https://scilett-fsg.uitm.edu.my/
Vol. 14(1) JANUARY 2020

ISSN: 1675-7785
eISSN: 2682-8626
DOI: 10.1234/jmpc.v14i1.7777

pH Condition Influence Nanotube Structure of TiO_2 by Anodizing Titanium Substrate

Nur Aimi Jani[1,2]*, Izzatul Syifa Azizan[1], Nur Fatin Razak[1], Mohd Muzamir Mahat[1], Weesiong Chiu[2]*, Saadah Abdul Rahman[2]

[1]*Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia*

[2]*Low Dimensional Materials Research Center, Department of Physics, Faculty of Science, University Malaya, Kuala Lumpur 50603, Malaysia*

Corresponding author: nuraimi_jani@uitm.edu.my; w.s.chiu@um.edu.my

Received: 11 September 2019; Accepted: 3 December 2019; Published: 31 January 2020

ABSTRACT

The influence of pH of the electrolyte used during anodization of Titanium substrate has been investigated in order to determine the optimum pH condition to form self-organized Titanium dioxide (TiO_2) nanotubes (NTs) structure. The TiO_2 NTs was formed by anodizing Titanium substrate in an electrolyte containing 1M of sodium sulfate (Na_2SO_4) with 0.7 g of ammonium fluoride (NH_4F) for 180 minutes with potential 20 V. The optimum conditions were determined by characterization using FESEM and XRD analysis. As shown in the result, it can be summarized that pH of the anodization electrolyte can affect the length and diameter of the NTs as confirmed by FESEM images. FESEM result shows that, the length of nanotubes increased as the pH increased which are from 50 nm to 424 nm for pH 5 and pH 7, respectively. However, at higher pH more than 7, the nanotube structure was collapsed and only form bulk oxide film. The FESEM result also supported by the XRD result as the peak at 24° increased up from pH 3 to pH 7 and drop at pH 9.

Keywords: *Nanotubes; TiO2; Anodization; Nanotubes length; Titanium*

INTRODUCTION

The development of nanostructured materials in the industry has grown rapidly for many applications that are useful to the people, microorganisms, environment and the others. As for the example, Titanium dioxide (TiO_2) is in the process that involves in antimicrobial activity to prevent or reduce the amount of microbes present in the photocatalytic activity in order to manage the waste pollutants treatment [1] and solar cells applications [2-6].

Compared to other nanostructured materials, TiO_2 nanotubes (TiO_2 NTs) is the structure of semiconductor material that is found to be the most well-known for the widespread environmental applications due to its

https://scilett-fsg.uitm.edu.my/
Vol. 14(1) JANUARY 2020
ISSN: 1675-7785
eISSN: 2682-8626
DOI: 10.1234/jmpc.v14i1.7777

low cost, non-toxicity, and the high level of inertness against the reaction that involved in corrosion [7-10]. There are three polymorphs phase that often presents in the crystal structure of TiO_2 which are, rutile, anatase, and brookite [11]. These three phases contain the six coordinated titanium. Mostly, anatase is the phase that exhibits the most photocatalytic activity. There was a study conducted by the previous researchers about those three phases in the efficiency of water splitting by using one sun illumination [6, 13-16]. From the study, it was found that anatase-rutile-brookite of TiO_2 nanotubes are the most efficient than anatase-rutile and anatase TiO_2. This is because they exhibit different bandgap energy in each phase [12].

TiO_2 NTs have drawn much attention for the applications of TiO_2 NTs in the formation of lithium dendrites for lithium-ion batteries. It is where TiO_2 will become the anode material in the storage device because of having a little volume change which is about 4% [17]. Other than that, the tubular pores of the anodized structure of TiO_2 are uniformly straight and vertically aligned to the substrate surface. This property gives a better microstructure and hence enhances the performance of photocatalytic microreactor [13]. To determine the efficiency and the performance of the TiO_2 NTs, some parameters such as morphology, crystallinity, structure are studied by many researchers. To produce TiO_2 NTs, several methods have caught the attention based on their dimensional nature, ways of handling and preparation. The mentioned methods are sonoelectrochemical, anodization, sol-gel, RF magnetron sputtering, chemical vapor deposition, microwave irradiation, and hydrothermal [13, 18-20].

Among all the methods, anodization is being a method of choice since it is cost-effective, higher electrical conductivity, great mechanical adhesion, and cell proliferation and good corrosion resistance [6, 13]. Moreover, the growth of TiO_2 NTs can be justified under a wide range of electrochemical conditions. For anodization, several parameters can be used as references to determine the efficiency of TiO_2 NTs formation as well as to control its limited thickness such as applied voltage, pH of the electrolyte, the concentration of the electrolyte and annealing temperature [21]. This study is focusing on the morphological and structural studies of TiO_2 NTs depending on the acidic and alkaline condition (pH).

EXPERIMENTAL

Titanium foil with thickness 0.25 mm from Sigma-Aldrich was used for anodizing. Firstly, the Ti foil was ultrasonically cleaned with acetone followed by ethanol and water for 5 minutes each condition. Then the foil was dried in an oven for 5 minutes. Anodization process was started by conventional two-electrode electrochemical process under stirring condition at room temperature. The potential was set as 20V for 180 minutes. The electrolyte used is 1M Na_2SO_4 and 0.7g of NH_4F. The pH for acidic and alkaline condition were controlled by adding chemical with high hydrogen ion content and hydroxide ion content, respectively. After anodization, the sample was immediately rinsed with deionized water, air dried and annealed for 3 hours at 450 °C to produce the required phase. Lastly, all the samples were characterized by using FESEM (for top and cross-sectional view) and XRD (for structural properties).

RESULTS AND DISCUSSION

Anodization pH play a crucial role in allowing the grow and dissolution process happened throughout anodization process. Figure 1 shows the FESEM images of TiO_2 NTs that were anodized in different pH

https://scilett-fsg.uitm.edu.my/
Vol. 14(1) JANUARY 2020
ISSN: 1675-7785
eISSN: 2682-8626
DOI: 10.1234/jmpc.v14i1.7777

condition. The pH of the electrolyte is the kind of parameter that reveals the condition of the electrolyte whether it is acidic, neutral or alkaline. A study found that the formation of the nanotubes became successful at neutral conditions specifically at pH over 6 but did not work at low pH which is an acidic condition[11]. Due to this insignificant parameter controlled, thus in this study, several pH ranges from acidic to neutral and alkaline was used for anodization which are in range from pH 3 to pH 9. In order to determine the diameter and the length of the nanotubes, top view image and cross-sectional view images was taken by FESEM characterization technique. Others method is HRTEM technique. Since this is low magnification images, therefore FESEM was conducted.

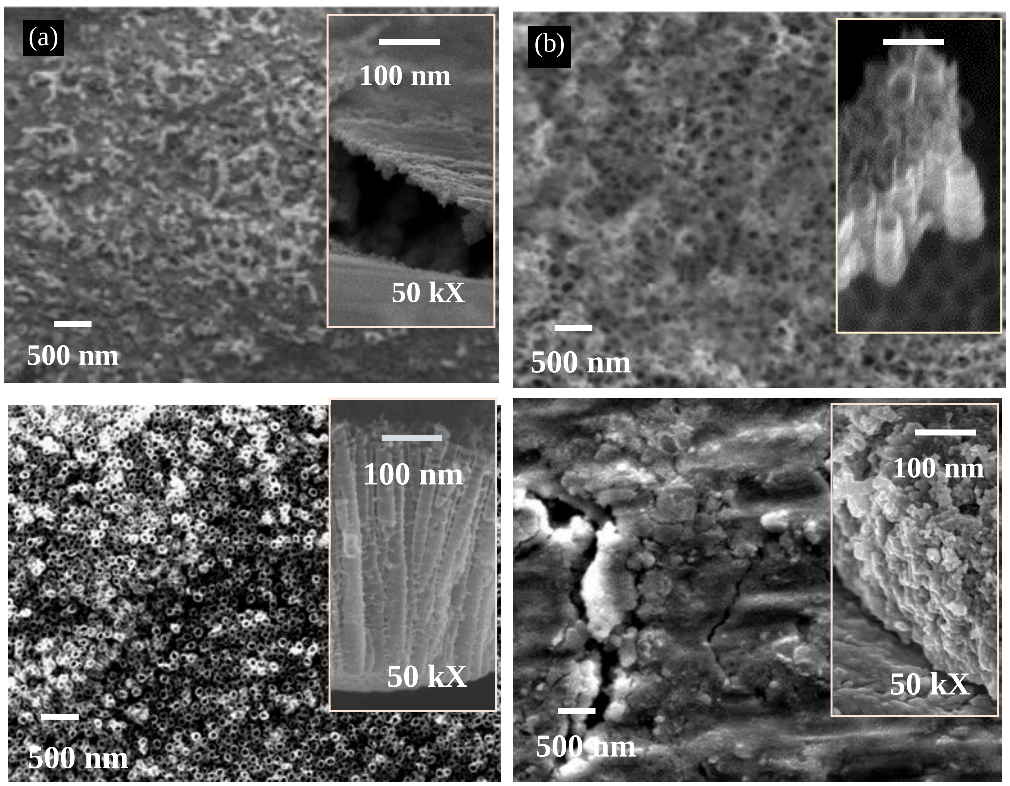

Figure 1: The morphological of top view images at magnification of 30 kX of anodized Ti substrate in electrolyte with different pH condition at (a) pH 3, (b) pH 5, (c) pH 7, and (d) pH 9 for the formation of TiO_2 NTs. The inset in each image represent the cross-sectional view images for TiO_2 NTs (This sample was prepared at potential 20V for 180 minutes of anodization process)

As seen in Figure 1a, at pH 3, the rougher porous structure was formed. This was happened due to the high dissolution rate at low pH has a high concentration of H^+ ion that caused the ability of oxidation reduced. As in inset, only thin layer was formed. As the pH 5 was used as in Figure 1b, the TiO_2 nanotubes was formed but they were just about to start to develop and grow. As in inset, the length growth up to 50 nm. The nanotubes grew well, and almost perfect structure of nanotubes was formed in pH 7 as in Figure 2c.

ISSN: 1675-7785
eISSN: 2682-8626
DOI: 10.1234/jmpc.v14i1.7777

The inset shows well growth nanotubes with maximum length achieved is 424 nm. However, the nanotubes denatured and collapsed at pH 9 as seen in Figure 2d and as in the inset. The nanotubes cannot grow in high pH conditions; this might be due to the high oxidation rate that potentially form thick film instead. The best length of the nanotubes formed in this study is about 424 nm at pH 7. In conclusion, TiO_2 nanotubes worked best in neutral condition but did not familiar in neither too low pH nor too high pH conditions. To support this finding, the sample was characterized using XRD as in Figure 2.

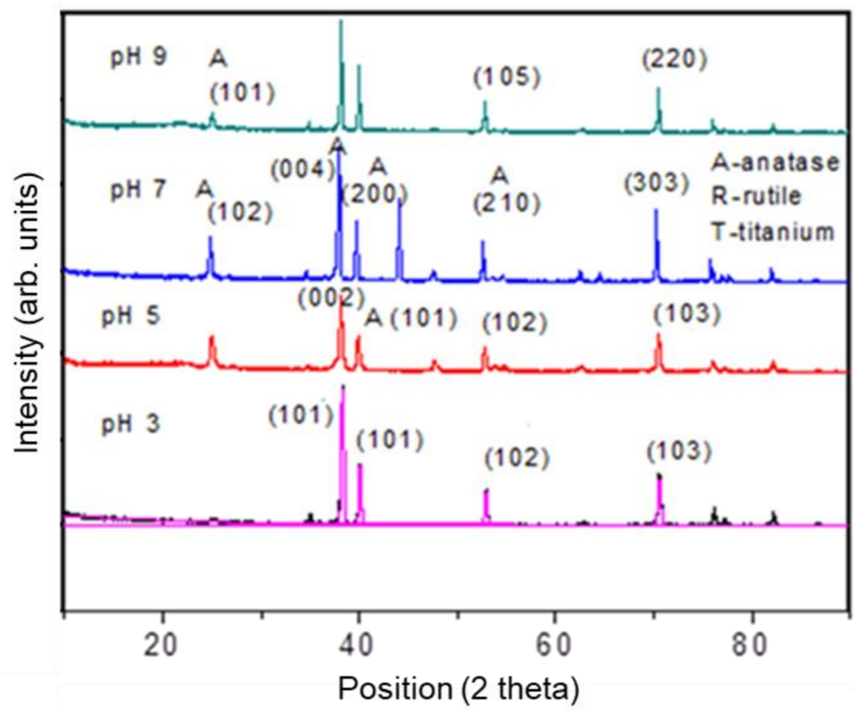

Figure 2: The XRD pattern of anodized Ti substrate in electrolyte with different pH condition at pH 3, pH 5, pH 7, and pH 9 for the formation of TiO_2 NTs

Figure 2 shows the XRD pattern of the TiO_2 NTs grown by anodization at different pH of electrolytes traces of anatase and rutile phase. It was proved that TiO_2 NTs are crystalline material due to the formation of sharp intensity peaks in the XRD pattern. Correspond to 2 theta position, the diffraction peaks involved are 25.08°, 37.80°, 38.58°, 48.05° and 53.89° at (101), (004), (112), (200), and (105) crystal plane, respectively. The diffraction peaks show the formation of anatase phase of TiO_2 [6].

This is confirmed with the reference standard JCPDS 21-1272 for Anatase-TiO_2 and 21-1276 for Ti. By increasing the pH value from pH 3 to pH 7, the intensity of the peak increased, especially at peak 27.5°. This is due to the strong identification of anatase phase as related to the existence of longer TiO_2 NTs formed at pH 7. However, at pH 9, the intensity of the peak decreased as the structure was collapsed as shown in inset in Figure 1d.

ISSN: 1675-7785
eISSN: 2682-8626
DOI: 10.1234/jmpc.v14i1.7777

CONCLUSIONS

In summary, a TiO_2 NTs anodized on Ti substrate has been successfully synthesized and characterized. The influence of pH to the formation of NTs structure has been examined. The result based on FESEM and XRD analysis shows optimum condition for pH was at pH 7 with length about 424 nm. The length of the nanotubes is increasing with an increasing anodization pH. Nanotubes are not suitable to grow in too acidic and too alkaline conditions as they show no sign of growing at pH 3 and collapsed at pH 9. The possible mechanism that contribute to the enhancement of length is oxidation and dissolution process competition in acidic and alkaline electrolyte during anodization.

ACKNOWLEDGMENTS

This study was funded by Ministry of Education (FRGS: FP-038-2014B), University Malaya Research Grant (UMRG-AFR Frontier Science-Project Number: RG390-17AFR; Postgraduate Research Fund (PG135-2014B)), Ministry of Education (MOE) together with Universiti Teknologi MARA for SLAB/SLAI Ph.D. Scholarship and UiTM Internal Research Grant (600-IRMI 5/3/LESTARI (030/2019)).

REFERENCES

[1] Zhang X., Xiao G., Wang Y., Zhao Y., Su H., Tan T., Preparation of chitosan-TiO_2 composite film with efficient antimicrobial activities under visible light for food packaging applications, *Carbohydrate Polymers*, **169**:101-7 (2017).

[2] Malevu T.D., Mwankemwa B.S., Motloung S.V., Tshabalala K.G., Ocaya R.O., Effect of annealing temperature on nano-crystalline TiO_2 for solar cell applications, *Physica E: Low-dimensional Systems and Nanostructures*, **106**:127-32 (2019).

[3] Agarwala S,, Ho G.W., Self-ordering anodized nanotubes: Enhancing the performance by surface plasmon for dye-sensitized solar cell, *Journal of Solid State Chemistry*, **189**:101-7 (2012).

[4] Bian H., Wang Y., Yuan B., Cui J., Shu X., Wu Y., Wu Y., Zhangab X., Adelojuc S., Flow-through TiO_2 nanotube arrays: a modified support with homogeneous distribution of Ag nanoparticles and their photocatalytic activities, N*ew Journal of Chemistry*, **37**:752 (2013).

[5] Chen X., Mao S.S., Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications, *Chemical reviews*, **107**:2891-959 (2007).

[6] Jani N.A., Haw C.Y., Chiu W.S., Rahman S.A., Lim Y.C., Khiew P.S., Yaghoubif A., Understanding the effect of plasmonic enhancement on photocatalytic activity of TiO2 nanotube arrays, *Materials Characterization*, **128**:134-41 (2017).

[7] Wang M., Zhang H., Zu H., Zhang Z., Han J., Construction of TiO_2/CdS heterojunction photocatslysts with enhanced visible light activity, *Applied Surface Science*, **455**:729-35 (2018).

[8] Comini E., Galstyan V., Faglia G., Bontempi E., Sberveglieri G., Highly conductive titanium oxide nanotubes chemical sensors, *Microporous and Mesoporous Materials*, **208**:165-70 (2015).

[9] Ibrahim M.Z., Sarhan A.A.D., Yusuf F., Hamdi M., Biomedical materials and techniques to improve the tribological, mechanical and biomedical properties of orthopedic implants – A review article, *Journal of Alloys and Compounds*, **714**:636-67 (2017).

ISSN: 1675-7785
eISSN: 2682-8626
DOI: 10.1234/jmpc.v14i1.7777

[10] Liu Y., Goebl J., Yin Y., Templated synthesis of nanostructured materials, *Chemical Society reviews*, **42**:2610-53 (2013).

[11] Chang F., Zhang J., Xie Y., Chen J., Li C., Wang J., Luo J., Deng B., Hu X., Fabrication, characterization, and photocatalytic performance of exfoliated g-C_3N_4–TiO_2 hybrids, *Applied Surface Science*, **311**:574-81 (2014).

[12] Preethi LK, Mathews T, Nand M, Jha SN, Gopinath CS, Dash S. Band alignment and charge transfer pathway in three phase anatase-rutile-brookite TiO2 nanotubes: An efficient photocatalyst for water splitting. Applied Catalysis B: Environmental;218:9-19.(2017)

[13] Nagamine S., Inohara K., Photocatalytic microreactor using anodized TiO_2 nanotube array, *Advanced Powder Technology*, 29:3100-6 (2018).

[14] Gong D., Grimes C.A., Varghese O.K., Hu W., Singh R.S., Chen Z., Dickey E.Z., Titanium oxide nanotube arrays prepared by anodic oxidation, *Journal of Materials Research*, **16**:3331-4 (2011).

[15] Macak J.M., Hildebrand H., Marten-Jahns U., Schmuki P., Mechanistic aspects and growth of large diameter self-organized TiO_2 nanotubes, *Journal of Electroanalytical Chemistry*, **621**:254-66 (2008).

[16] Nischk M., Mazierski P., Gazda M., Zaleska A., Ordered TiO_2 nanotubes: The effect of preparation parameters on the photocatalytic activity in air purification process, *Applied Catalysis B: Environmental*, **144**:674-85 (2014).

[17] Zu G., Li H., Liu S., Li D., Wang J., Zhao J., Highly efficient mass determination of TiO_2 nanotube arrays and its application in lithium-ion batteries, *Sustainable Materials and Technologies*, 18:e00079 (2018).

[18] Cui L., Hui K.N., Hui K.S., Lee S.K., Zhou W., Wan Z.P., HaThuc C.N., Facile microwave-assisted hydrothermal synthesis of TiO_2 nanotubes, *Materials Letters,* **75**:175-8 (2012).

[19] Hernandez-Alonso M.D., Garcia-Rodriguez S., Sanchez B., Coronado J.M., Revisiting the hydrothermal synthesis of titanate nanotubes: new insights on the key factors affecting the morphology, *Nanoscale*, **3**:2233-40 (2011).

[20] Uchida S., Chiba R., Tomiha M., Masaki N., Shirai M., Hydrothermal Synthesis of Titania Nanotube and its Application for Dye- Sensitized Solar Cell, *Studies in Surface Science and Catalysis*, **146**:791-4 (2003).

[21] Lu L., An X., Silver nanoparticles synthesis using H_2 as reducing agent in toluene–supercritical CO_2 microemulsion, *The Journal of Supercritical Fluids*, **99**:29-37 (2015).