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Fabrication and Characterisation of Titanium Dioxide (TiO_2) with Different Synthesis Temperatures for Solar Cell Applications

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In this investigation, the effects of various synthesis temperatures of titanium dioxide (TiO_2) on the structural, optical, and electrical properties of Dye-Sensitised Solar Cell (DSSC) were investigated. As an organic dye for DSSC, Beetroot plant was chosen. The TiO_2 solution was prepared using the sol-gel method and deposited on glass using the spin coating technique. Several compounds, including absolute ethanol, Titanium Isopropoxide (TTIP), Glacial Acetic Acid (GAA), Triton X-100, and deionised water, were combined to create the TiO_2 solution. Using a Scanning Electron Microscope (SEM), an Ultraviolet-Visible (UV-Vis) spectrometer, and a Keithely 2450 Sourcemeter, the structural, optical, and electrical properties of TiO_2 were determined. The results indicate that the TiO_2 thin film synthesised at a temperature of 60°C has the most porous structure and the smallest particle size when compared to others. This temperature also produces TiO_2 with the sharpest peak absorption of 0.40 at a wavelength of 575.50 nm, resulting in a bandgap energy of 3.10 eV. Furthermore, it has a higher Field factor (FF) value that results in the highest energy conversion efficiency, η of 0.34 %.

Keywords: Dye-Sensitised Solar Cell (DSSC); Titanium dioxide (TiO_2); band gap energy; energy conversion efficiency; sol-gel method

I. INTRODUCTION

Population growth is driving a significant increase in the worldwide energy consumption rate. This subsequently led to a rise in demand for natural resources such as petroleum and natural gas. However, the rising demand for these natural resources may result in an increase in harvesting costs. This generation has relied on fossil fuels to generate a respectable amount of energy, but their emissions of harmful gases contaminate the environment and contribute to global warming and climate change. Therefore, individuals began to utilise other energy sources. The solar cell, which is also known as a photovoltaic cell, is one of the most environmentally friendly energy sources. A solar cell is recognised as a clean energy device because it does not produce carbon dioxide and is renewable. Dye-Sensitised Solar Cell (DSSC) was first developed by O'Regan and Gratzel in 1991, a new type of photochemical solar cell (Grätzel, 2005). DSSC is a low-cost solar cell with a simpler fabricating process. Because of these advantages, the DSSC has become a promising alternative solar cell. To fabricate DSSC, a semiconductor electrode is the most crucial one. One of the major factors in fabricating the DSSC is to choose the

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photoanode materials (Song *et al.*, 2014). Many researchers have found semiconductor materials such as Graphene, reduced Graphene Oxide (rGO), Zinc Oxide (ZnO), and Titanium dioxide (TiO_2) for DSSC application (Casaluci *et al.*, 2016; Wei *et al.*, 2016; Zhang *et al.*, 2018). TiO_2 was widely used in DSSC due to its larger band gap, relatively nontoxic material and has higher photoactivity (Zulkifli *et al.*, 2015). However, the lower efficiency of DSSC is caused by the lower electron transfer in TiO_2 which is due to less optimal contact between particles (Trihutomo *et al.*, 2019). In addition, the fabrication techniques are the utmost important to improve the performance of DSSCs (Song *et al.,* 2014). Improved performance of DSSC can be achieved by depositing a good quality of TiO_2 on the film. Many parameters should be taken into account to produce high-quality TiO_2 film. It has been reported that the potential application of titania nanomaterial are affected by the particle size and morphology (Shang *et al.,* 2009; Chen *et al.,* 2007). Several processes have been studied and investigated to develop titania nanoparticles (Baek *et al.,* 2009; Simonsen *et al.,* 2010). Sol-gel method is one of the preparation methods that has been extensively used to prepare TiO_2 nanoparticles (Ojstrsek *et al.,* 2013). Theoretical and experimental showed that the size of particle has been influenced by temperature, pH solution and metal precursor (Zhang *et al.,* 2008). In addition, it was confirmed that the process temperature of sol-gel method has an impact on the nucleation growth of TiO_2 nanoparticles (Morteza *et al.,* 2017). In addition, a combination of organic dye and TiO_2 showed a promising result. Our previous research showed the turn-on voltage increases from 0.2 V to 1.2 when integrating turmeric and TiO_2 for DSSC application (Sahari *et al.,* 2017).

Therefore, this study aims to investigate the effects of different synthesis temperatures of TiO_2 on the structural properties of TiO_2. The correlation between structural properties and performance of DSSC was further investigated from optical and electrical characteristics. The structural properties of TiO_2 thin film was characterised by Scanning Electron Microscopy (SEM), while the optical properties were measured by UV-Visible spectroscopy (UV-Vis). Meanwhile, the electrical properties (I-V characteristic) was measured by Keithely 2450 Sourcemeter.

II. MATERIALS AND METHOD

A. Synthesis of Titanium Dioxide (TiO_2) by Sol-Gel Method

The fabrication process of DSSC is illustrated in Figure 1. First, the photoanode was prepared from TiO_2. The TiO_2 film was prepared by depositing the TiO_2 solution on the substrate. The TiO_2 solution was prepared by mixing ethanol or ethyl alcohol (C_2H_6O), Glacial Acetic Acid (GAA), titanium isopropoxide (TTIP), distilled water and Triton X-100 in a Schott Bottle Blue Cap.

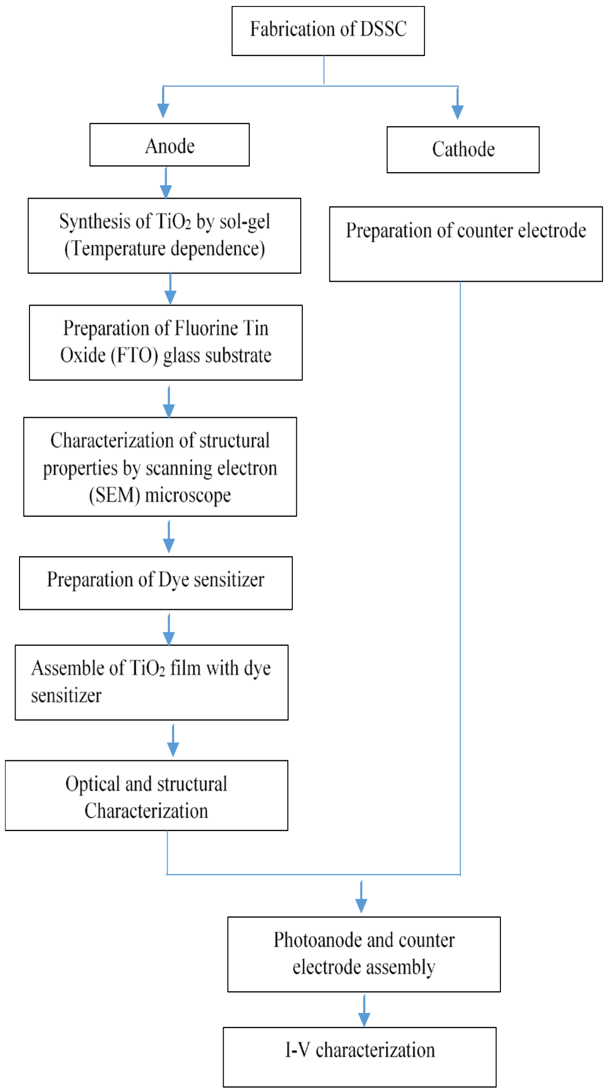


Figure 1. The flow process of DSSC fabrication.

The solution was continuously stirred for two hours at different synthesis temperatures (50 °C, 60 °C or 70 °C) at 600 rpm. The stirring process at a certain temperature (50 °C, 60 °C or 70 °C) in 2 hours is very important to break the carbon chain and to avoid from agglomeration (Vaiciulis *et al.,* 2012). In this method, TTIP was used as a precursor, ethanol as a solvent, GAA as a stabiliser or chelating agent, while Triton X-100 act as a surfactant to avoid precipitation (Maarof *et al.,* 2013). Besides that, Triton X-100 is very important in order to increase the conductivity of the thin films. The overview of synthesis process of TiO_2 by sol-gel method is shown in Figure 2.

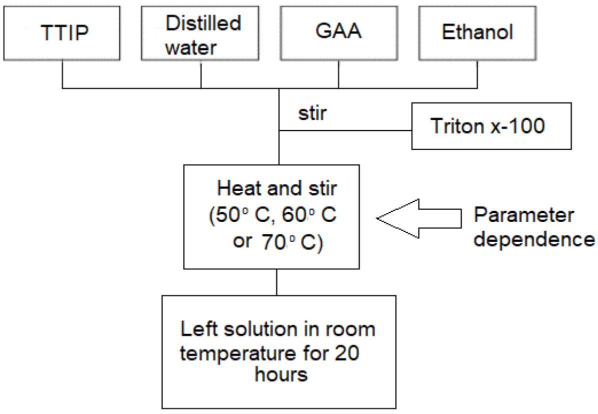


Figure 2. Overview of the synthesis process of TiO_2.

B. Preparation of Glass Substrates

The glass substrates were cut carefully in the dimension of 2 cm x 1.5 cm. Then, the glass substrates were cleaned by using acetone and distilled water in ultrasonic bath for 10 minutes each to remove any contaminants on the glass surface. The substrates were dried using blower (Giuseppe *et al.,* 2008). For FTO glass substrates, they were cleaned by using acetone and isopropanol in ultrasonic bath for 10 minutes each.

C. TiO_2 Thin Film Deposition

The deposition of TiO_2 solution was done by spin coating method to the FTO conductor glass surface with polishing area of 1cm x 1cm in size which functions as the active area of solar cell. The spin coater was set at speed 3000 rpm for 30 seconds. By using a micropipette, the TiO_2 solution was dropped at the middle of the glass substrate. Then, the glass was heated at a temperature of 100°C for 5 to 10 minutes on the hot plate. Finally, the samples were annealed at 450°C for 2 hours.

D. Extraction of Natural Dye Solution

The natural dye used in this experiment was the beetroot plant. Beetroot plants contain anthocyanin dye pigment with high light absorption capability (Elumalai *et al.,* 2015). The beetroot plant was cut into small pieces and crushed using mortar. The mixture was immersed with 100 ml of ethanol and the solution was kept in away from light illumination for one week at room temperature. After a week, the solution was filtered by using filter paper. The extracted dyes solution was stored away from the sunlight for future use.

E. Fabrication of Dye-Sensitised Solar Cell (DSSC)

Both anode and cathode electrodes are prepared for fabrication of DSSC. TiO_2 was used as a photoanode. The FTO glass substrate with TiO_2 coated was immersed in the dye solution and left in a dark place at room temperature.

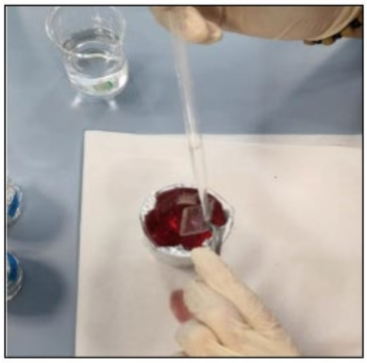
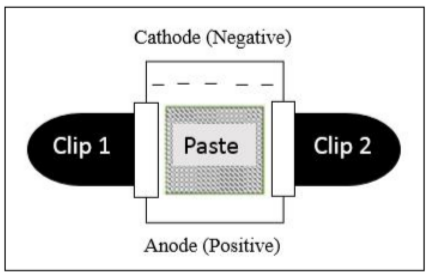


Figure 3. The process of removing excess dye by using ethanol.



clipsby using ethanol

Figure 4. Top view of DSSC with binder clips using ethanol.

After 24 hours, the substrate was removed from the solution. Then, the substrate was rinsed off with ethanol. This process is shown in Figure 3. For the cathode electrode, graphite was coated on the FTO glass. Both anode and cathode were bound together to form DSSC as shown in Figure 4. The electrolyte solution of iodide was injected between the electrodes, drop by drop to prevent the substrates from drying out. The iodide provides ions that will carry the current flow through the solution (Lee *et al.,* 2017). The structure of DSSC is like a sandwich configuration that consist of photoanode, cathode, dye and electrolyte as shown in Figure 5.

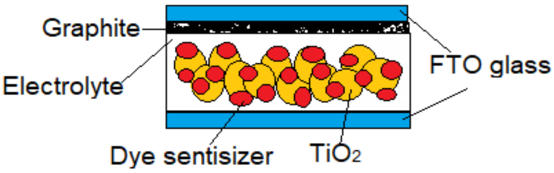


Figure 5. Structure of DSSC.

F. Characterisation of TiO_2

The structural properties of TiO_2 were observed by using SEM with a magnification of 10 000 X. The optical properties were observed using UV-Vis. Meanwhile, the electrical properties of TiO_2 were measured by using Keithely 2450 Sourcemeter.

III. RESULTS AND DISCUSSION

Figure 6 shows the SEM images for different synthesis temperature of TiO_2 solution at 50°C, 60°C and 70°C obtained via SEM.

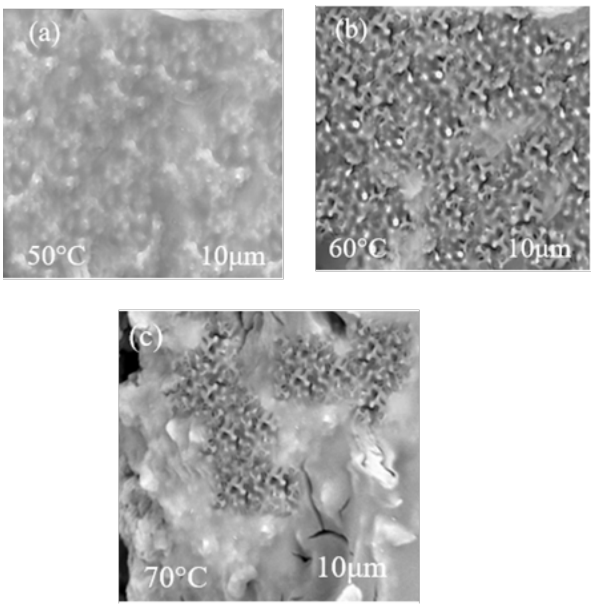


Figure 6. The TiO_2 structure with different synthesising temperature.

It shows that the porosity of TiO_2 was affected by different synthesis temperatures of TiO_2. The TiO2 thin film synthesised at a temperature of 60°C has the most porous structure compared to others. The finding indicates that the surface of the TiO_2 thin film is covered with a rough, grain-like structure that is dispersed across the whole surface. Increased porosity of the particles will boost the infiltration of dye sensitiser on the surface area, resulting in enhanced light absorption capacity (Byranvand *et al.,* 2012).

Further increase in the synthesis temperature leads to the cracked surface, which can be observed at sample with synthesis temperature of 70°C as shown in Figure 6(c). This crack may be due to the formation of higher-density particles, which caused by collapse events in higher temperature. The higher temperature can increase the collision of particle and increase the diffusion rate according to the collision theory as reported in previous research (Jean *et al.,* 1986).

Figure 7 shows the optical properties of TiO_2 thin films at different synthesis temperature.

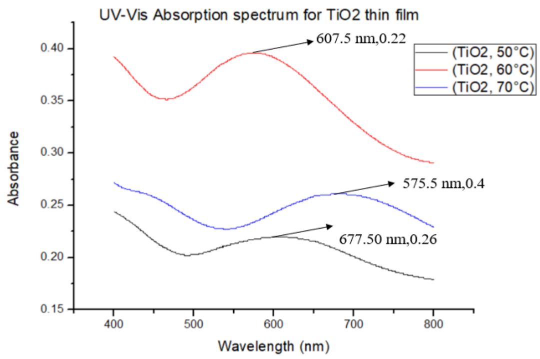


Figure 7. UV-Vis absorption spectrum of TiO_2 thin film at different synthesising temperatures.

The peak absorbance is clearly seen at a wavelength of 607.50 nm for 50°C while 60°C and 70°C have peak absorbance at wavelength at 575.50 nm and 677.50 nm, respectively. It also shows that the TiO_2 with a synthesis temperature of 60°C also exhibits the highest absorption peak of UV light, as shown in Figure 7. This result implies that the 60°C is the optimum synthesis temperature compared to others.

The Tauc method is based on the assumption that the energy-dependent absorption coefficient, α can be written as the following equation:

$$(\alpha h\nu)^{1/\gamma}=\beta(h\nu\text{-}E_g) \qquad (3)$$

where h, ν, E_g, β are Planck constant, photon's frequency, energy band gap and constant, respectively. The γ value is 1/2 or 2 for direct and indirect transition band gap, which depends on the nature of electronic transition (Pankove, 1971). Figure 8 shows $(\alpha h\nu)^2$ versus $h\nu$ for TiO_2 (an indirect band gap semiconductor) transformed according to equation (3).

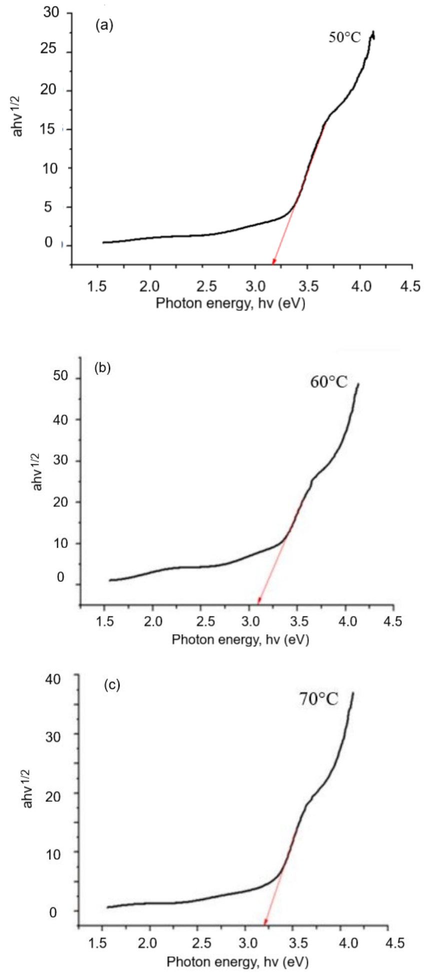


Figure 8. Tauc plot for band gap energy estimation of TiO_2 thin film at different synthesising temperature.

The band gap energy can be estimated by the intersection point of the linear fit of Tauc plot at x-axis as summarised in Table 1. TiO_2 synthesised at 60°C showed lower energy band gap. This result can be related to the crystal quality of TiO_2 formation at this synthesise temperature that may be due to the oxygen vacancy, oxygen interstial, and impurities that has been discussed in previous research (Vanheusden *et al.*, 1996).

To measure the efficiency of solar cell, the three samples of TiO_2 based DSSC prepared are then tested with the presence of light with an illumination of 100 mW/cm². Current density (J) versus applied voltage (V) graph is plotted as in Figure 9.

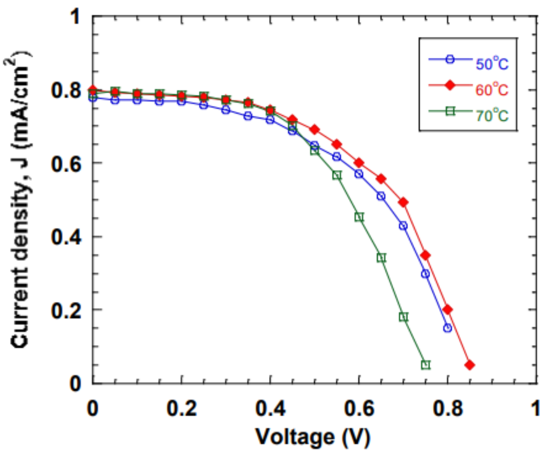


Figure 9. The photocurrent-voltage curve of DSSC with different synthesis temperatures.

From this graph, open voltage (V_{oc}), short circuit current (J_{sc}) and fill factor, FF, which are the main parameters for solar cell can be determined. The current through solar cell when the net voltage is zero is called short circuit current, while open circuit voltage is the voltage when the current through the circuit is zero. FF and the energy conversion efficiency, PCE can be calculated by using Equations (1) and (2) as similar to the previous study (Byranvand *et al.*, 2012).

Here, V_{oc} is open circuit voltage (V), J_{sc} is short circuit current (mA/cm²), and FF is fill factor and Pin (mW/cm²):

$$\mathrm{FF} = \frac{\mathrm{P_{max}}}{\mathrm{J_{sc}V_{oc}}} \qquad (1)$$

where V_{max} and I_{max} are voltage and current at the point of maximum power output of cell. The entire energy conversion efficiency, PCE, is calculated by means of the following equations:

$$PCE = \frac{\mathrm{J_{sc}V_{oc}FF}}{\mathrm{P_{in}}} \qquad (2)$$

Table 1. Solar performance parameters of DSSC with different synthesis temperatures.

Synthesis temperature (℃)	**Short circuit current, J_{sc} (mA/cm²)**	**Open circuit current, V_{oc} (V)**	**Energy band gap, E_g (eV)**	**Fill Factor (FF)**	**Energy Conversion Efficiency, PCE (%)**
50	0.78	0.82	3.3	0.44	0.28
60	0.8	0.85	3.1	0.50	0.34
70	0.8	0.75	3.4	0.49	0.29

The DSSC with 60°C of synthesis temperature exhibits higher solar efficiency than others. The fill factor degrades with lower and higher synthesis temperature of 50°C and 70°C. The highest power conversion efficiency, PCE of 0.34 % was achieved at the synthesis temperature of 60°C due to the high porosity of TiO_2 structure was formed at this temperature. The surface structure that is more porous are possible to provide wider surface area that can promote a deeper infiltration of the dye (Park *et al.,* 2010). Hence, higher surface area of TiO_2 thin film will be infiltrated by the dye sensitiser, which results in higher absorption of light.

IV. CONCLUSION

Dye-Sensitised Solar Cell (DSSC) based beetroot dyes was successfully studied with different synthesis temperatures of TiO_2. The structural, optical and electrical properties were affected by the synthesis temperatures. It can be concluded that 60°C was the optimum temperature to synthesise TiO_2 solution. At this temperature, a high porosity structure of TiO_2 film was formed that leads to more absorbance of light and improve the performance of DSSC. It was also observed the higher temperature of synthesis temperature leads to the crack of the TiO_2 structure. This is due to the increased of collision and diffusion rate of the particles. To improve the performance of DSSC, continuous optimisation of parameter through process modification should be taken into account.

V. ACKNOWLEDGEMENT

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