

Effect on Different Amount of TiO₂ P25 for Dye-Sensitized Solar Cell

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Abstract—Titanium Dioxide (TiO₂) has been successfully prepared using the spray pyrolysis method. Then it was optimized by conducting several repetition procedures and deposited on fluorine tin oxide (FTO) substrate. The amount of TiO₂ P25 was varied from 0.1 grams (g) to 0.5 g in order to study the exact amount of TiO₂ P25 needed to produce the highest efficiency solar cell result. All the thin films were annealed at fixed temperature at 500°C within 3 hours. The thickness of the thin film was measured through a surface profiler. From the measurement, it can be concluded that the utilization of different amount of TiO₂ P25 affects the thickness of thin film. The properties of TiO₂ thin film were investigated by Field Emission Scanning Electron Microscopy (FE-SEM), X-ray Diffraction (XRD) and Four Point Probes. The amount of TiO₂ P25 shows the notable effect on morphological and structural of deposit-TiO₂. The optimum porosity of thin film was observed when 0.3g of TiO₂ P25 has been used while XRD patterns exhibit anatase and rutile structures based on the peak existed. The adsorption of dye molecules increased when the thickness of thin film increased due to the increase in crystal size. Hence, it improves the short circuit density respectively. The efficiency of Dye-Sensitized Solar Cell increased as short circuit density and film thickness increased. Based on this research, the amount of 0.3g TiO₂ P25 with thickness 17.89 μm can be used in Dye-Sensitized Solar Cell applications with the optimum power conversion efficiency measured by solar simulator which is 1.84%.

Index Terms—Dye-Sensitized Solar Cell; TiO₂; Thickness; Efficiency.

I. INTRODUCTION

Titanium Dioxide (TiO₂) promising a good efficiency result and it has been widely used in Dye-Sensitized Solar Cell (DSSC) technology. Generally, photoanode plays an important role in enhancing the efficiency of the solar cells, thus, this study was conducted to investigate the effect of different amounts of TiO₂ P25 for dye-sensitized solar cell. Based on previous research that used TiO₂ P25 as a photoanode, some of the researcher used 0.25g [1] and 0.3g [2] of TiO₂ P25 and it gives a different efficiency for the different amount of TiO₂ P25 used. The amount of TiO₂ P25 used is directly proportional to the thickness of the thin film as more nanoparticles of TiO₂ P25 is utilized. Further, paper [1] was revealed that the optimum thickness, which exhibits the best photovoltaic performance are ranging from 5.57μm to 12.73μm. Recently, a lot of fundamental researches were

done on zinc oxide (ZnO) single crystal as an alternative electrode in DSSC which need high cost for the preparation [3]. Apart from that, a research has proven that the aligned rutile TiO₂ is able to produce the highest light to electric energy conversion efficiency. However, in DSSC the cell efficiency that measured still in below 11%. The others had suggested that replacing nanoparticle with nanorods or nanowire should improve the performance of solar cell [1]. However, the efficiency was less compared to nanoparticles based film due to very low I_{sc}. Therefore, one way to enhance the performance on DSSC is to improve the dye molecule absorption on TiO₂ film. The randomly porous structure of TiO₂ produced by sol-gel methods has some disadvantages such as low conductivity and enhanced electron recombination. These problems are all due to the random microstructure and different orientation of the nanoparticles [4].

In this paper, the optimum thickness and amount of TiO₂ P25 that produces a high efficiency of DSSC, as well as surface morphology, structural properties and electrical properties of TiO₂ thin film are reported. The variety of TiO₂ thin film thickness was obtained from Spray Pyrolysis Deposition (SPD) method by utilizing different amount of TiO₂ P25 as the precursor. DSSC fabricated with these TiO₂ as photoanodes has been tested using a solar simulator to retrieve the efficiency results.

II. EXPERIMENTAL

The TiO₂ layer was deposited on an FTO-coated glass substrate using TiO₂ P25 powder by spray pyrolysis method. There are five steps to fulfil the objective of this study which includes substrate preparation, TiO₂ P25 solution preparation, spray pyrolysis deposition, annealing process, deposit characterization and efficiency measurement. Firstly, the FTO glass substrate was cut approximately into 1.0 cm x 2.5 cm. Then, the FTO-coated glass substrate was immersed in the cleaning solution (the mixture of Deionized (DI) water, ethanol as well as acetone with ratio 1:1:1) and cleaned using an ultrasonic cleaner for 10 minutes. After that, the cleaned FTO was taken out from the cleaning solution and dried inside the oven at 60°C for a few minutes. TiO₂ P25 solution was prepared by dissolving the desired amount of TiO₂ P25, 5.5ml of acetic acid, 20ml of Titanium Colloid Solution

(TKC), 30ml of ethanol and 5 drops of triton. The amount TiO_2 P25 was measured using weight scale. Next, TiO_2 P25 powder sample mixed with the acetic acid solution and it was ground using a mortar and a pestle until it becomes a paste. Meanwhile, a mixture of ethanol and triton is produced inside another beaker. Both pastes, as well as the mixture of ethanol and triton were assorted in the light-proof bottle. The TiO_2 solution in the light-proof bottle was further dissolved in ultrasonic machines for 30 minutes.

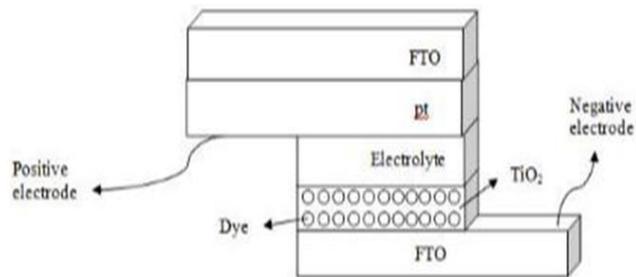


Figure 1: Schematic structure of DSSC with TiO_2 nanoparticles thin film as photoanode.

III. RESULT AND DISCUSSION

The results of this study were discussed and analyzed. The result was divided into six parts which included the sample of TiO_2 P25 thin film obtained, the thickness of the thin film for each different amount of TiO_2 P25 used, morphological characteristic, structural characteristic, electrical properties and the efficiency of Dye-Sensitized Solar Cell (DSSC).

A. TiO_2 P25 thin film

Figure 2 (a)-(e) indicate two version of the deposited TiO_2 thin film with a very thin white color layer growth on every surface FTO glass substrates at the end of spray pyrolysis deposition (SPD) method and annealing process. The substrate with round white layer (masked) which diameter 0.25cm^2 were prepared for DSSC assembly and conversion efficiency measurement. On the other hand, the rest of the characterization and experimental procedure were tested by using all fully covered white layer (unmasked) substrates produced via the same preparation method. From the observation in Figure 2 (a) – (e). 0.5g of TiO_2 thin film sample implies the brightest white layer that growth on the FTO substrate compared to all the TiO_2 thin film appearances while 0.1g of TiO_2 thin film sample is the dimmest among all the samples. Hence, it can be concluded that as the amounts TiO_2 P25 used increases, then, the TiO_2 thin film appearances were getting brighter and whiter.

B. Thickness optimization of TiO_2 Thin Film

The thickness optimization of TiO_2 thin film is the key factor for the enhancement in Dye-Sensitized Solar Cell. Thicknesses of this thin film were measured using a surface profiler. From the data arranged in Table 1, it can be concluded that the increases of amount TiO_2 P25 used, has increased the thickness of this thin film. When the thickness increased, the large amount of dye molecule can be absorbed on particles of TiO_2 thin film and eventually, produce high efficiency of the conversion of light into electrical energy.

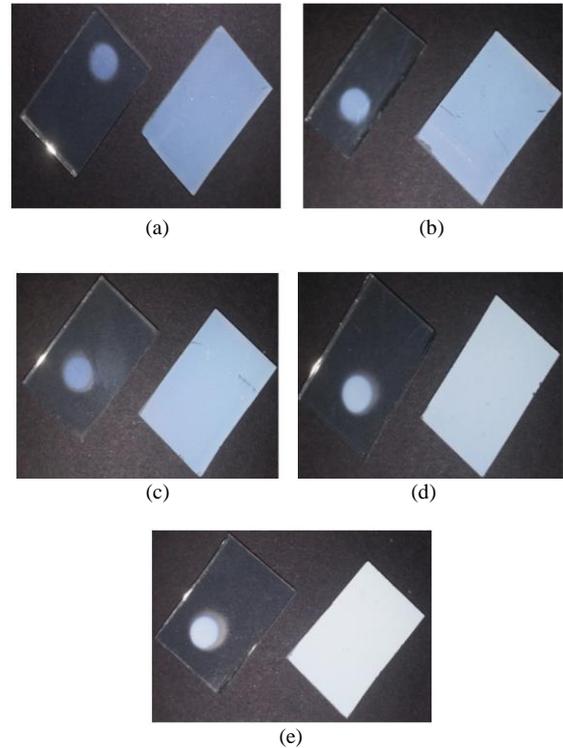


Figure 2: Physical appearance of TiO_2 thin film after SPD and annealing process prepared at different amounts of TiO_2 P25 powder used which is (a) 0.1g , (b) 0.2g , (c) 0.3g , (d) 0.4g and (e) 0.5g .

Table 1
The Thickness of TiO_2 Thin Film Resulted from Different Amounts of TiO_2 P25 Used.

Amount TiO_2 P25 used	Thickness
0.1g	$3.95\mu\text{m}$
0.2g	$7.70\mu\text{m}$
0.3g	$17.89\mu\text{m}$
0.4g	$36.95\mu\text{m}$
0.5g	$46.43\mu\text{m}$

C. Morphological Characteristics

Photoanode of the deposited TiO_2 thin films were prepared with various amounts of TiO_2 P25 on this study, Figure 3 below shows the result of surface morphology under FE-SEM observation. The rough estimation of particle reveals a spherical shape and the size of that particle range from 25nm to 40nm . From the observation on FE-SEM image, the distribution of particle for 0.1g TiO_2 thin film sample is just enough to fulfil the FTO substrate, but with the increasing amount of TiO_2 P25 used, the distribution particle seems crowded and became thicker. Based on (c), the morphology TiO_2 thin film with 0.3g of TiO_2 P25 exhibits the TiO_2 particles grown was successfully covered on the conductive side of the FTO-coated glass substrate layer compared to FE-SEM images retrieved for 0.1g and 0.2g of TiO_2 thin film samples. Furthermore, 0.3g of TiO_2 P25 was more porous compared to other samples. The element of porosity is crucial in fabricating these samples to increase the surface area of the thin film. Hence, it increased the dye adsorption as well as the efficiency of the solar cell. However, starting 0.4g until 0.5g of TiO_2 P25 samples shows the morphological structure of TiO_2 thin film getting more compact and this is not good as packed structure of TiO_2 particles are blocking the porous surface. The amount of TiO_2 nanoparticle affects the thickness of TiO_2 layer as well as the efficiency of DSSC. The thickness of thin film plays an important role to the

efficiency of DSSC as it can give a compact structure for TiO₂ film nanocrystalline. That film directly has an ability to absorb the dye molecule much as possible.

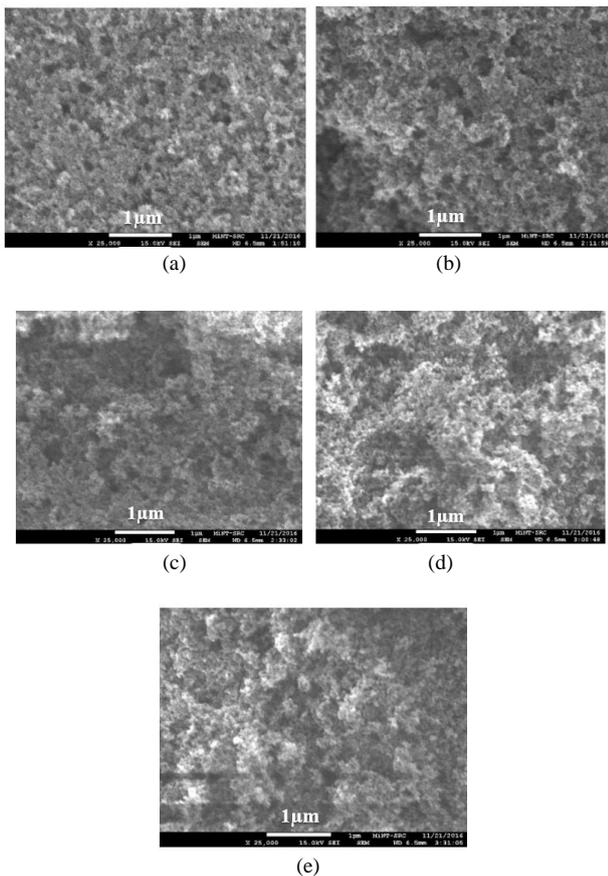


Figure 3: FE-SEM images of TiO₂ thin film prepared at different amount of TiO₂ P25 used which is (a) 0.1g, (b) 0.2g, (c) 0.3g, (d) 0.4g and (e) 0.5g.

D. Structural Characteristics

XRD pattern of the samples TiO₂ P25 were taken by BRUKER-binary V3 X-ray diffractometer using copper radiation (40mA, 40kV) with scanning rate of 8 degree/min which is 0.133 step degree. Peak intensity was measured by integration of the given peak, 25.30 degree (101) and 27.40 degree (110) for all the sample. Figure 4 below shows the XRD spectra of the products synthesized at 400°C under a variety amount of TiO₂ P25.

From Figure 4 it shows that the reading for 0.3g of TiO₂ P25 thin film fabricated was anatase structure that corresponding to the peak of spectrum. The peak found at 2theta value of 25.34°, 37.80°, 41.80° and 55.14° correspond to anatase plane which is (111), (004), (200) and (211). The data obtained quite similar with the data file for anatase structure. However, this TiO₂ P25 contains 80% of anatase and 20% of rutile [6]. It is proven by rutile peaks that were found at 36.09°, 41.23° and 54.32° which match with rutile plane (101), (111) and (211). For sample 0.3g of TiO₂ P25, the peaks observed was matched to the rutile and anatase plane data file. The spectrum of this sample showed a good crystallinity. However, for the overall sample, the increasing amount of TiO₂ P25 has increased the crystallinity of the sample only up to 0.3g TiO₂ P25. Meanwhile, for sample 0.4g and 0.5, the XRD pattern depicted the decreasing of the theta value and it has affected the peak value as well as the crystallinity of the samples.

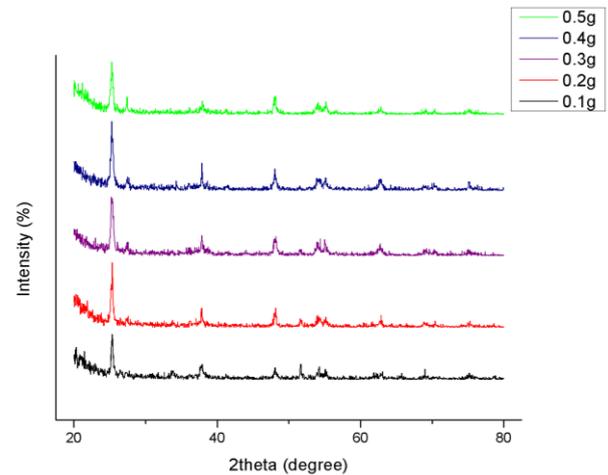


Figure 4: XRD patterns of TiO₂ thin film prepared at different amount of TiO₂ P25 used

E. Structural Characteristics

The resistivity decreases as the thickness of thin film increases. The conductivity of this thin film is the reciprocal inverse for the resistivity. Their relationship is shown by the following equation.

The value of the electrical resistivity for reading 0.1g TiO₂ P25 is $0.87 \times 10^{-2} \Omega\text{-cm}$ and the electrical conductivity is 114.94 S/cm. Based on the experimental observation, it can be said that the value of conducting will increase when the amount TiO₂ P25 increases while the resistivity value decrease.

$$\rho = 1/\sigma \quad (1)$$

F. Solar Cell Efficiency

From data in Table 2, it clearly shows that when the amount of TiO₂ P25 increased, the efficiency of solar cell also increased due to the thin film thickness and the ability of porous surface in creating more dye adsorption. However, the improvement of efficiency exhibits sharp decrease with an increase of thickness beyond 17.89μm. This study was revealed, the efficiency of these TiO₂ P25 DSSC become higher when more TiO₂ P25 used, unfortunately, decrease when 0.4g of TiO₂ P25 was used to fabricate TiO₂ thin film. For sample 0.1g, it is enhanced by only 0.12%; while for 0.2g the efficiency has increased up to 0.24%. The efficiency graph rapidly increases at 0.3g usage of TiO₂ P25 where it produced the highest efficiency result which is 1.84%. For the thin film with 0.4g and 0.5g of TiO₂ P25, the efficiency has declined to 0.318% and 0.256%, respectively. The decreasing of solar efficiency at the end of this experimental has indicated that the thickness of TiO₂ photoanode layer made in this study has very little influence on the performance of the DSSC. In addition, the fill factor (FF) is one of the parameters which have an effect on the efficiency. In general, the DSSC which has high efficiency shows good fill factor (higher value). The fill factor is affected by the internal resistance in DSSC. Therefore, in the case of the large-sized cell, the fill factor is poor because of an increased internal resistance, compared to a small sized cell. For this study, the large size cell refers to the film with an amount of TiO₂ P25 equal to 0.4g and 0.5g TiO₂ P25. Besides, data in Table 2 also display the Four Point Probes measurement results and performances of prepared DSSC. The value of short-circuit current density J_{sc} (mA/cm², at $U = 0$ V)

depends directly on charge injection and collection at TiO₂ electrode, on the amount of absorbed dye and layer thickness. For this study of TiO₂ electrodes with different amount of TiO₂ P25 (0.1g, 0.2g, 0.3g, 0.4g and 0.5g) the measured value of J_{sc} was 0.63, 2.40, 3.05, 2.35 and 1.031 mA/cm². The highest value of J_{sc} for the sample 0.3g of TiO₂ P25 and lowest for the sample with 0.1g TiO₂ P25. All in all, the solar efficiency, η is a product of the short-circuit current density, J_{sc} with the open-circuit photovoltage, V_{oc} and Fill Factor, FF divide by P_{in} (the solar power incident on the cell 100mW cm⁻² for mass (AM) 1.5 a) as the equation (2) written below. Hence, to enhance the power efficiency, the only way is to improve J_{sc} , V_{oc} and /or the FF component as well as maximize the product of these three component .

$$\text{Efficiency, } \eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \quad (2)$$

Table 2
Data Obtained from Solar Simulator

Amount TiO ₂ (g)	Voc (V)	Jsc (mA)	Fill Factor	Efficiency (%)	Thickness (μm)
0.1	0.71	0.63	43.69	0.115	3.95
0.2	0.71	2.40	46.86	0.244	7.70
0.3	0.75	3.05	67.11	1.839	17.89
0.4	0.77	2.35	34.57	0.318	36.95
0.5	0.78	1.03	30.27	0.256	46.43

IV. CONCLUSION

The sample of the TiO₂ thin film with a different amount of TiO₂ P25 used as precursor were successfully fabricated onto the FTO-coated glass substrate by Spray Pyrolysis Deposition method. The confirmation of the presence of TiO₂ was made via FE-SEM and XRD observations. The thickness of the thin film has been measured using surface profiler in order to study the dependence of amount TiO₂ P25 needed for the photoanode film thickness on the performance of dye-sensitized solar cell (DSSC). As a conclusion based on the results obtained through entire experimental procedures as the amount of TiO₂ P25 increased, the film thickness increased and the optimum thickness to attain the highest efficiency for this study were 17.89μm. Besides, the efficiency of the DSSC increases as the short circuit current (J_{sc}) and TiO₂ P25 thin film thickness increases. However, the conversion efficiency started to decline when more than 0.4g TiO₂ P25 applied in this study (thickness obtained beyond 17.89μm), the short-circuit current decreases and resulting in the decreasing solar cell efficiency. A thick

photoanode induces a large surface area enhancing dye molecules to adsorb on it. Hence, a thick photoanode captures more light to generate photoexcited electrons. However, the J_{sc} requires that these electrons successfully transport to the FTO substrate (electrode) without recombination at the dye/photoanode or photoanode/ electrolyte interfaces; therefore, electron diffusion length is also a key point that needs to be considered. Though a thick photoanode enhances the generation of photoexcited electrons, a long electron diffusion length is inevitable for those photoexcited electrons generated in the deep layer. Thus, the J_{sc} is a compromise between the two conflict factors: enlarged surface area by increasing photoanode thickness and increased thickness resulting in a long electron diffusion length. The probability of recombination of injected electrons and the iodides in the electrolyte is smallest in this case. Lastly, as mentioned previously, the DSSC's fabricated using 0.3g of TiO₂ P25 powder with 17.89μm thickness exhibited the best photovoltaic performances with highest incident photon-to-current conversion efficiency, highest short-circuit photocurrent as well as highest fill factor.

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