The influence of TiO$_2$ film thickness in Dye-Sensitized Solar Cells (DSSC) performance based on TiO$_2$/Ag@TiO$_2$-ZnO

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Abstract. The effects of TiO$_2$ film thickness in double layer TiO$_2$/Ag@TiO$_2$-ZnO as the photo-anode, on the performance of dye-sensitized solar cells have been investigated. Dye adsorption and band gap of the electrode are paramount importance to enhance the efficiency. With the increase of TiO$_2$ film thickness is expected to increase dye adsorption while silver (Ag) doping in semiconductor electrode is proposed to reduce the band gap. Experimentally, TiO$_2$ nanoparticle was deposited on ITO glass by a spin coating method as a first layer with varying number of spin coating to obtain different of thickness. Ag@TiO$_2$-ZnO was deposited above the first layer by the doctor blade method. The sample was characterized by using X-Ray Diffraction, SEM cross-sectional, UV-vis spectroscopy, and solar simulator. It is found that the increases TiO$_2$ film thickness in double layer TiO$_2$/Ag@TiO$_2$-ZnO electrode increase the efficiency linearly. The optimum efficiency of 0.31747% was obtained in a double layer DSSC with TiO$_2$ film thickness of 42.54 µm.

Keywords: DSSC, double layer, thickness, efficiency.

1. Introduction

Solar energy can be converted into electrical energy directly through photovoltaic processes. One of them is by solar cell device[1]. Solar cells have been developed into several generations, The first generation is solar cells based on single crystalline or polycrystalline of silicon[2], the second generation based on thin film[3] and the third generation is dye-sensitized solar cells (DSSC)[4]. DSSC attracts attention because of low prices[5], environmentally friendliness[6], ease of fabrication[7], and still possible to increase the efficiency[4]. In general DSSC is composed of several components, e.g. photo-anode[8], electrolytes[9], dye[10], and the counter electrode[11].

DSSC works based on the concept of photosynthesis, where the photon energy is needed to release electron bonds[12]. The dye functions to absorb photons, so that electrons is excited[13]. The thickness of photo-anode film can affect the amount of dye adsorption[14]. On the other hand an increase in thickness has also resulted in a decrease in thin film transmittance thereby reducing light intensity[15]. Many studies have been conducted examining the effect of photo-anode thickness on DSSC efficiency[16,17]. However, to have better thickness information on DSSC efficiency, it is necessary to examine different photo-anode.
Photo-anodes are usually composed of semiconductor material that has a large band gap such as ZnO[18] and TiO$_2$[19]. TiO$_2$ has three main structures they are rutile, anatase, and brookite[20]. In its application as a photo-anode, brookite in thermodynamically is unstable phase while anatase is considered to be more photoactive than rutile phase[21]. In addition, a mixture of silver (Ag) wrapped in TiO$_2$ has been shown to increase the efficiency of DSSC[22]. The band gap of Ag@TiO$_2$ is smaller than pure TiO$_2$, so the electron mobility is better[23]. The use of Ag@TiO$_2$ in DSSC is limited due to possibility degraded[24]. So far, it is hard to find the literature for the study of layer thickness on double layer DSSC. In this work, we report the influence of double layer thickness composed of ZnO, TiO$_2$, and Ag as photo-anode on its performance.

2. Materials and Methods

2.1. Materials

The material used in this research is Zinc acetate dehydrate, Titanium(IV)-isopropoxide (TTEAIP) 80 wt%, β-carotene, and Titanium dioxide (TiO$_2$) 99% from Sigma-Aldrich, Deionized (DI) water, Sodium hydroxide (NaOH), ethanol 96%, 2-propanol, Dimethyl Formamide (DMF), Nitric acid (HNO$_3$), and Silver nitrate (AgNO$_3$) powder.

2.2. Methods

2.2.1 Synthesis of ZnO nanoparticles. The synthesis of ZnO nanoparticles prepared by the sol gel method. Firstly, we dissolved 16 grams of zinc acetate dehydrate in 80 mL of DI water followed by stirred using a magnetic stirrer 600 RPM. After one hour, NaOH 3M was added little by little under a drip method to reach a pH of 13. The solution was heated at 90°C for one hour then washed using ethanol to obtain a neutral pH and subsequently. Heated 90°C for 30 minutes. After that, the solution was deposited then filtered. The suspension was dried in an oven at 100°C to yielded a ZnO white powder.

2.2.2 Synthesis of Ag@TiO$_2$. The synthesis of Ag@TiO$_2$ nanoparticles were prepared by the reflux heating method by dissolving 2.174 mL of Titanium (IV) - (triethanolaminato) isopropoxide solution (TTEAIP) in 87.828 mL 2-propanol and then stirring using a magnetic stirrer at 500 RPM. On the other hand, we dissolved 0.764 grams of AgNO$_3$ powder in 30 mL of DI water and then stirred at 500 RPM. After 15 minutes, the two solutions were mixed and stirred for 15 minutes. After that, Dimethyl Formamide (DMF) solution was added to the mixture and followed by reflux heating at 85°C, at 500 RPM for 90 minutes. When the solution indicated a dark brown, the heater was turned off. We used ethanol to wash the solution and followed by centrifugation process to get the suspension. The washing process was repeated three times, then the sediment was dried in the oven with a temperature of 100°C. After that, the vacuum calcinations was carried out at 450°C for 3 hours. The result was a dark brown of Ag@TiO$_2$ powder.

2.2.3 Fabrication of TiO$_2$/Ag@TiO$_2$-ZnO. The photo-anode was composed of three layers i.e. TiO$_2$ as compact layer, TiO$_2$ as first layer, and Ag@TiO$_2$-ZnO as the second layer. The compact layer was made from deposition of a prepared solution of 0.5 grams of TiO$_2$ nanoparticles in 3 mL of HNO$_3$ 0.1 M. The homogenous solution was deposited on ITO glass substrate using spin coating at 2500 RPM for 30 seconds followed by heated at 450°C for 30 minutes. The first layer of DSSC was created on the TiO$_2$ compact layer with the spin coating method by 1500 RPM by varying the number of spin coating 1-5 times to obtain different thickness. The last layer of ZnO-Ag@TiO$_2$ was made by the mixture of 0.75 grams of ZnO and 0.075 grams of Ag@TiO$_2$. The mixture was dissolved in 3 mL of 0.1 M HNO$_3$ and ground for 2 hours. The second layer was deposited on first layer using the doctor blade method. Furthermore, the deposited layers were calcined in the furnace at 450°C for 30 minutes. The samples were characterized by X-Ray Diffractometer to obtain information of crystal parameters, SEM cross-sectional to extract the thickness of our samples, UV-vis spectroscopy to get band gap, and Solar simulator test to obtain the efficiency.
3. Results and Discussion

3.1. X-Ray Diffraction studies
The diffractograms of TiO$_2$/Ag@TiO$_2$-ZnO of various spin coating is represented by Fig.1. All samples were characterized using Cu anode, 1 degree slit divergence, 0.2 mm receiving slit X’Pert PRO (Pan Analytical). The peak intensity appears at the 2θ value of 25.384, 31.901, 34.543, 36.388, 38.216, 44.470, 47.677, 56.694, 62.978, 68.099, and 69.238°. The diffraction peak corresponds to the miller index (hkl) of the TiO$_2$ phase (011), the ZnO phase (010), (002), (011), (012), (110), (013), (112), (021), and the Ag phase (111) (002) (022). The crystallite sizes of TiO$_2$/Ag@TiO$_2$-ZnO with different thickness by varying the different spin coating times of 1 to 5 were calculated from a debye scherrer formula:

\[
D = \frac{K \lambda}{\beta \cos \theta}
\]

where D is the crystal size, K is constant, \( \beta \) is the full width at half maximum (FWHM), and \( \theta \) is diffraction angle[25]. We obtained the crystal size of samples 1, 2, 3, 4, and 5 is 10.39, 12.03, 16.54, 17.28, 17.78 nm, respectively. The crystal size of TiO$_2$/Ag@TiO$_2$-ZnO photo-anode increases with increasing the thickness of TiO$_2$.

![XRD of TiO$_2$/Ag@TiO$_2$-ZnO with 1-5 times the spin coating.](image)

3.2. SEM studies
Morphology of all TiO$_2$/Ag@TiO$_2$-ZnO photo-anodes were studied by the image obtained from SEM in Fig.2. It is clearly show that the films have relatively uniform shape with different sizes. Porosity is the ratio between the volume of crystal space with the overall crystal volume. So that the greater of crystal size the porosity crystal will be enlarged. Based on Fig.2 porosity increases with increasing thickness and sample 5 had the highest porosity. Pores were needed to absorb dye. The high porosity can absorb more dye and increase the efficiency. For all of the samples with different thickness respectively 10.295, 14.859, 19.045, 29.335, and 42.542 micrometers did not peel off from the ITO surface. The thickness of TiO$_2$/Ag@TiO$_2$-ZnO film is shown in Fig.3. It was successful to obtain different thickness by varying the number of spin coating 1-5.
Figure 2. SEM of TiO$_2$/Ag@TiO$_2$-ZnO with 1-5 times the spin coating.

Figure 3. SEM cross-sectional of TiO$_2$/Ag@TiO$_2$-ZnO with 1-5 times the spin coating.

3.3. UV-vis spectroscopy

UV-vis characterization is useful for calculating the band gap of TiO$_2$/Ag@TiO$_2$-ZnO 1-5 times spin coating. The band gap can be calculated from the samples with the following Equation 2.
\[ (\alpha h\nu)^2 = C(h\nu - E_g) \] (2)

where \( \alpha \) is the absorbance coefficient, \( C \) is constant, \( h\nu \) is the energy of the photon and \( E_g \) is the band gap[26]. The absorbance pattern of TiO\(_2\)/Ag@TiO\(_2\)-ZnO 1-5 with different thickness is shown in Fig.4. Based on the absorbance pattern of Fig.4, it can be seen that samples 1 and 2 have a pattern similar to ZnO while samples 3-5 are similar to the pattern Ag@TiO\(_2\). This shows more TiO\(_2\) phases in samples 3-5 and the dominant ZnO phase in samples 1-2. To obtain the band gap can be performed by the linear fitting in the graph of \( (\alpha h\nu)^2 \) Vs \( h\nu \). Using this method the band gap of samples 1, 2, 3, 4, and 5 is 3.134, 3.132, 3.126, 3.127, and 3.116 eV, respectively. From the results, it can be concluded that the band gap of the TiO\(_2\)/Ag@TiO\(_2\)-ZnO photo-anode is decreases with thickness. Reduction in the band gap increases the conductivity of the material since the electrons will require less energy to travel from valence to the conduction band of the material[27]. Therefore, by reducing the band gap of the photo-anode will result in better efficiency of DSSC.

![Absorbance pattern](image)

**Figure4.** The normalized absorbance pattern of TiO\(_2\)/Ag@TiO\(_2\)-ZnO with 1-5 times the spin coating.

### 3.4. Solar simulator studies

The solar simulator test is useful to determine the efficiency of TiO\(_2\)/Ag@TiO\(_2\)-ZnO 1-5 times spin coating. The power input which is used is 28 mW/cm\(^2\) while the electrode work area was 0.25 cm\(^2\).
Figure 5. I-V curve for DSSC TiO$_2$/Ag@TiO$_2$-ZnO with Different TiO$_2$ Thickness by varying the number of spin coating 1-5.

The efficiency of DSSC based on TiO$_2$/Ag@TiO$_2$-ZnO photo-anodes can be calculated with a linear fitting of Fig.5. The efficiency of DSSC based on TiO$_2$/Ag@TiO$_2$-ZnO photo-anodes of sample 1, 2, 3, 4, and 5 are 0.11387, 0.20663, 0.22816, 0.22879, 0.31747%, respectively. The optimum efficiency is obtained in the thickest photo-anodes. With the increase of TiO$_2$ film thickness can increase dye adsorption [14]. On the other hand an increase in thickness has also resulted in a decrease in thin film transmittance thereby reducing light intensity[15]. From the results, The increasing of the thickness of TiO$_2$ increases the efficiency of double layer DSSC based on TiO$_2$/Ag@TiO$_2$-ZnO photo-anodes.

4. Conclusion

The increase of the thickness of TiO$_2$ give rise to increase in grain size range from 10.39, 12.03, 16.54, 17.28, and 17.78 nm for sample of 1, 2, 3, 4, and 5 respectively. An increase in the number of spin coatings has been successfully made electrodes with TiO$_2$ thickness respectively 10.295, 14.859, 19.045, 29.335, and 42.542 µm. The similar effect also shows by the bandgap of the layers. The increasing of the thickness of TiO$_2$ increases the efficiency of DSSC.

5. References

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