but ZnO has higher electron mobility and high exciton binding energy (60 meV) that permits exciton emission at room temperature [5].
Research on previous TiO$_2$ / ZnO composites has been largely done by some other researchers. Mane et al [6] performed DSSC fabrication by wet chemical coating technique at room temperature resulting in a TiO$_2$/ZnO composite with an efficiency of 0.67% and high stability for 25 min. Giannouli et. al. creates TiO$_2$/ZnO composition in different variations TiO$_2$ (100%), TiO$_2$/ZnO (75%:25%), TiO$_2$/ZnO (50%:50%), TiO$_2$/ZnO (25%:75%), and ZnO (100%) with doctor blade coating technique. It was reported that ZnO has higher electron mobility than TiO$_2$, this research synthesized the TiO$_2$/ZnO composition with different composition ratio to test its effect on DSSC performance.

2. Methods
This research was conducted in some steps covering such steps as formulating TiO$_2$/ZnO paste, depositioning TiO$_2$/ZnO paste on FTO substrate as the working electrode followed by soaking in the red spinach extract, preparing standard electrode, assembling DSSC device, and testing TiO$_2$/ZnO optical characteristics and DSSC electrical characteristics.

TiO$_2$/ZnO paste formulation was done by dissolving TiO$_2$ and ZnO powder into an ethanol solution by using a magnetic stirrer. This research used TiO$_2$: ZnO active substance with different compositions; 2:0, 1:1, and 0:2. The homogeneous paste was then deposited on the FTO substrate using doctor blade method and heated at 250 °C. for four hours in an oven. Furthermore, characterization using SEM was done to determine the surface morphology of TiO$_2$/ZnO thin film. Optical characteristic measurement covering the absorbance spectrum of TiO$_2$/ZnO thin film was also done by using UV-Vis spectrometer. The standard electrode was prepared using sputtering technique and the indicator electrode was soaked in red spinach extract for 24 hours. The series of DSSC devices was performed by the assembly method, wherein the standard electrode was placed over the indicator electrode to form a sandwich structure and then heated in an oven for five minutes at 100 °C. As the final step, the electrolyte solution was dripped on the space between the two electrodes and the electrical properties was also tested to test the DSSC performance using I-V characterization.

3. Results and discussion
3.1. TiO$_2$/ZnO Thin Film Optical Characteristics
The characteristics of TiO$_2$/ZnO Thin Film Optical Characteristics is presented in Figure 1. the maximum absorbance value in the ZnO sample was 5.38 at a wavelength of 677 nm. there is an increase in maximum absorbance value and wavelength shift after dye administration on TiO$_2$/ZnO. In general, TiO$_2$/ZnO without dye can only absorb photons in the ultraviolet light region in the wavelength of 350-420 nm. With the addition of dye, there is a wavelength shift of light absorption at 600-700 nm which is the area of visible red-light color.
The intensity of dye absorption by TiO$_2$/ZnO has an effect on the electron dispersion at the surface. This is because the dye acts as a solar absorber which will in turn inject the electrons into the TiO$_2$/ZnO conduction band. Soaking for 24 hours was done so that the dye can absorb completely on the TiO$_2$/ZnO layer, because long-lasting soaking results in greater absorption intensity [8]. The wavelength shifts for the three semiconductor coating compositions is shown in Table 1.
Figure 1. Thin Film Optical Absorbance (a) TiO₂, dye Spinach, TiO₂+spinach (b) TiO₂/ZnO (1:1), dye spinach, TiO₂/ZnO+spinach and (c) ZnO, dye spinach, ZnO+spinach

Table 1. TiO₂, ZnO, TiO₂/ZnO maximum absorbance before and after red spinach dye application

| Composition          | λ maximum (nm) | Maximum absorbance | Absorbed color | Spectrum area   |
|----------------------|---------------|--------------------|----------------|----------------|
| Red spinach          | 439           | 4.28               | purple-blue    | Visible light  |
| TiO₂                 | 393           | 3.32               | purple         | ultraviolet    |
| ZnO                  | 408           | 3.31               | purple         | ultraviolet    |
| TiO₂/ZnO             | 400           | 2.98               | purple         | ultraviolet    |
| TiO₂+ red spinach    | 655           | 3.94               | red            | visible light  |
| ZnO + red spinach    | 677           | 5.38               | red            | visible light  |
| TiO₂/ZnO + red spinach | 677        | 4.98               | red            | visible light  |

3.2. TiO₂/ZnO Thin Film Surface Morphology

SEM image of thin film with TiO₂/ZnO composition variation is shown in Figure 2. Surface morphology based on the SEM image TiO₂ / ZnO (2: 0) indicates a small pore formed on TiO₂, and the TiO₂ aggregate is more evenly distributed when deposited on the FTO substrate. The average pore size produced by TiO₂ is 0.758 μm. Pore size greatly affects the absorption of photons because of its role in binding dye; the larger and fewer pores are produced, the less dye will be bound so that the photons will not be optimally absorbed. In TiO₂/ZnO (1:1), more pores are formed with an average pore size 0.821 μm and uneven aggregate.

In a thin layer of TiO₂/ZnO (0:2), there are many pores produced with a more evenly distributed ZnO aggregate structure. The pore size produced by ZnO is smaller than the pore size produced by the composition of TiO₂ / ZnO (2: 0), and (1: 1) by 0.649 μm. The smaller the pore size becomes, then the active surface area that plays a role in the dye up taking process will increase and it will increase the light absorption [9].
3.3. \textit{TiO}_2/ZnO thin film electrical Characteristics with different variations

Electrical characteristics are measured by using the voltage-current curve (I-V) which further becomes the basis for determining the efficiency of DSSC conversion. The DSSC conversion efficiency testing results are summarized in Table 2. The best electrical properties of the I-V test are shown by DSSC with the TiO2 / ZnO (0: 2) composition. This is in accordance with the reference which states that the electrical properties produced ZnO is greater than TiO2 when applied to DSSC solar cells. Nonetheless, ZnO stability is lower than that of TiO2 [7]. This corresponds to previously reported optical properties, in which the maximum absorbance is produced by a thin layer of ZnO. The optimum dye absorption in ZnO maximizes the absorption of photons so that more electrons will be formed. This is also supported by the SEM image showing that ZnO produces the largest number of pores and evenly distributed aggregate. As more pores are produced, more dye will be attached to this composition and more photons will be absorbed by dye and will result in better electrical properties of DSSC.

| TiO2/ZnO compositions | Efficiency |
|-----------------------|------------|
| 2:0                   | 0.0044     |
| 1:1                   | 0.0015     |
| 0:2                   | 0.0515     |

4. Conclusion

In this research, DSSC fabrication has been successfully done with various composition of TiO / ZnO indicator electrode. Best optical absorption by a thin layer of ZnO and there is a maximum absorption shift of the wavelength of 408 nm before the addition of dye to 677 nm after the addition of dye. The
surface morphology of the ZnO thin film is also in a good shape, indicated by the average produced pore size by 0.649 μm. Based on the electrical characteristics, the efficiency value produced by TiO₂/ZnO (0:2) is the better compared to other two compositions by producing 0.0515% conversion efficiency

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