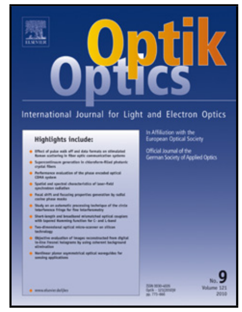

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Dye-sensitized Solar Cell using Pure Anatase TiO_2 Annealed at Different Temperatures

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Abstract

The performance of pure anatase titanium dioxide (TiO_2) annealed at different temperatures as photoanode in the application of dye-sensitized solar cell (DSSC) was investigated and discussed. All samples of TiO_2 were deposited on fluorine-doped tin oxide (SnO_2) on glass substrate using spray pyrolysis deposition (SPD) method. Characterizations of the DSSCs fabricated were executed on their surface morphology, structural property, and energy conversion efficiency. In the DSSC preparation, anatase TiO_2 thin films, platinum (Pt), ruthenium-based dye N719 and DPMII triiodide couple electrolyte were used as photoanodes, cathode/counter electrode, dye sensitizers and liquid electrolyte, respectively. All of the TiO_2 photoanodes were annealed at 300ºC, 400ºC and 500ºC with a set left without any heat treatment. The thickness of anatase TiO_2 photoanodes measured were in between 23µm and 41µm. The power conversion efficiency of DSSCs performed under visible light with intensity of 100 mW/cm^2 shows that DSSC with pure anatase phased TiO_2 annealed at 500ºC as photoanode yields the highest efficiency of 3.25%.

Keywords: DSSC, Titanium Dioxide, SPD method, Anatase

1. Introduction

Titanium dioxide (TiO_2) exists in nature as an oxide of titanium and is fairly abundant. It occurs in a lot of phases and forms with the three most common being rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic) [1]. For macroscopic crystals, rutile is said to be more thermodynamically stable form of TiO_2 if compared to anatase [2]. But for nanocrystals about 10-20nm in size, anatase is found to be more stable form. This condition regarding their sizes is similar to a research conducted to relate diamonds and graphite [3]. Since rutile is generally the most stable phase of TiO_2, it is not suitable for the application of DSSC due to the dye not being able to attach properly on the surface of the structure [4]. Nanostructured rutile has better optical and electrical properties but the amount of researches on rutile as a DSSC photoanode is not plenty [5, 6]. Anatase is also said to be the better option for DSSC as it provides higher surface area due to its crystallographic orientation other than lower recombination rate than rutile for its higher indirect band gap [4, 7]. However, it is said that anatase and rutile might have a synergy up to a certain ratio to produce a better working photoanode [8].

Annealing of TiO_2 thin films can improve their surface morphology and crystallinity which can heavily influence the electron transport rate and effective surface area [9]. Annealing process evaporates the solvent used in the preparation of the thin film, resulting in purer and more crystalline structure aside from creating porous structure into the films. The annealing process may affect the thickness of the film but not necessarily as reported in a previous research. Instead of thinning the film, annealing process changes the structure of the film from amorphous to a more porous and crystalline structure [10]. It was also reported that annealing of the films makes the grain size becomes larger, lowers the transmittance of the film, increase the value of refractive index and allowed indirect optical band gap [11, 12]. Other than that, annealing process was also reported to make the surface rougher as the temperature increase [9].

In this research paper, we discuss the optimum annealing temperature for anatase TiO_2 thin film. A lot of researches came to an optimum temperature of 450ºC for annealing. We also investigated the reasons why a higher annealing temperature might be the better option as a treatment to photoanodes in DSSC.

2. Experimental

2.1. Preparation of anatase phased TiO_2 solution

The preparation of anatase phased TiO_2 solution starts with mixing 0.3g of Sigma-Aldrich TiO_2 anatase powder with 5.5ml of acetic acid in a mortar. The mixture is grinded with the pestle until thoroughly combined. This process takes about 5 to 7 minutes. Then, 20ml of diluted TKC-303 solution ($5 \geq pH \leq 6$) is poured and stirred into the mixture. The solution is then transferred into a lightproof bottle. An organic solvent was needed to dilute the solution and thus, 30ml of ethanol was added into the solution along with 5 drops of Triton X-100 to fully disperse the nanoparticles and as a stabilizer to increase the TiO_2 thin film conduction. The bottle is lidded and put into the ultrasonicator for 30 minutes with the heat off to obtain a homogeneous solution.

2.2. Deposition of TiO_2 thin films

Fluorine-doped SnO_2 (FTO) coated glass was used as a substrate with dimension of 10mm x 25mm and FTO thickness of 0.5µm. The substrates are cleaned by sonicating method in acetone, ethanol and deionized water with volume ratio of 1:1:1 for 10 mins and later dried in air. The deposition of the TiO_2 thin films is by spray pyrolysis deposition (SPD) technique. A regular air compressor airbrush is used to spray the TiO_2 solution onto the FTO substrates. The substrates are placed on a hotplate with the temperature set at 150ºC. Once the substrate temperature reached 150ºC, the TiO_2 solution is poured into the airbrush. The brush is held so that the nozzle is about 10cm vertically above the substrates. The spraying of the TiO_2 solution is done using the left to right motion until all of the solution is deposited. The heat is turned off and the samples are immediately annealed. In order to study the effect of annealing temperature, the prepared nanostructured films were annealed at 300ºC, 400ºC and 500ºC. A set of samples are also left as deposited.

2.3. Characterization

Surface morphology of the prepared TiO_2 films were analyzed by using field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7600F) at an accelerating voltage of 20 kV. X-ray diffraction (XRD) was performed by using PANalytical X'Pert^3 Powder with Cu Kα radiation (λ= 1.5418 Å). The XRD profiles were measured at a 2º/min scanning speed in the 2θ range from 20º to 60º to determine the crystal phases and crystallinity of TiO_2 films. The efficiency of the solar cells fabricated is determined from the photocurrent versus voltage (I–V) characteristics measured by using solar simulator under 1.5 AM (ORIEL Sol1A). For the aforementioned efficiency study, the prepared TiO_2 photoanode with working area of 0.25 cm^2 was immersed in 0.3 mM of N719 dye for about 24 h at room temperature. The platinum, Pt counter electrode was prepared by sputtering method. In order to assemble the DSSC, the electrolyte prepared from 1.59 g of 1,2-dimethyl-3-propylimidazolium iodide, 10 ml of iodolyte AN 50, 10 ml of 4-tert-butylpyridine, 0.01 g of guanidine thio-cyanate and 5 ml of valeronitrile was inserted between the two electrodes before clamped for the solar cell measurement.

3. Results and discussion

3.1. FESEM characterization of anatase phased TiO_2 nanoparticles

The annealing temperature used to anneal the samples can affect the porosity and roughness of the TiO_2 samples. Fig. 3(a)-(d) shows FESEM images of anatase TiO_2 films on FTO as deposited and with annealing temperatures of 300ºC, 400ºC and 500ºC respectively. The as deposited film shown in Fig. 3(a) seems to not have particle shape as the particles seem to have coalesced due to the high amount of solvent in the film. There are almost no gaps between particles and the film appears to be compact and not porous. The gaps between particles increased as annealing temperature increased; creating porous structure into the films as seen in Fig. 3(b)-(d). The particle shape can be clearly seen after the process of annealing as the heat evaporates the solvent in the films and leaves pores in the films. The surface also seems rougher and more uneven. This uneven surface of the films may be an advantage for its application in DSSCs as the incident light can be scattered to increase the absorbed photon by the dye molecules [14]. The particles in the films annealed at 300ºC to 500ºC have the diameters of 24nm-35nm. The process of annealing also made the films thinner from the solvent evaporation [15]. The as deposited films have thickness of 38µm-41µm. The annealed films have thickness of 23µm-38µm with the film annealed at 500ºC being the thinnest as documented in Table 1.

3.2. XRD characterization of anatase phased and mixed-phased TiO_2 nanoparticles

The XRD profiles of the anatase TiO_2 films as deposited and annealed at different temperatures; 300ºC, 400ºC and 500ºC are shown in Fig. 4. From the figure, it was found that all the films are of polycrystalline anatase type tetragonal symmetry (PDF No. 98-015-4604). The diffraction peaks at 25.3º, 37.7º, 48.1º, 53.9º and 55.1º are found to correspond to the (101), (004), (200), (105) and (211) anatase planes. No rutile peaks were detected due to the purity of the TiO_2 anatase film fabricated. The intensity of peak (101) for all the samples was noted to have slightly increased as the annealing temperature increased. The spectra also indicate that the films are all well crystallized regardless of the annealing temperature since the commercialized anatase powder used is already crystalline. This characterization proves that the films are all of pure anatase as the minimum temperature for the transition of anatase to rutile is between 700ºC-900ºC [16].

3.3. Efficiency of anatase phased and mixed-phased TiO_2 as photoanode in DSSC

The efficiency of the TiO_2 films is determined from the photocurrent-voltage characteristics shown in Fig. 5 under a simulated sunlight at 100 mW/cm^2. The details of the performances of the DSSCs are as summarized in Table 1 for pure anatase phased photoanode. The current density (Jsc) of the anatase photoanode increased with the annealing temperature along with the conversion efficiency (η). The highest conversion efficiency of 3.25% was given by the sample annealed at 500ºC.

An increase in the current density is the main cause for the increasing efficiency. The current generated is determined by the amount of photoelectrons from the dye molecules. Higher amount of dye molecules naturally will generate more photoelectrons. The amount of dye molecules adsorbed onto the TiO_2 can easily be influenced by the surface area and the surface morphology of the TiO_2 samples. From the increased porosity seen from the FESEM images, it can be said that the amount of dye molecules adsorbed also have increased [17]. The annealing process can also eliminate the contaminants that may have deposited onto the films, thus improving the overall adsorption process.

The Fill Factor (FF) value of the samples are calculated using formula (1):

$$FF = \frac{Vmax\ X\ Imax}{Voc\ .\ Isc} \tag{1}$$

The main factor that can influence the value of FF is related to the series resistance, R_S within the cell. This resistance may be affected by the poor electron mobility in FTO, large distance between TiO_2 film and Pt electrode which can be caused by thick layer of electrolyte, and an incompetent Pt electrode [18]. Fill Factor value is also directly influenced by the recombination rate of the photoelectrons [19]. As shown in Table 1, the value of FF increased as the annealing temperature increased which indicated lower resistance and recombination with increasing annealing temperature. Thicker photoanode will increase the chances of recombination and as can be seen in Table 1, the thickness of the films decreased as the annealing temperature increased which explains the increase of Jsc value.

4. Conclusion

We have successfully fabricated pure anatase TiO_2 photoanode for dye-sensitized solar cell. All samples are deposited on top of FTO glass and annealed at different temperatures; 300ºC, 400ºC and 500ºC. The performance of each samples for both types of TiO_2 are summarized in Table 1. The current density (Jsc) and conversion efficiency for anatase TiO_2 photoanodes increased as the annealing temperature increased with the highest values achieved by sample annealed at 500ºC. Higher annealing temperature created a more porous surface and thinner film thus creating higher surface area for dye attachment and lower recombination rate.

Acknowledgements

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Figure captions

Figure 1. Schematic diagram of dye-sensitized solar cell with TiO2 photoanode deposited on FTO [13].

Figure 2. A schematic diagram of spray pyrolysis deposition (SPD) method.

Figure 3. FESEM images of fabricated pure anatase TiO_2 (a) as deposited, annealed at (b) 300ºC, (c) 400ºC and (d) 500ºC

Figure 4. XRD spectra of pure anatase TiO_2 as deposited, annealed at 300ºC, 400ºC and 500ºC.

Figure 5. I-V measurements of pure anatase TiO_2 as deposited, annealed at 300ºC, 400ºC and 500ºC.

Figure 1

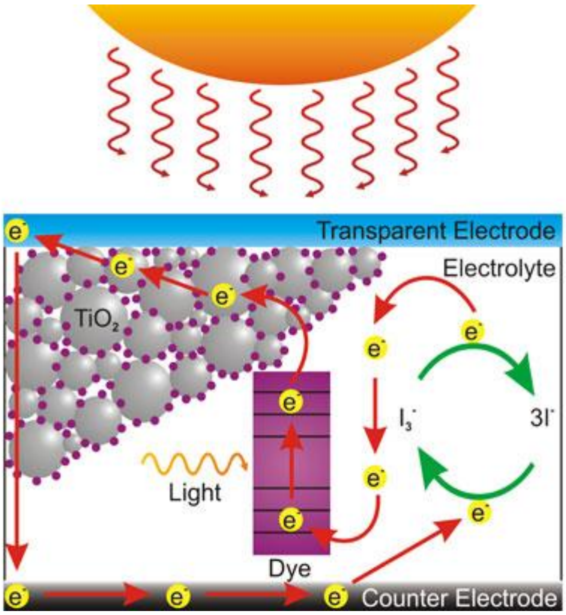
Transparent Electrode
Electrolyte
TiO2
e-
I3-
3I-
Light
Dye
Counter Electrode

Figure 2

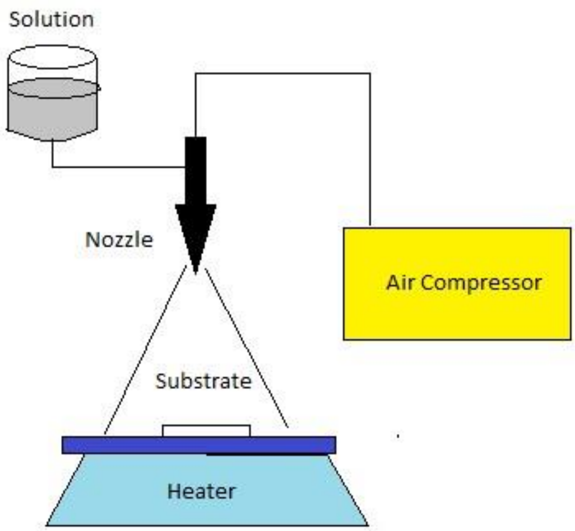

Figure 3

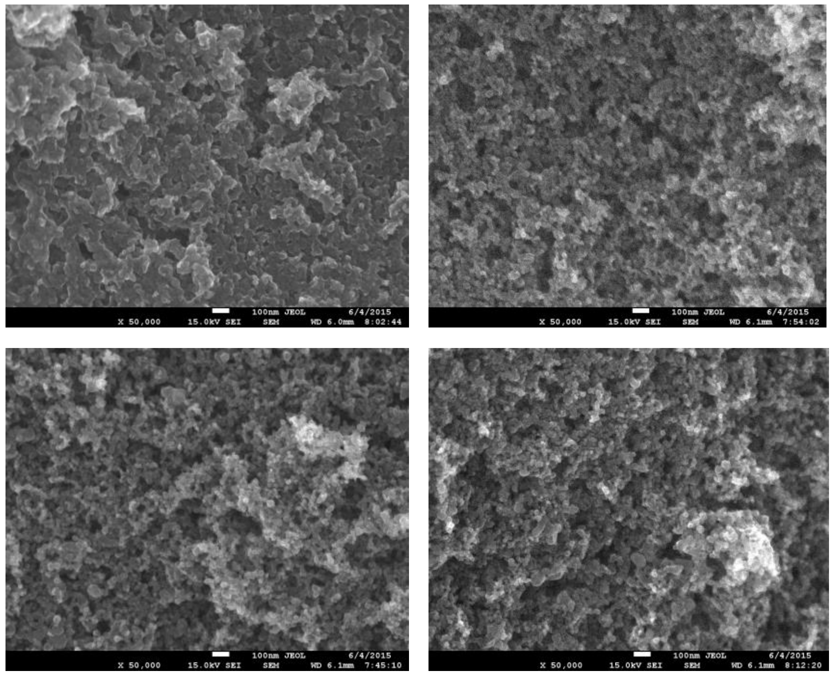
100nm JEOL 6/4/2015
X 50,000 15.0kV SEI SEM WD 6.0mm 8:02:44
100nm JEOL 6/4/2015
X 50,000 15.0kV SEI SEM WD 6.1mm 7:54:02
100nm JEOL 6/4/2015
X 50,000 15.0kV SEI SEM WD 6.1mm 7:45:10
100nm JEOL 6/4/2015
X 50,000 15.0kV SEI SEM WD 6.1mm 8:12:20

Figure 4

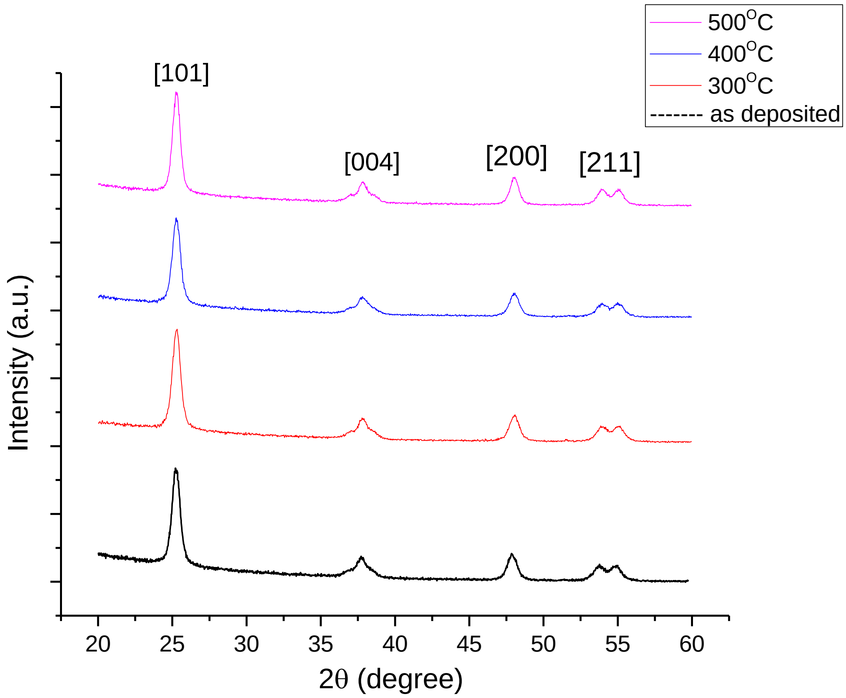
500^{O}C
400^{O}C
300^{O}C
as deposited
[101]
[004]
[200]
[211]
Intensity (a.u.)
20
25
30
35
40
45
50
55
60
2θ (degree)

Figure 5

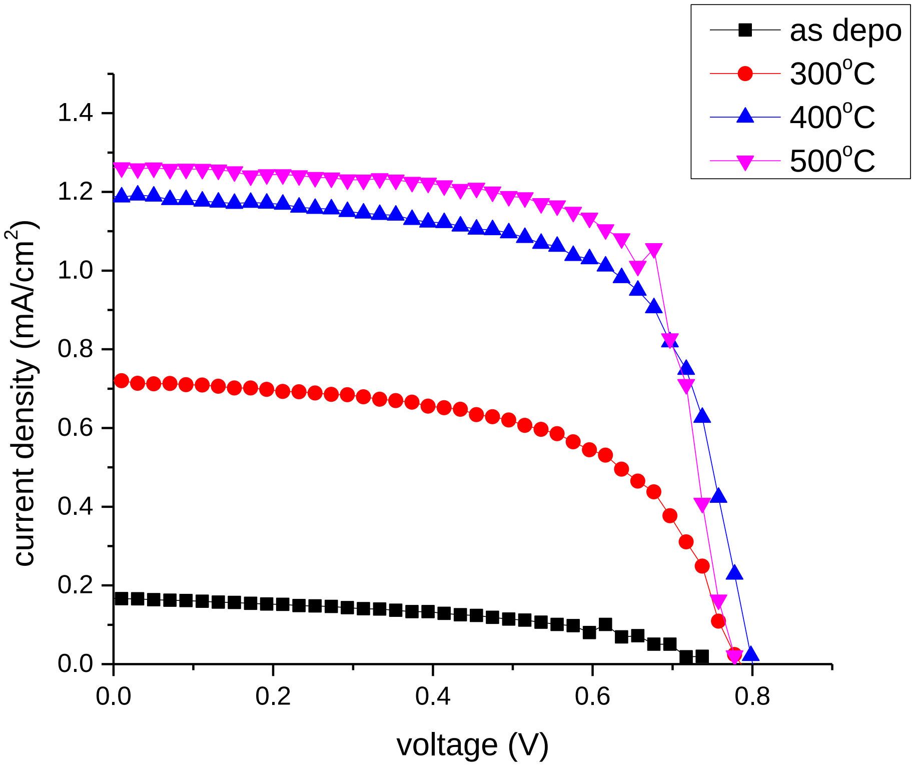
as depo
300°C
400°C
500°C
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
current density (mA/cm2)
0.0
0.2
0.4
0.6
0.8
voltage (V)

Table 1
I-V measurements of DSSC using pure anatase TiO_2 photoanode annealed at different temperature.

Sample	Voc (V)	Jsc (mA/cm2)	Fill Factor	Thickness (µm)	Efficiency, η (%)
As deposited	0.7374	0.6689	0.5120	40.589	0.2870
300ºC	0.7718	2.8809	0.5885	37.115	1.4870
400ºC	0.7929	4.7544	0.6665	28.745	2.8553
500ºC	0.7793	5.0468	0.7269	23.514	3.2488