International Journal of Integrated Engineering, Vol. 10 No. 1 (2018) p. 109-113
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DOI: https://doi.org/10.30880/ijie.2018.10.01.017

TiO_2 Based Dye-Sensitized Solar Cell Prepared by Spray Pyrolysis Deposition (SPD) Technique

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Received 1 January 2018; accepted 1 March 2018, available online 30 April 2018

Abstract: Titanium dioxide (TiO_2) thin films have been produced on Fluorine-doped Tin Oxide (FTO) glass substrates by using the technique of spray pyrolysis deposition and annealed at different temperatures. The film was annealed for 3 hours for each thin film. The different temperatures used for annealing were 300℃, 400℃, and 500℃. This study showed that, when the temperature increased, the efficiency of the thin film also increased. The temperature annealing at 500℃ shown the highest efficiency with 3.3093% compared to others temperature. Morphological properties of TiO_2 DSSC thin film was examined by using FESEM and conversion efficiency by solar simulator . It is shown that the porosity of TiO_2 thin film and the I-V characteristic increased as the annealing temperature is increased. This results in more surface area of TiO_2 for dye adsorption which leads to an increase in efficiency.

Keywords: Titanium dioxide (TiO_2), Dye-sensitized Solar Cell (DSSC), Spray Pyrolysis Deposition (SPD), Solar Cell

Introduction

A dye-sensitized solar cell (DSSC) is another version of energy conversion device other than common solar cell which is silicon solar cell. DSSC can be made with lower cost because of its simple manufacturing techniques [1]. It also classified under the group of thin film solar cell and is made from non-toxic materials. The theory of using dye molecules to generate electricity came from a previous research study conducted by Gericher et al [2]. The part that contributes to the cell and for the general function of a DSSC is the metal oxide semiconductor thin film that act as a charge collector and also as a base for molecules to be adsorbed onto. The basic structure of DSSC consists of two conducting glass electrodes in a sandwich arrangement. These electrodes are transparent, which allows the light to pass through it [1].

In this experiment, titanium dioxide (TiO_2) is used as a part of the device. TiO_2 has been one of the most attractive materials in the experimental investigation during the last decades due to its scientific and technological importance [3]. The electrochemical photolysis, sterilization and sewage disposal are the typical applications of TiO_2 as catalysts. A recent interest is focused on an amphiphilic TiO_2 surface induced by ultraviolet irradiation, which is expected to be applicable to a windshield and a mirror for vehicle. In the field of alternative energy, a dye-sensitized solar cell is now a hot topic due to its high conversion efficiency produced with a porous TiO_2 electrode that is composed of several tens of nanometer-sized particles, which is also known as Titanium (IV) Oxide or Titania. It exists in a lot of different forms with

three most accessible forms being rutile, anatase and brookite. The crystal system for rutile and anatase is tetragonal. The other one of TiO_2 form which is brookite, the crystal form is orthorhombic. One of the application of TiO_2 is as a pigment in white paints, for brightness and high refractive index which is applicable for antireflective coating research, such as hydrophobic characteristic for self-cleaning application [4-5]. TiO_2 naturally has high transport mobility of the charge carrier that reduces the electro-transport resistance but its performance can be improved.

The method used in this experiment is spray pyrolysis deposition (SPD) which is a physical technique. The technique is one of the most promising ones, since the structure of the apparatus is quite simple and the technique is applicable to produce thin films on a large scale [3]. The technique is also known as pyrosol technique in which the solution was sprayed onto the substrate deposited as a film. In other words, when a source solution is atomized, small droplets splash and vaporize on the substrate and leave a dry precipitate in which thermal decomposition occurs [6].

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1. Experiment Details

A. Preparation of the TiO_2 films

The TiO_2 thin film had been prepared by spray pyrolysis deposition. Spray pyrolysis deposition (SPD) method involves spraying the solution onto substrate [7] placed over a heated surface where the solvent will evaporate to form a solid chemical compound. The compound used to produce a thin film by this method should be volatile at the temperature of deposition. In a previous study, the sample is heated at different temperature from 325°C upto 500°C [8]. SPD technique is one of the easiest and cost-effective method [7, 9] in the preparation of thin films with different thickness for ceramic coating and powder. This method usually does not require special type of substrates and its suitable for a wide range of material of the thin film. This method also can be used in producing porous film, multilayered [10] and also powder production [11].

The step of preparing TiO_2 solution started with P25 TiO_2 nanoparticle powder mixed with acetic acid. The mixture was grounded until completely dissolved. Then, TKC-303 solution was poured into the mortar and stirred into the mixture. After that, the solution transferred into a lightproof bottle. Ethanol along with Triton X-100 were added to fully separate the nanoparticle and to increase the TiO_2 thin film conduction. After that, the bottle was lidded with parafilm and put into an ultrasonicator to obtain a homogenous solution.

The TiO_2 solution were sprayed on top of the FTO substrates, using a regular spray. The substrate is arranged on the hot plate set at 150°C is illustrate like in Fig.1. The TiO_2 solution was poured into the container then attach to airbrush. The brush was held about 10-20cm above the substrates to spray. The spraying was done by making a left and right motion until all of the solution was deposited onto substrates.

After the spraying process was done, the TiO_2 films that had been fabricated were put in the furnace for annealing process. The temperature was set at 300°C, 400°C and 500°C. The period for annealing is 3 hours. Then, the samples were taken out from the furnace and let to cool down to room temperature before dipped into the dye.

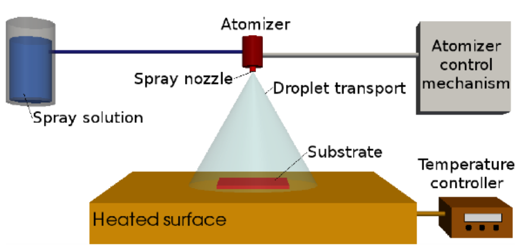


Fig. 1 Spray pyrolysis deposition technique

B. Preparation of the solar cells

In the DSSC, dye molecules act as photosensitizers that will absorb light energy and excite electrons into the conduction band of TiO_2 and produce electrical energy. The best dye with a wide range absorbance commonly used in researches is the N719 dye. N719 is a dye with improved solar conversion efficiency. TiO_2 films were immersed overnight in the N719 dye fabricated. The N719 powder (Ruthenizer 535-bis TBA) was a product of Solaronix. The dye solution was made by mixing 0.0178g of N719 with 25 ml of acetonitrile and 25 ml of 1-butanol. Then, the mixture was stored at low temperature. It is to prevent evaporation that will cause changes in molarity.

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, 10ml of butyl pyridine (TBP), 10 ml of Iodolyte AN 50, 1.597 g DMPII and 0.01 g guanidine thiocyanate (GT).

The DSSC is assembled for characterization using the Solar Simulator. After the TiO_2 thin films were left overnight in dye, the sample was dipped into ethanol to remove the excess dye before clamped with Platinum counter electrode together in a sandwich structure. A drop of the electrolyte was injected between the electrodes.

C. Characterization

The surface morphology of the as-prepared surface was analyzed using a field-emission scanning electron microscope (FE-SEM, JEOL, model JSM-7600F). The Raman spectral analysis of the samples was carried out using a (Raman Spectroscopy machine model XploRA PLUS). Electrical properties and efficiency were measured by Solar Simulator and 2-point probe.

2. Result and Discussion

A. Morphological Properties of TiO_2 thin films

The surface morphology of TiO_2 thin films was taken by Field Emission Scanning Electron Microscopy (FESEM). Fig. 2 shows the magnification with different annealing temperatures. The magnification at 50k showed that, when the annealing temperature increases, the grain size becomes larger. The film also seems rougher and more uneven with the increasing temperature. For the particle structure, the particles seem to merge with each other as annealing temperature rises. The higher the temperature, the more agglomerated are the particles. Furthermore, comparing all the figures the porosity of thin film seems to be increased. The porosity obtain from 500 °C temperature is the highest than other temperature. The average size of particles for all film is 25 nm, it is because of the use of Titanium Dioxide P25. Due to the small size of the resulting TiO_2 particle, TiO_2 film surface area would be bigger [12]. This will give an advantage and improved the efficiency of the conversion since more dye molecules can be adsorbed onto the TiO_2 particles.

For the as deposited sample, the particle from the sample is dense. The gap between particles is closes. It is because when in as deposited stage, the porosity of the element is low. For the 300°C and 400°C of the annealed temperature, the gap between particles become larger. It is because the porosity increased

[13]. It also can be seen in Fig. 2 D that showed sample that annealed at 500°C temperature. The gap between the particles is larger than 300°C and 400°C. When the gap is larger, it means that the porosity of the sample is greater than 300°C and 400°C sample. From this observation, it can be concluded that, the porosity of TiO_2 thin films increased when the annealed temperature is increased.

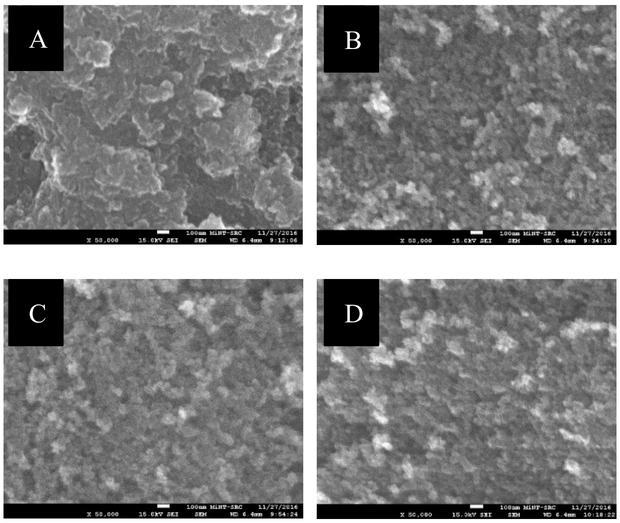


Fig. 2 FESEM image of TiO_2 thin films with diameter at 50k magnification. a) as-deposited, b) annealed at 300°C temperature, c) annealed at 400°C temperature, d) annealed at 500°C temperature

B. Electrical properties and Efficiency

From the data shown in Table 1 and Fig. 3, the data of voltage shows that the sample of solar cell achieved the optimum voltage for DSSC. 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 (V) [14] [15]. That is, if an illuminated DSSC is connected to a voltmeter in an "open circuit", it would read about 0.7 V. In terms of voltage, DSSCs offer slightly higher voltage than silicon, about 0.7 V compared to 0.6 V. It also shows that the higher the temperature of anneal, the efficiency of DSSC will increase. The efficiency can be calculated by using equation (1).

$$\text{Efficiency, } \eta = \frac{P_{out}}{P_{in}} \times 100 = \frac{J_{sc} V FF}{I_{sc}} \times 100 \qquad (1)$$

The I-V graph and the efficiency of the films indicate that the films annealed at higher temperature provides higher current and better efficiency. From the data, the Isc for the as deposited was around 1.0 mA/cm^2. It is because, during the as deposited stage, the element is amorphous. Amorphous phase happens at the temperature below 300^o [13]. When in the amorphous state, the electron in the TiO_2 cannot move freely because the element is still well dispersed. So, the resistance will increase, thus the Isc is low. Compared to the samples annealed at 300°C, 400°C and 500°C the Isc is around 4.0 mA/cm^2 range. As the annealing temperature increased from 300°C to 500°C, the Isc also increased. The increasing of Isc occurs when the electron can move freely in the element with low resistance. When the temperature is increased, the surface area also increased thus the dye absorption increased resulting in more photoelectron and current flow. Therefore, the Isc is increased since the dye is covered the area of porous.

Table 1 I-V measurement of DSSC with TiO_2 samples annealed at different temperatures

Sample	Voltage (V)	Isc (mA/cm^2)	Fill factor	Efficiency (%)
As deposited	0.7679	1.4130	54.9	0.6939
300°C	0.7937	4.4296	70.1	2.8696
400°C	0.8012	4.9153	70.4	2.9380
500°C	0.8048	4.9226	71.8	3.3093

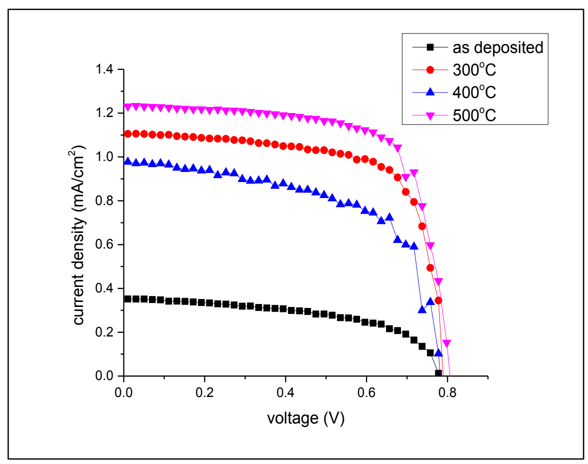
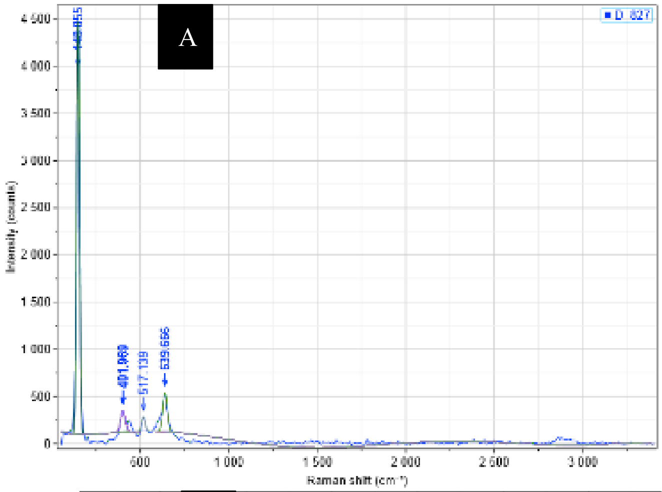


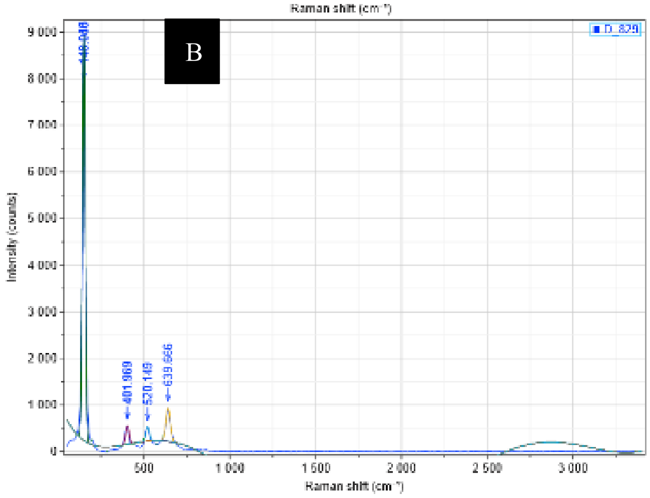
Fig. 3 voltage versus current density

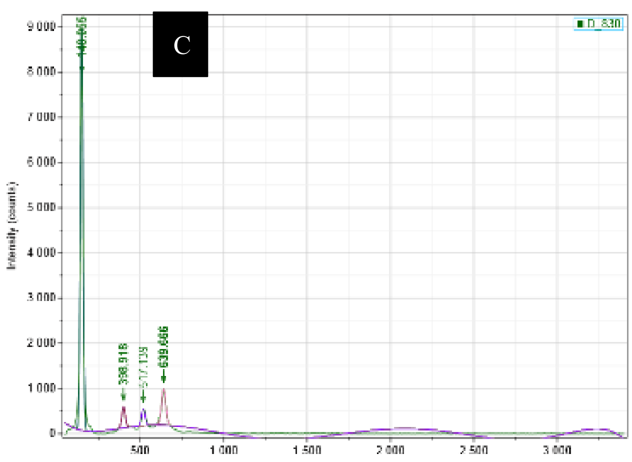
C. Anatase properties of TiO_2 nanostructured

By using Raman spectroscopy, the crystal structure of TiO2 can be determined, where the polymorphism of TiO_2 were analyzed. The peak shown in Fig. 4 proved the evident of TiO_2 crystalline structure deposited on FTO. Fig. 4(a), (b), (c) and (d) show the result of samples as-deposited, and annealed at 300°C, 400°C and 500°C.

From the Raman spectra, the peak of the anatase phase became well defined after annealing. The anatase structure is tetragonal. The appearance of film crystallization was assumed to be induced by annealing temperature. From this result, Raman Spectroscopy shows the TiO_2 nanoparticles at the surface of thin film has a strong peak of anatase for the intensity with shifting at $148cm^{-1}$ for all spectra. According to reference of wavenumber of TiO_2 [16], it can be conclude that anatase TiO_2 thin film is successfully deposited on the surface of FTO.







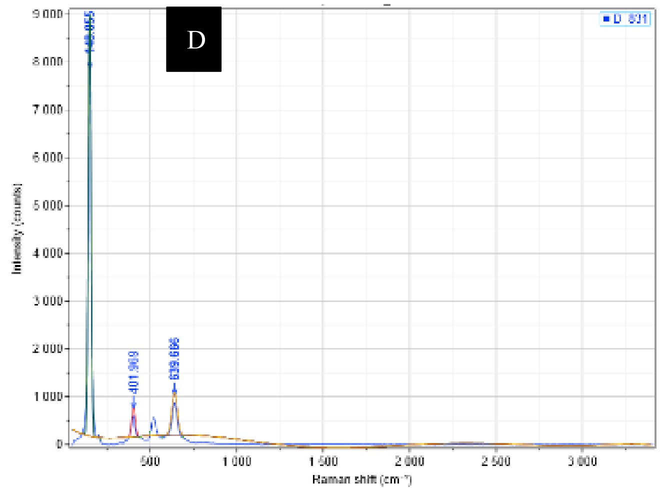


Fig. 4 Raman Spectra of TiO_2 thin films (a) As-deposited 0℃, (b) 300℃ annealing temperature, (c) 400℃ annealing temperature and (d) 500℃ annealing temperature.

3. Conclusion

This project is conducted to show that, the annealing of TiO_2 film can increase its efficiency in a DSSC. In this research, the TiO_2 thin film shows better result after annealing. With the increase in temperature during annealing process, the films will become more porous as shown in the FESEM images. The porosity of the film contributed to the conversion efficiency, as can be seen in the data from the Solar Simulator.

Spray pyrolysis deposition method has been selected to produce TiO_2 thin film. By annealing with different temperature, the 500℃ is found to be the best temperature for annealing TiO_2 thin film, based on the electrical properties and surface morphology result. For the spraying technique, it will be altered to achieve film with better structure and porosity.

For the electrical properties and efficiency, it can be concluded that when the annealing temperature is increased, the result for voltage and current also increased due to dye molecules adsorbed on the TiO_2 particles. It is affected by resistivity that decrease when the film is annealed at high temperature. So, to conclude when the annealing temperature is higher, the efficiency is also increased.

This research is expected to produce high efficiency TiO_2 thin films using low cost and environmental friendly materials and method. For the conclusion, the study concluded that an increase in temperature will increase the efficiency of TiO_2 thin film in DSSC. It also proves that the fabrication of TiO_2 thin films by spray pyrolysis deposition method is successful.

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