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Performance of post-hidrothermally treated xerogel TiO_2 dye-sensitized solar cell (DSSC) and its nanostructure characteristic

B Priyono[1*], A H Yuwono[1], A Z Syahrial[1], M H Mustofa[1], R S Bawono[1]

[1] Department of Metallurgical and Materials Engineering, University of Indonesia, Depok, 16425, Indonesia

bambang.priyono@ui.ac.id

Abstract. Dye-sensitized solar cell (DSSC) is one of photovoltaic solar cells, which is very favorable as alternative renewable energy source to anticipate the diminishing the fossil fuel due to its low-cost, ease of production and eco-friendliness. This work is aimed to investigate the correlation between TiO_2 nanostructure properties i.e.: crystallite size, surface area, band gap energy to obtain the optimum parameter for best performance as DSSC prototype. At this study, TiO_2 nanoparticles were synthesized via sol-gel process using titanium tetra-n-butoxide, ethanol, hydrochloric acid and deionized water with the ratio of (0.4 : 0.83 : 1 and 1.39) respectively upon sol preparation. The followed with multi-step calcinations to obtain anatase phase and post-hydrothermal process with various temperatures (100, 120, and 150 ˚C). As comparison, TiO_2 of P25 Degussa was used and also assembled to make DSSC. The X-ray diffraction, BET (Brunauer-Emmett-Teller) and UV-Vis DRS (diffuse reflectance spectroscopy) tests were taken to characterize the samples. The performance of DSSC was investigated using open voltage circuit (Voc) measurement. The characterization results of synthesis powder shows indication at temperature 150ºC was optimum process of post-hydrothermal with crystallite size 10.55 nm, surface area 95.38 m^2/grams, and band gap energy 3.16 eV. Nevertheless, the open circuit voltage (V_{OC}) measurement reveals that the DSSC fabricated with post-hydrothermal at temperature process 120˚C provide the highest voltage (250 mV).

1. Introduction

To overcome the polution problem and world energy crisis, the usage of solar energy would be inevitable due to its cleanliness and abundance resources. Dye-sensitized solar cell (DSSC) is one of the solar cell types which gain more attention today due to economic cost, high photon conversion efficiency and good stability [1]. Many development has been achieved to improve the DSSC performance [2]. One important approach is focussed on the photo-anode field. The DSSC performance improvement in this field relates to base material which is influenced by the structure of oxide layer having characteristic of the high surface area to absorb sensitizing dyes to maximize the performance required. One of semiconductor layer most commonly used in DSSCs is TiO_2 [3]. Many methods have been developed to make the DSSC components, i.e.: photoanodic oxide. Sol-gel method is one of most useful techniques that provide nanoparticles with high purity of precursor, high surface

area, larger pore volume and uniform pore-size distribution. In our previous study [4], it has been learned how to synthesize nanoparticle with sol-gel method followed with multi-step calcinations and post-hydrothermal treatment to obtain high crystallinity and well-ordered Ti-O-Ti network. Beside, one important component of dye-sensitized solar cell (DSSC) is the photo-anode, which consists of a monolayer of highly porous semiconductor oxide layer. This study was carried out to develop a preparation technique that should increase the nanostructure properties to be integrated in the DSSC prototype. The method made use of xerogel combined with multi-step calcination followed by post-hydrothermal process as an effort to improve the crystallinity all of samples while maintaining minimum loss in the surface area [5]. The results of post-hydrothermally treated samples would be compared to P-25 Degussa.

The objective of the present study is to investigate the correlation between TiO_2 nanostructure properties such as: crystallite size, surface area, band gap energy, and their performance as a semiconductor material in the DSSC prototype. Hydrothermal process is employed to obtain high temperature and pressure for nucleation and crystallization of nanoparticles. This method is favorable for the formation of a better TiO_2 nano-particles crystallization [6]. On the other hand, super critical extraction technique (SCE) involves CO_2 as the extraction solvent has the potential to augment the surface area of nanoparticles but has a low degree of crystallinity.

This article describes the effects of temperature parameters on the properties of TiO_2 powder prepared by sol-gel method and post-hydrothermal method is used to control the properties and the reaction efficiency of TiO_2 nanoparticles, which are used in dye sensitized solar cells and performance of these cells.

2. Experimental method

TiO_2 sol was prepared by hydrolysis of titanium tetra-n-butoxide (Kanto Chemical, JPN) that was previously mixed with hydrochloric acid in ethanol solution under vigorous stirring and the water was added drop-wise to the precursor until the appropriate ratio was obtained. The molar ratio of Ti-but, ethanol, hydrochloric acid and deionized water were determined as (0.4 : 0.83 : 1 and 1.39), respectively. The mixture was stirred for 3 hours to stabilize the solution, and then sealed in a container for 1-2 days at room temperature. TiO_2 P-25 Degussa nanoparticles powder was obtained using P-25 Degussa Merck™. Next, the gel was processed using a multi-step calcination method in a tube furnace. The multi-steps was carried out at two different conditions, i.e. the first and second temperature were carried out under vacuum condition, while the third one was performed by injecting air for regaining the white powder of the TiO_2 nanoparticle. The first step was conducted at 150 ˚C in which the solvent would evaporate, whereas the second step was carried out at 300 ˚C in order to remove the entire remaining organics compound, and subsequently the final step was carried out at 420 ˚C under an air-injection condition. After calcination process the gel was prepared to undergo a post-hydrothermal treatment in a Teflon-lined stainless steel autoclave which is equipped with a special stand-holder for sample, sealed and placed in an oven at 100˚, 120˚ and 150 ˚C for 14 hours. Afterwards, it was dried at 70 ˚C for 24 hours.

Post-hydrothermal samples and P-25 Degussa samples were characterized by XRD method to identify the phase of TiO_2 anatase and to determine the crystallite size via Scherrer's equation analysis. The BET (Brunauer-Emmet-Teller) testing was used to determine the surface area, and UV-Vis with Diffuse Reflectance Spectroscopy (DRS) method is used to determine the band-gap energy calculated via Kubelka-Munk function that transformed to Tauc's equation analysis. After characterization, both samples were prepared to be assembled as DSSC. The performance of dye-sensitized solar cell (DSSC) assembled from the nanoparticles resulted from both of methods tested through the measurement of open circuit voltage (V_{oc}), taken under the light beam source of an overhead projector.

3. Results and discussion

In order to improve the crystallinity of sol-gel, the multi-step calcinations were conducted. After that, samples were post-hydrothermally treated to increase the order of Ti-O-Ti bond. It was confirmed that all of samples which post-hydrothermally treated shows anatase phase. For P-25 Degussa, it shows combination of anatase and rutile phases because of higher manufacturing process above 600 ^{0}C [7].

The XRD patterns of samples of P25 Degussa sample and post-hydrothermal treatment at 100 ˚C, 120 ˚C, and 150 ˚C were shown in the Figure 1.

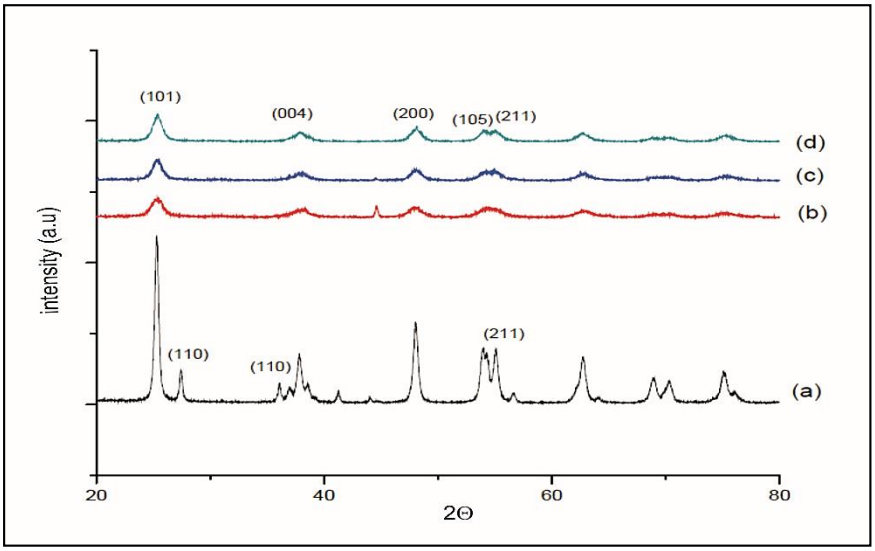

Figure 1. XRD Pattern of (a) P-25 Degussa and Post-hydrothermally treated at temperature, (b) 100 ^{0}C, (c) 120 ^{0}C, (d) 150 ^{0}C.

In Figures 1 (b), (c) and (d), are shown the XRD patterns of as-prepared TiO_2 powders post-hydrothermally treated at different temperatures (100 °C, 120 °C and 150 °C). The as-prepared sample show reflection peaks at 2θ of 25.65°, 37.60°, 38.95°, 48.37°, 54.23°, 55.60°, 63.20°, 68.99°, 70.78° and 75.37°, which are assigned to (101), (004), (112), (200), (105), (211), (204), (116), (220) and (215) lattice planes of anatase TiO2 phase (JCPDS Card no. 21-1272). The well-formed peak shows clearly that the anatase phase was successfully formed by multi-step calcinations process at 150, 300, and 420°C respectively.

Meanwhile, ss comparison, in Figure 1 (a), the P25 Degussa has additional peaks at 27.5°, 36.04°, 41.18°, 44.14°, 61.79°, 68.99°, 70.17° and 76.80° which are assigned to the (110), (101), (111), (210), (002), (301), (112) and (202) lattice planes of rutile phase (JCPDS Card no. 21-1276). The peak intensities of the anatase phase do not diminish even with the appearance of the rutile phase.

Based on those peaks, the broadening on each of peak was measured and furthermore was used to estimate the crystallite size of TiO2 nanoparticles by using the Scherrer equation by measuring the widening of the peak, that is the full width at half of the maximum intensity (FWHM). The results are summarized in Figure 2.

As the temperature of post hydrothermal treatment increases, the crystallite size of the respective samples also increased. The calculated crystallite size shows that the largest size was possessed by the 150°C post-hydrothermally treated sample, i.e. 10.55 nm with a surface area of 95.38 m^2/g. The second largest one is the 120 °C post-hydrothermally treated sample with a value of 8.85 nm, accompanied with a surface area of 92.25 m^2/g. Finally the last sample is a 100 °C post-hydrothermally treated sample, i.e. 5.49 nm, but the surface area was only 117.96 m^2/g. This result is possibly caused as a consequence of an attempt to suppress the fast development of stiff Ti-OH by pre-hydrothermal treatment which led to a largely amorphous particle [8]. The highest crystallite size was obtained by post-hydrothermally treated sample at 150 ^{o}C. Enhancement in

crystalline size refers to hydrothermal growth at higher temperature [7]. However, P-25 Degussa samples still has higher crystallite size due to high crystallinity compared to post-hydrothermal samples. The crystallite size of 7.29 nm was obtained by calculation for the noncalcinated TiO_2 powder. The XRD patterns of TiO_2 nano-powders calcinated at different temperatures show that the anatase phase was detected for the calcinated samples till a calcinated temperature below 500 ºC.

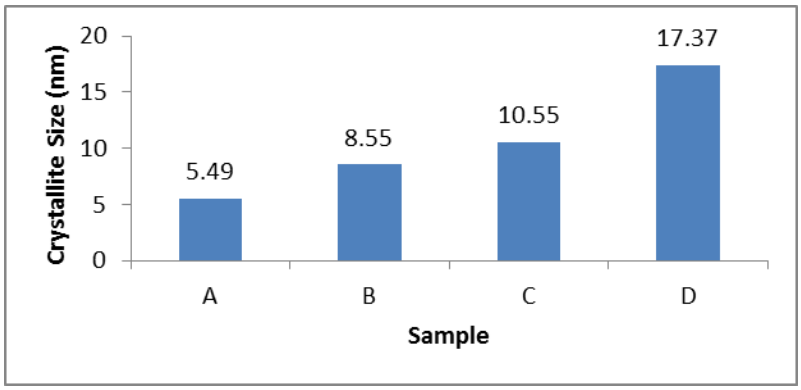

Figure 2. Crystallite Size estimation of TiO_2 nanoparticles Post-hydrothermally treated at temperature of 100 ^{0}C, (b) 120 ^{0}C, (c) 150 ^{0}C and (d) P-25 Degussa.

The result of BET testing is depicted in Figure 3. Based on BET testing, it could be established how extensive the size of the surface area is, which is obtained via those processes. One also would then understand how effective the multi-step calcinations process is, to minimize the drop of surface area while gaining the crystallinity of the nanoparticles.

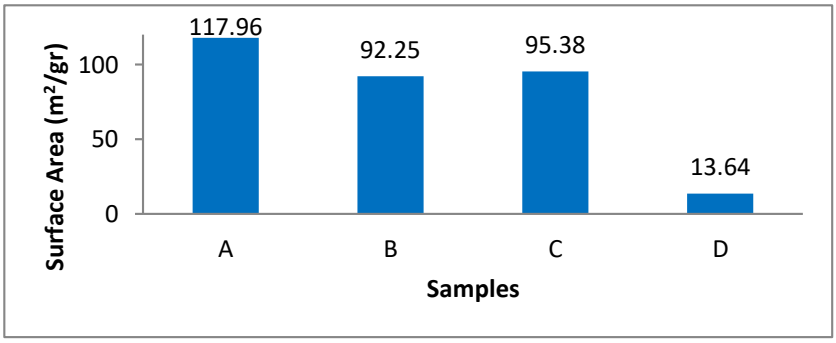

Figure 3. Surface Area of TiO_2 nanoparticles Post-hydrothermally treated at temperature 100 ^{0}C, (b) 120 ^{0}C, (c) 150 ^{0}C and (d) P-25 Degussa.

As the temperature increases, there is an indication that the surface area of the post-hydrothermally treated sample has decreased which causes the growth of the crystal grains. However, a unique result obtained by a post-hydrothermally treated sample at 150 ºC shows that there is a slight increase compared to the 120 ºC treated sample. P-25 Degussa sample has the lowest surface area due to high crystallinity and also the lowest value of crystallite size because of the presence of the rutile phase, where the average rutile′s diameter size is greater than the diameter size of the anatase [9] .

The optical characterization by UV-Vis with DRS mode was aimed at observing optical response of TiO_2 synthesized nanoparticles. Figure 4 shows the absorbance spectra of all four samples.

From the figure bellow, it can be seen that the post-hydrothermal 150 ^{0}C move toward to red shift compared to 120 ^{0}C sample. DR/UV–vis directly provides some insight into the interactions of the photocatalytic materials with photon energies [10]. The obtained result of UV-vis spectroscopy is the UV spectral intensity versus wavelength of each sample which is then converted into band-gap energy.

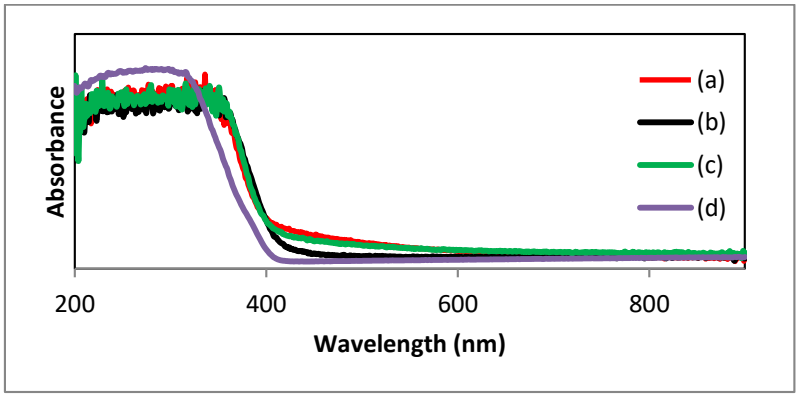

Figure 4. Photo-activity of TiO_2 nanoparticles Post-hydrothermally treated at temperature 100 ^{0}C, (b) 120 ^{0}C, (c) 150 ^{0}C and (d) P-25 Degussa.

This finding is in accordance with the quantum size effect, where the nanocrystals with larger size exhibited lower energy and displayed red shift. Conversely, the nanocrystals with smaller size displayed blue shift because of their higher energy. In our experiments, a red shift was observed for the products consisting of rutile nanorods compared with pure anatase particles, because the size of rutile nanorods was larger than anatase particles [11]. As a comparison, P-25 Degussa has very smooth line which was blue shifted from post-hydrothermal samples. The band gap energy of samples was further determined by using Kubelka-Munk equation and the result is shown in Figure 5.

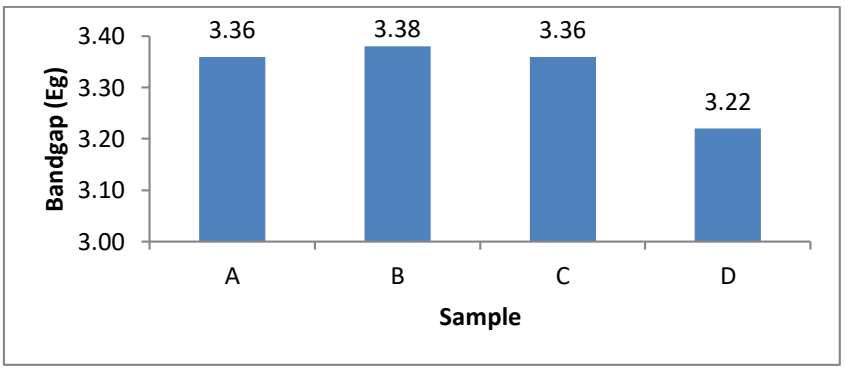

Figure 5. Band gap energy of TiO_2 nanoparticles Post-hydrothermally treated at temperature 100 ^{0}C, (b) 120 ^{0}C, (c) 150 ^{0}C and (d) P-25 Degussa.

Figure 5 shows that post-hydrothermally treated sample at temperature 100 °C and 150 °C has the lowest band gap value among post-hydrothermal samples. Both samples obtained band gap energy i.e. 3.36 eV. The lower band gap energy value indicates that the sample has higher crystallinity. In Figure 5, it is shown that the higher crystallite size belonging to the 150 °C post-hydrothermal sample did not

provide the lowest band gap energy value. To clarify this phenomenon further investigation and more accurate calculation must be performed.

Moreover, the DSSC performance of the sample was examined by measuring the open voltage circuit (V_{oc}) of the prototype upon exposed in 50 W projector lamp. The result of open circuit voltage is shown at Figure 6.

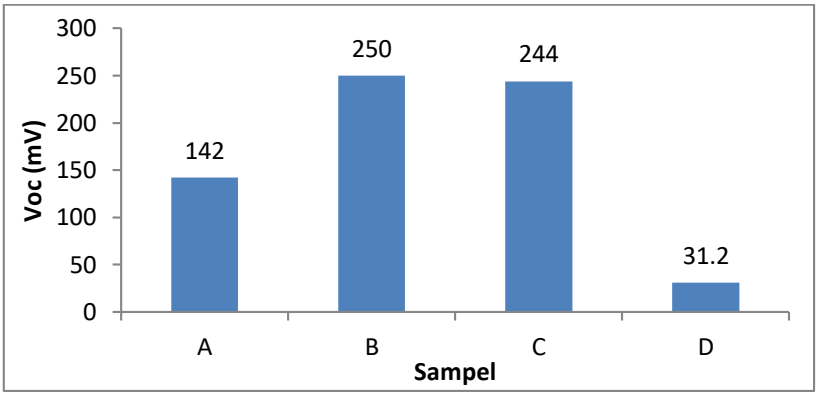

Figure 6. Open Circuit Voltage (V_{OC}) of TiO_2 nanoparticles Post-hydrothermally treated at temperature 100 ^{0}C, (b) 120 ^{0}C, (c) 150 ^{0}C and (d) P-25 Degussa.

DSSC performance of open voltage circuit correlates with crystallinity, surface area, and band gap energy. From Figure 1, the highest crystallite size was achieved by the Post-Hydrothermal-150 treated sample at 10.55 nm, but the V_{OC} value of the sample does not show the maximum value. Post-Hydrothermal-120 shows the highest open voltage circuit at 250 mV. The lowest band gap energy, high crystallite size of up to 8.85 nm and also a high surface area value of 92.25 m^2/gr which also makes this sample to achieve the highest V_{OC}. P-25 Degussa should have achieved highest V_{OC} due to highest crystallite size (17.33 nm) and lowest band gap energy to compared TiO_2 anatase (3,2 Ev) [12], but due to the lowest surface area V_{OC} value of P-25 Degussa obtained the lowest value i.e 31.2 mV.

Based upon these indications, it seems proper to suggest that post-hydrothermal process has made the stiff Ti-OH network to become more flexible and to be arranged as Ti-O-Ti after completion of the hydrolysis process. Ti-O-Ti rearrangement has helped to make the degree of crystallinity of the TiO_2 higher and for the sample to achieve a better performance. The effect of this phenomenon has improved the distribution of Ti-O-Ti network in the hydrothermally treated. The highest V_{OC} of post-hydrothermal at 120 °C sample indicates that in this temperature at 120 °C is the optimum condition of post-hydrothermal treatment in this study.

4. Conclusion

All the TiO_2 xerogel samples in the present study have been successfully synthesized by sol-gel process, and in this work have been successfully assembled to become DSSC and have displayed their activity in converting the light spectrum into electrical energy as shown by their open circuit voltage (V_{OC}) values. The TiO_2 xerogel possesses good nanostructure characteristics in terms of relatively large surface area and a sufficiently high crystallinity and post-hydrothermal treatment with operating parameters and conditions. The increase of the post-hydrothermal temperature gives the effect of increasing the diameter of crystallite size of the samples. However, conversely the surface area and energy band gap values obtained have not shown any downward trend.

The nanostructure TiO_2 properties obtained at temperature 150 °C shows the highest crystalline size (10.55 nm), high surface area (95.28 m2/gr), and bandgap energy (3.36 eV), so it is considered as the optimum value of the present post-hydrothermal process. The performance test of open circuit voltage revealed that the DSSC fabricated with P-25 Degussa provides 3.14 mV, while the highest

result belongs to post-hydrothermal at 120 °C with 250 mV followed by post-hydrothermal at 150 °C and 100 °C.

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