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Research paper

Rutile-phased Titanium Dioxide (TiO_2) Microstructures by Hydrothermal Method for Dye-Sensitized Solar Cell (DSSC)

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Abstract

This paper presents rutile-phased titanium dioxide (TiO_2) microstructures fabricated by hydrothermal synthesis for the application as a photoanode in DSSC. The amount of precursor, titanium (IV) butoxide (TBOT) was varied from 0.5 to 2 ml and the changes on the surface morphology, structural and electrical property as well as their performance in DSSC were evaluated by using FE-SEM, XRD, 4-point probeand solar simulator respectively. Since the amount of precursor is too low, no rods were able to grow from the FTO substrates used, but flower formations can be seen on sample with 2 ml of TBOT. The structural analysis revealed rutile spectra for all samples with the peaks gradually increased as the amount of precursor increased. The conductivity decreases as the film thickens with increasing precursor amount, while the resistivity and sheet resistance decreased as the amount increase; as rutile structure is known to have good electron mobility. The performance of the TiO_2 films in DSSC was evaluated, and the sample with the best performance was found in the film with 2 ml TBOT precursor at 0.234 % with Jsc and Voc of 0.759 and 0.643 respectively. Increased TBOT precursor is concluded to increase the efficiency of DSSC but the limit is yet to be studied and further research will be needed.

Keywords: *DSSC; Hydrothermal; Microstructure; Titanium Butoxide; Titanium Dioxide*

1. Introduction

Following the green technology trend, the increase in demand of clean energy led to many researches regarding clean energy to substitute the old way of energy harness which is using fossil fuel. Fossil fuel is an effective source that can generate million watts of power. However, many problems surfaced when using this type of sources such as pollution, area needed, and the limited resources that dwindles day by day [1]. One of renewable and clean energy sources is solar power [2].

The solar power technology has evolved following many researches emerging everywhere trying to resolve the disadvantages of solar energy. One of the technologies that is being researched nowadays is DSSC [3-5]. The researches regarding DSSC started in late 1960s when it was discovered that illuminated organic dyes can generate electricity on oxide electrodes in electrochemical cells. Since then, many researchers start their own researches to improve the technology until DSSC was demonstrated in 1972 [6].

DSSC is a low cost solar cell belonging to the group of thin film solar cell. The modern day DSSC mainly uses titanium dioxide (TiO_2) nanoparticles covered with molecules of dye to absorb sunlight [7]. The more popular structure of TiO2 for DSSC application is anatase but rutile has its own attractive points for DSSC [8, 9]. Following that, many researches has been done to improve its performance in DSSC [8–10]. The main purpose of the research is to study the effect of different titanium (IV) butoxide (TBOT) volume on the performance of TiO_2 film in DSSC.

2. Experimental

2.1. Sample preparation

The nanostructured TiO_2 thin film was prepared by using hydrothermal method [13]. The precursor solution for the hydrothermal solution consists of distilled water as solvent, hydrochloric acid as the chelating agent and titanium (IV) butoxide as the titanium precursor.

The solutions were mixed accordingly before the hydrothermal process. The performance of DSSC based on nanostructured rutile phased TiO_2 depends on different chemical ratio of the precursor solution will be evaluated. The investigation on obtained nanostructured TiO_2 and DSSC were characterized by FE-SEM, XRD, solar simulator and four-point probe for morphological, structural and electrical properties as well as their performance in DSSC. Table 1 shows the samples prepared and ratio of chemicals used.

Table 1: Sample and ratio chemicals

Sample	Ratio of chemicals
1	80 ml Deionized water : 80 ml Hydrochloric : 0.5 ml Titanium(IV) Butoxide
2	80 ml Deionized water: 80 ml Hydrochloric : 1.0 ml Titanium(IV) Butoxide
3	80 ml Deionized water: 80 ml Hydrochloric : 1.5 ml Titanium(IV) Butoxide
4	80 ml Deionized water: 80 ml Hydrochloric : 2.0 ml Titanium(IV) Butoxide

2.2. Cleaning process

The first process is the cleaning of the FTO substrate (1.0 cm x 2.5 cm) and substrate mask with circular hole (Ø = 0.25 cm^2) for the substrate. The ultrasonic machine is used to clean the FTO glass substrate and mask as described in Figure 1. 10 ml of acetone ($(CH_3)^2$ CO) solution, 10 ml of ethanol and 10 ml of deionized water were consequently used for each cycle of sonication. The ultrasonic cleaning process for the FTO glass substrate and substrate mask takes 5 minutes per cycle.

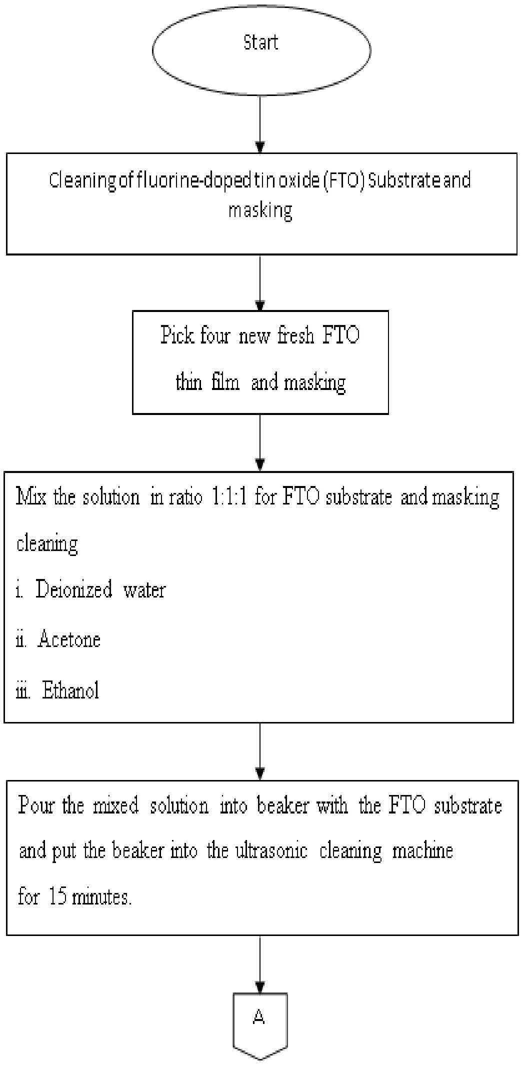


Fig 1: Flow chart of the substrate cleaning process.

2.3. Hydrothermal process

Precursor solution was prepared according to Figure 2. The solution was made by mixing 80 ml deionized water (DI) and 80 ml hydrochloric acid (HCl) in a beaker before adding 0.5 ml titanium(IV) butoxide (TBOT) dropwise. The second, third and fourth variation of solution uses the same volume of DI water & HCL but the TBOT precursor were increased to 1.0 ml,1.5 ml and 2.0 ml. All solution was stirred for 10 minutes to ensure that the solution is homogeneous. Cleaned FTO substrates were put into Teflon lined autoclave with the conducting side of the substrate facing upwards. The autoclave is then filled with the precursor solution and put into the oven. This hydrothermal synthesis was conducted at constant temperature of 150 ºC for 18 hours. After synthesis, the FTO film was taken out, rinsed extensively with DI water and dried at 50 °C in oven for 10 minutes. The samples were then characterized for morphological properties and electrical properties.

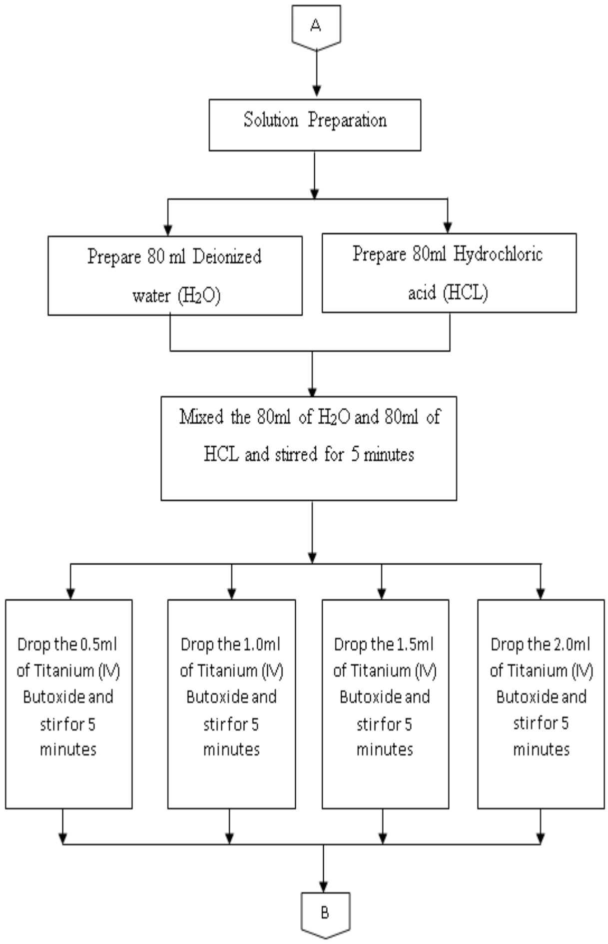


Fig 2: Flow chart of the TiO_2 precursor solution preparation.

2.4. Preparation of electrolyte

The electrolyte used in this study is the 1.2-dimethyl-3-propylimidazolium iodide (DMPII) which has the triiodide/iodide redox couple. The mixture consists of 5 ml of veloronitrile, 10 ml of butyl pyridine (TBP), 10 ml of iodolyte AN 50, 1.597 g DMPII and 0.01 g guanidine thiocyanate (GT). After the chemicals are mixed, it was put into the ultrasonicator for 10 minutes for thorough mixing.

2.5. TiO_2 thin film dye immersion

For this experiment, the experiment used synthetic (N-719) ruthenium dye for its outstanding absorbance range of photons in the visible light [14]. The N719 powder (Ruthenizer 535-bis TBA) was a product of Solaronix. The dye solution was made with the blend of 0.0178 g of N719 with 25 ml of acetonitrile and 25 ml of 1-butanol. Then, the mixture of solution was kept or stored at low temperatures to prevent evaporation that will cause changes in molarity. In DSSC, dye molecules act as photosensitizers that will absorb light energy and excite electrons into the conduction band of TiO_2 to produce electrical energy. The films were immersed in the dye prepared for 24 hours.

2.6. DSSC assembly

The DSSC is assembled for making characterization using the Solar Simulator. The TiO_2 thin films were dipped into ethanol to remove the excessive dye before clamped with the Pt counter electrode. The electrolyte is injected between the electrodes. Then, the excess electrolyte is wiped off and the solar cell is clamped.

3. Results and discussion

3.1. Morphological analysis

The Field Emission Scanning Electron Microscopy (FE-SEM) is used to observe the surface morphology of TiO_2 thin films. The presence of TiO_2 thin film on the surface of FTO can be determined through FE-SEM and the morphology such as shape, size and thickness can be characterized. Figure 3 shows the FE-SEM images at 50, 0000 magnification and the cross section images of TiO_2 thin films with different TBOT volume. It is indicated from figure ‘a’ and ‘b’ that films with 0.5 ml TBOT produced some misaligned rods with diameter from 0. 21 µm to 0. 31 µm. At 1.0 ml, there are still some misaligned rods obtained as shown in figure ‘c’ and ‘d’. The average diameter of rods is 51.6 nm. When TBOT was increased to 1.5 ml and 2.0 ml, flower structure can be seen on the surface based on ‘e’ to ‘h’. The highest thickness obtained is from sample with 1.5 ml TBOT at 7.13 µm as shown in Figure 1(f). A few TiO_2 nanoflowers are observed on sample with 2.0 ml of TBOT.

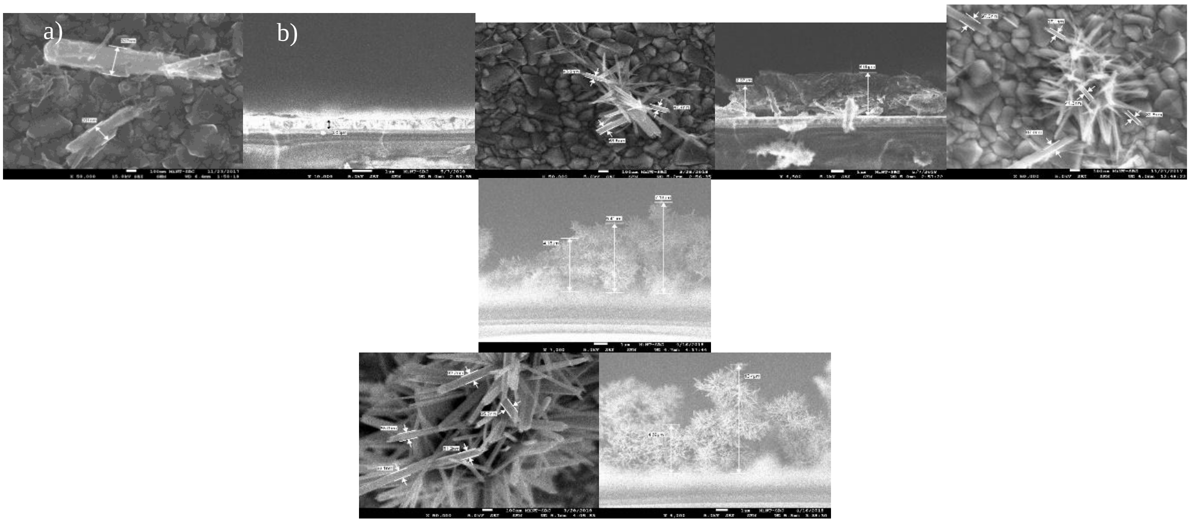


Fig 3: FE-SEM image of TiO_2 grown on FTO substrate at top view 50,0000 magnification and cross section. (a & b) 0.5ml, (c & d) 1.0 ml, (e & f) 1.5ml and (f & g)2.0 ml of TBOT.

The different morphologies obtained are rods and nanoflowers. The growth of TiO_2 is based on titanium reaction with oxygen at low temperature with high pressure in a closed system. At 0.5 ml and 1.0 ml, less rods are obtained because of the low volume of TBOT. When volume of TBOT increased to 1.5 ml and 2.0 ml, nanoflowers formed. The FE-SEM results showed that the growth of TiO_2 nanorods diminished on the FTO substrate and only nanoflowers left on the substrate because of low titanium precursor concentration, the rods were not as aligned as rods grown using higher amount of titanium precursor [15]. More flowers will increase the effective surface area for dye adsorption and the amount of adsorbed dye is crucial as dye molecules provide electrons to produce current. From this analysis, sample with 2 ml TBOT is the best as it showed the most flower formation.

3.2. X-Ray diffractometer (XRD) analysis

The analysis of structural properties of TiO_2 thin film were carried out with Cu-Kα radiation. Figure 4 shows XRD spectra of thin film with different TBOT volume. The XRD patterns obtained from the samples exhibited strong diffraction peaks at 27.43º, 36.12º, 41.31º corresponded to the rutile [110], [101] and [111] crystal planes, respectively. All the rutile peaks matches with datasheet PDF No. 98-016-7953. When the volume of titanium precursor increases, the peaks become narrower and sharper which indicate better crystallinity with increasing TBOT volume. Increased crystallinity will improve electron mobility as well as reducing sheet resistance which will result in higher current density in DSSCs. The results prove that all the samples are rutile. Theoretically, rutile can be better for the application of DSSC since the rutile phase exhibits an excellent combination of physical properties, including exceptional light scattering efficiency, a high refractive index, opacity, chemical inertness and photocatalytic properties [16]. In a nutshell, according to the XRD spectra, sample with 2 ml TBOT exhibits the best spectra.

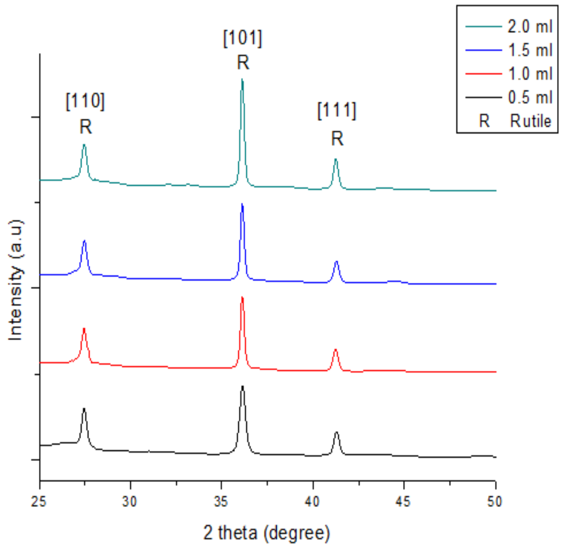


Fig 4: XRD profiles of thin flm with different TBOT volume ;(a) 0.5 ml, (b) 1.0 ml, (c)1.5 ml and (d)2.0 ml

3.3. Photovoltaic properties of DSSC

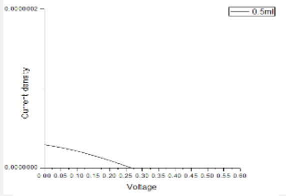
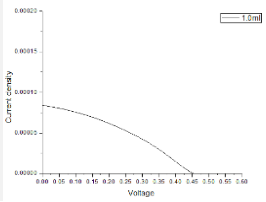
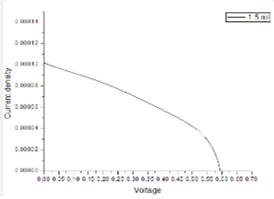
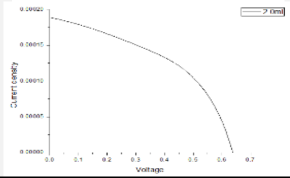
Table 2 shows the photovoltaic properties of DSSC with different TBOT volumes, where Jsc is short circuit current density, Voc is open circuit voltage and η is power conversion efficiency. It is confirmed that DSSC based on TiO_2 nanoflowers film fabricated from 2.0 ml of TBOT gives the highest efficiency, and that efficiency is increased as the precursor volume increased. The increase in efficiency is mainly due to an increase in Jsc which indicates an increase in dye adsorption. The dye absorption is closely related to surface morphology of the film itself. As the concentration of TBOT increases, the current density of DSSC increases as shown in Table 3.

Table 2: Photovoltaic properties of DSSC with different TBOT volume

TBOT content (ml)	Jsc (mA/cm^2)	Voc (V)	Fill factor	η (%)	Thickness (μm)
0.5	0.000125	0.289759	29.1048	0	0
1.0	0.345386	0.432281	36.6546	0.0547	4.05
1.5	0.398053	0.592961	38.96	0.092	7.13
2.0	0.75936	0.643937	47.8577	0.234	10.4

The increase in the amount of nanostructure might increase the surface area of the film and thus resulting higher dye adsorption. Although the efficiency of 0.234% is much lower compared to other research [17], an increase in thickness and the controlled growth of the TiO_2 nanoflowers could enhance the dye adsorption and photovoltaic properties, and finally increase the DSSC efficiency. In theory, the maximum voltage generated by such a cell is simply the difference between the quasi-Fermi level of the TiO_2 and the redox potential of the electrolyte, about 0.7 V under solar illumination conditions. From the results, the sample with the closest Voc value to the theoretical 0.7 V is the sample with 2.0 ml TBOT volume at 0.64 V, which also produced the highest Jsc and efficiency at 0.76 mA/cm^2 and 0.23%, respectively.

Table 4: I-V graph of DSSC using TiO_2 with different TBOT volume

Sample	TBOT volume	I-V graph
1	0.5 ml	
2	1.0 ml	
3	1.5 ml	
4	2.0 ml	

3.4. Current-voltage (I-V) measurement

The resistivity of the TiO_2 thin film is measured by using four-point probe. In order to obtain a more accurate value, four points were characterized on the surface of TiO_2 thin film. When all the values of thickness are gathered, the average sheet resistance, R_s resistivity, ρ and conductivity of the TiO_2 thin film can be calculated. Table 4 tabulates the average sheet resistance, average resistivity and also the conductivity of deposited TiO_2 thin film on the FTO substrates with different TBOT volume.

Table 5: Average sheet resistance, average resistivity and conductivity of TiO_2 thin film with different TBOT volume

TBOT volume	Average sheet resistance, R_s (Ω/sq)	Average resistivity, ρ (Ω-cm)	Conductivity, σ (S/cm)
0.5 ml	5.96×10^0	3.34×10^{-4}	2.99×10^3
1.0 ml	5.58×10^0	3.10×10^{-4}	3.23×10^3
1.5 ml	5.45×10^0	3.08×10^{-4}	3.24×10^3
2.0 ml	4.87×10^0	2.73×10^{-4}	3.66×10^3

From the table, the TBOT volume of 0.5 ml shows the lowest average sheet resistance with value 5.96×10^0 Ω/sq while the 2.0 ml gives the highest value of average sheet resistance at 4.87×10^0 Ω/sq. Besides that, the average resistivity of TiO_2 thin film is inversely proportional to the TBOT volume. The average resistivity of the thin film is found to decrease with the increase of TBOT volume in the range of 3.34×10^{-4}Ω-cm to 2.73×10^{-4}Ω-cm. From these results, the sample with the lowest resistivity is the best since it will be easier for the current to flow. The TBOT volume at 2.0 ml shows the lowest average resistivity compared to others. For the conductivity, the result shows that the conductivity of the TiO_2 thin film is directly proportional to the TBOT volume. The conductivity of the thin film is observed to increase when the TBOT volume increase in the range of 2.99×10^3S/cm to 3.66×10^3 S/cm. From this result, it can be concluded that the resistivity of TiO_2 thin film is inversely proportional and the conductivity of TiO_2 thin film is directly proportional to TBOT volume.

4. Conclusion

This paper has presented rutile-phased titanium dioxide (TiO_2) microstructures by hydrothermal method for dye-sensitized solar cell (DSSC). Overall, this research is capable to aid in the understanding of rutile TiO_2 in DSSC and of the simple method for TiO_2 thin film deposition by using hydrothermal method. This research is to study the effect of different TBOT volume to the characteristic of TiO_2 thin film. For this experiment, the volume of TBOT was varied to be 0.5 ml, 1.0 ml, 1.5 ml and 2.0 ml and the fabrication condition is fixed with the temperature set at 150 ^{0}C for 18 hours. This research focused on the effect on nanostructure TiO_2 thin film characteristic such as thin film surface morphology, structural property, photovoltaic and also electrical properties by varying the different TBOT volume. The increment of TBOT volume can increase the efficiency in a DSSC.

The TiO_2 nanostructures have been successfully deposited on the FTO coated glass substrate using hydrothermal method. From FE-SEM images, the thickness of the nanostructured TiO_2 increased when the amount of precursor increased. XRD pattern suggest that all peaks for sample with 0.5 ml, 1.0 ml, 1.5 ml and 2.0 ml of TBOT corresponded to rutile phase. It is confirmed that the efficiency of DSSC based on TiO_2 using 2.0 ml of TBOT gives the highest efficiency, and the efficiency is mainly caused by an increase in Jsc, which indicates an increase in the dye adsorption on the nanostructure thin film. The dye adsorption is closely related to the surface morphology of film. As the volume TBOT increase, the density of TiO_2 nanostructure also increase as shown in Figure 1. The increase in nanostructure might increase the surface area of the film thus giving higher dye adsorption. Though the efficiency of 0.234% is much lower compared to other research [18], an increase in the thickness and the controlled growth of the nanostructure could enhance the dye adsorption and photovoltaic properties, and finally increasing the DSSC efficiency.

Furthermore, the characterization of TiO_2 thin film by four-point probe shows that the resistivity of the thin film is inversely proportional to the TBOT volume. The resistivity obtained is in the range of 3.34×10^{-4} Ω-cm to 2.73×10^{-4}Ω-cm. Meanwhile, the conductivity of the TiO_2 thin film increased with the increase of the TBOT volume.

A few recommendations for this research is to decrease the amount of HCL for hydrolysis process. When the HCL volume is too high, [Cl-] ions become very concentrated, the hydrolysis of titanium becomes restricted and restrains nucleation [19]. Another recommendation is to increase the volume of TBOT and learn more about cetyltrimethlyammonium bromide (CTAB) to be used as a surfactant. The sample also should never be taken out from the Teflon by using tweezers while still submerged in the solution because the contamination from tweezer can affect the performance of the sample. Lastly, shared autoclave with other students can also cause contaminations to the sample.

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