

Synthesis of TiO₂ Nanotube Arrays by Sonication Aided Anodization and Its Application for Hydrogen Generation from Aqueous Glycerol Solution

by Ratnawati Ratnawati

Submission date: 05-Feb-2023 09:09AM (UTC+0500)

Submission ID: 2006450377

File name: 1c._matecconf_icense2015_01001.pdf (597.24K)

Word count: 2708

Character count: 13592

Synthesis of TiO₂ Nanotube Arrays by Sonication Aided Anodization and Its Application for Hydrogen Generation from Aqueous Glycerol Solution

Ratnawati^{1,a}, Jamuzi Gunlazuardi², Slamet¹

¹Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia, Depok 16424, Indonesia
²Department of Chemistry, Faculty of Mathematics and Sciences, Universitas Indonesia, Depok 16424, Indonesia
³Department of Chemical Engineering, Institut Teknologi Indonesia, Tangerang Selatan 15320, Indonesia

Abstract. The sonication aided anodization in the TiO₂ Nanotube Arrays (TNTA) formation and its performance for photocatalytic hydrogen generation from glycerol–water solution (10 v%) has been examined. TNTA were prepared by anodization of Ti foil at 30 V, 50 oC with glycerol containing fluoride as an electrolyte solution. The anatase phase was obtained by annealing of amorphous TNTA at 500 oC under H₂ in Ar atmosphere for 3 h. TNTA have average tube's lengths and inner diameter approximately in the range of 0.5-1.5 μm and 70-84 nm respectively, and a comparable tube wall thickness of 14-20 nm was also observed. The elemental composition of TNTA observed are Ti, O, C, N, and F. In the range of 10 - 60 min anodization process, it was found that the average inner diameters and length of the tubes increase as anodization time increased. The photocatalytic H₂ generation test indicated that H₂ produced was found to depend on the tube dimension. Among the TNTA obtained, TNTA-U60 with 1.46 μm tube length showed the highest hydrogen production (47,22 mmol/m² photocatalyst).

1 Introduction

Nowadays, a steady depletion of fossil fuels source is caused by the growth of high energy demand as well as increasing world population. In addition, combustion of fossil fuel leads to a significant contaminant emission issue. As a consequence, it is very crucial to promote new alternative energy that is renewable and environmental friendly. Hydrogen produced by photocatalytic reaction over TiO₂ in ambient condition from glycerol-water solution is a potential candidate, as it is a renewable, clean energy, and low cost compared to traditional technology [1,2,3]. Huge quantities of biomass-derived waste such as glycerol solution can be considered as interesting renewable and sustainable source for producing H₂ [2,3]. Furthermore, glycerol can serve as a hole scavenger/an electron donor that can increase the H₂ generation [3,4]. The amounts of H₂ generated was found to be in agreement with the photo-spitting of water and photo-reforming of glycerol that take place simultaneously according to the overall reaction in Eq. 1 [2,3,4]:



TiO₂ is the most suitable photocatalyst due to its photo-stability, photo-corrosion resistance, nontoxicity, availability and relatively cheap [3,5]. Morphology modifications to increase surface area and the addition of non-metal doping to enhance photo-responsive to solar

spectra have been developed to minimize the drawbacks of TiO₂ [4,5,6]. Anodic oxidation of Ti foil produces TNTA that have larger surface area and provide superior electron – hole separation compared to the TiO₂ nanoparticles [5,6]. Therefore, it can enhance photon absorption and suppress recombination. The morphology and dimension of TNTA are determined by the net growth rate of the formation of TNTA from Ti foil and chemical dissolution of formed TNTA [6,7,8]. Formation of TNTAs in glycerol electrolyte solution with high viscosity result in low growth rate. However, by elongating the anodization time, increasing the tube length can be achieved [6]. In addition, sonication aided anodic oxidation could improve mass transport in the electrolyte solution, thus could affect the morphology and dimension of TNTA. Furthermore, by adding a certain amount of water that can decrease the viscosity of glycerol also influences the optimum growth rate [9]. Sonication changes diffusion process that could enhance the formation rate of TNTA with ethylene glycol and 1,2,3-propanetriol as electrolyte solution at room temperature [7,8]. As a result, longer TNTAs can be obtained with a short time.

Formation of TNTA in an organic electrolyte such as glycerol containing NH₄F may lead to the adsorption of this organic molecules on the TNTA during anodic oxidation process [4,9,10]. Annealing this anodized photocatalyst in 20% H₂/Ar atmosphere at 500 °C for 3 h resulted in C, N, and F incorporation (as doping) in the TNTA [4,9]. Carbon was supplied by thermal

^a Corresponding author: mwt63@yahoo.co.id

decomposition of glycerol [4,9,10], whereas Nitrogen and Fluoride were provided by NH_4F [4,9,11]. Annealing were performed to produce crystalline phase of TNTAs and may also lead to the incorporation of dopants that already available in the electrolyte solution along the anodic oxidation process (in-situ doping) [4,7,9]. This non-metal doping can reduce the band gap energy. Consequently, these TNTA provide a positive response to the visible light [4,7,9] or fully harvest to the solar energy since visible light accounts for approximately 45% of the incoming solar energy spectrum [3].

The aim of this research, presented in this paper, is to investigate the effect of sonication during anodization time on the morphology of TNTA in glycerol electrolyte solution (25 v% water) at 50°C. It is expected that by this method, the TNTA with the larger surface area that can absorb more photon can be obtained in a shorter time. The activity of TNTA produced by sonication is tested in producing H_2 from photo-reforming of 10 v% glycerol in water, which is still rarely investigated by researchers.

2 Experimental Procedure

2.1 Synthesis and characterization of TNTA

Ti sheet (99.6% purity) with 0.3 mm thick underwent anodization to obtain TNTA. To study the effect of sonication on the morphology, different time of 10; 30 and 60 min were performed during the anodization process (denoted as TNTA-U10, TNTA-U30, and TNTAs-U60 respectively). Meanwhile, anodization with magnetically stirring (150 rpm) for 60 min is denoted as TNTA-M60. Anodic-oxidation was performed by Ti foils in 60 ml of glycerol electrolyte solutions using ultrasonic waves (Telsonic TPC 015, 200 W, 65 kHz) at 50°C according to the maximum temperature achieved during sonication. More details information about anodization technique had been described previously [4,9]. All photocatalysts were then annealed to produce crystalline phase of TNTA. The morphology of TNTA was examined using a FESEM (FEI-Inspect F50). Energy dispersive X-ray spectroscopy (EDAX) is used to evaluate the elements that present in TNTA at 20 V. Glycerol solution with 25 v% water content and annealing under 20% H_2/Ar at 500 °C for 3 h are optimum conditions is examined by our previous experiment [9].

2.2 Photocatalytic hydrogen generation

The photocatalytic H_2 productions from 10 v% of glycerol in water were performed in a 500 ml Pyrex glass reactor that placed inside a reflector box. A thermocouple, magnetic stirrer, line purging was put in the reactor. A mercury lamp of Philips HPL-N 250 W/542 E40 HG ISL (17% of UV and 83% of visible light) was used as the light source. The reactions were carried out in 200 ml of solution for 240 min irradiation. Before each experiment, the reactor was purged with argon for 30 min to eliminate the air and to test the leakage. The reactor was equipped with Ar gas inlet/outlet to help in transferring H_2 products

to the analytical system. The H_2 was measured by on-line sampling every 30 min using Shimadzu Gas Chromatograph (GC 2014) with Thermal Conductivity Detector (TCD) to record the peak of H_2 , and it is connected to the computer. Molecular sieve (MS H_2 5A, 80-100 meshes) column is used to analyze the H_2 generated. High purity Ar (99.9%) with a velocity of 50 cm^3/min was used as a carrier gas.

3 Results and discussion

3.1 Morphology of TNTA

Fig. 1 and 2 show the top view and cross section image of TNTA at a different time of anodization prepared by sonication. Table 1 presents the dimensions of TNTA.

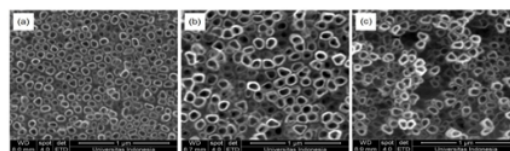


Figure 1. Top view FESEM image of (a) TNTA-U10, (b) TNTA-U30 and (c) TNTA-U60

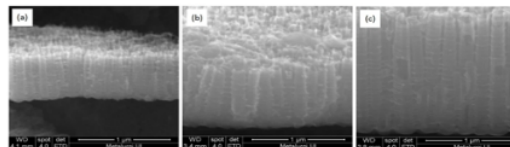


Figure 2. Cross view FESEM image of (a) TNTA-U10, (b) TNTA-U30 and (c) TNTA-U60.

Table 1. The Average of Inner Diameter, Wall Thickness, and Tube Length

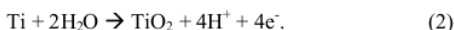
Photocatalyst	ID ^a [nm]	t ^b [nm]	L ^c [μm]
TNTA-U10	70	14	0.55
TNTA-U30	84	19	1.04
TNTA-U60	75	20	1.46
TNTA-M60	107	16	0.99

^aaverage inner diameter,

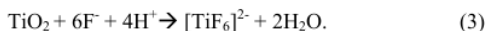
^baverage wall thickness,

^caverage tube length,

The two processes of TNTA formation can be represented in the following reactions. Oxidation of titanium result in TiO_2 film according to Eq. 2 as follows [6,8,12]



The mechanism of tube formation (chemical dissolution of TiO₂ film) due to F⁻ ion is presented by the reaction that can be seen in Eq. 3 [6,8,12]



The two above processes determine the morphology and the growth rate of TNTA and it is influenced by water content in the electrolyte solution, applied voltage, temperature, electrolyte composition, concentration of fluoride, mode of agitation, anodization time, etc. [6]. In this study, the variation of anodization time, ultrasonic or magnetically stirring influenced those two reactions, and, therefore, changed the TNTA morphology and the growth rate.

From Fig. 1, it is observed that the surfaces of TNTA are not flat/unevenness (tubes have difference length), and it is influenced by the duration of sonication time. The longer the sonication/anodization time, the greater the disorder of the tube length that caused by longer vibration of the ultrasound. Anodization time has a less significant effect on the wall thickness as it relatively remains unchanged. Increasing the inner diameter at longer anodization time is caused by increasing chemical dissolution at the tube wall. Whereas increasing the tube length occurs if the chemical dissolution rate at the tube bottom greater than that at the tube mouth. In the range of up to 60 min, the longer the anodization time, the longer the tube length. In the certain anodization time, the chemical dissolution rate at the tube bottom equals to at the tube mouth. In this condition, there is no addition of the tube length, meant that two above reactions achieve equilibrium [8,12]. From Fig. 2, it is obvious that self-organized of TNTA are perpendicular to the Ti substrate.

From Table 1, the growth rate of TNTA-U is reached the maximum at the first 10 min (0.055 μm/min), and followed by the decreasing growth rate until 60 min anodization time (0.024 μm/min). This could happen since in certain length, the diffusion at the mouth is greater than in the bottom tube [8]. TNTA-U60 performs faster growth rate (0.024 μm/min) compared with TNTA-M60 (0.016 μm/min) and, therefore, TNTA-U60 provides a longer tube (1.5 times) than TNTA-M60. A similar phenomenon also reported by other researchers [7,8]. To achieve around 1 μm length, TNTA-U needs 30 min anodization time; meanwhile TNTA-M needs 60 min. Ultrasonic waves that generate and subsequent destruct of cavitation bubbles increase ionic mass transfer/diffusion of F⁻ and H⁺ and effusion of the [TiF₆]²⁻ in the solution and, therefore, enhance the rate of TNTA formation [7,8]. In contrast, diffusion of ions is limited for magnetically stirring. Furthermore, Table 1 and Fig. 3 show that TNTA-U60 have a smaller diameter, and its tubes are closer to each other compared with TNTA-M60 since ultrasonic stirring is more homogeneous than magnetically stirring. As a result, more nucleation can happen that produce more tubular structure on the Ti surface of TNTA-U. With ultrasound, the disorder of the tubes length take place, but it is not for the one without ultrasound.

The EDAX analysis shows that the elemental composition of TNTA are Ti, O, N, C, and F. The

incorporation of C, N, and F in the lattice of TNTA were retained by annealing in H₂/Ar [4,9]. In our previous study, FTIR analysis indicated that C and N were incorporated in the lattice of TNTA. Consequently, the energy band gap was decreased [4,9]. In this study, reducing energy band gap also was evidenced since these TNTA gave a positive response to the visible light in generating H₂.

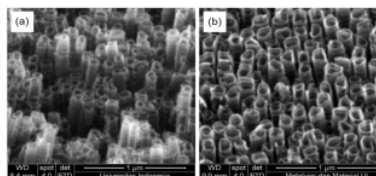


Figure 3. FESEM top view image with angle 45o of (a) TNTA-U60 and (b) TNTA-M60.

Photocatalytic hydrogen generation. Fig. 4 shows the effect anodization time toward the tube length of TNTA and H₂ production.

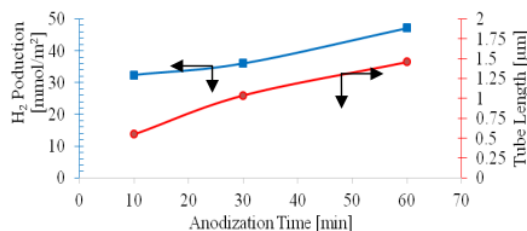


Figure 4. Effect of anodization time on the tube length of TNTA and H₂ production.

The hydrogen generation for the 10; 30 and 60 min irradiation time were 32,43; 36,07 and 47,22 mmol/m² photocatalyst respectively. From that Figure, it can be stated that the longer the anodization time, the longer the tube of TNTA. Consequently, the longer the tube length, the higher the H₂ generation since TNTA can absorb more photon that result in higher photocatalytic reaction rate. Compare to the TNTA-M60 (produces 29.5 mmol H₂/m² photocatalyst), the TNTA-U60 provided more H₂ generation (produces 47.22 mmol H₂/m² photocatalyst) as it has longer the tube. In our previous study, glycerol can act as a sacrificial agent that reduce electrons-hole recombination [4]. The mechanism of glycerol solution in TiO₂ to produce H₂ and CO₂ was proposed by previous researchers [13].

4 Conclusions

Sonication aided anodization could enhance the formation rate of TNTA. As a result, longer TNTA can be obtained with a short time of anodization. The difference in the TNTA dimension and morphology are caused by the competition of the oxidation reaction of Ti to TiO₂ and chemical dissolution of formed TiO₂ that is

influenced by time of anodization. The longer the anodization time, the wider the inner diameter of TNTA since the dissolution of the tube wall occur. In the range of up to 60 min, increasing the tube length still occurred as the dissolution at the tube bottom higher than that at the tube mouth. TNTA obtained in this study gained positive response to the 83% of visible light in the H₂ production, indicate that reducing band gap energy of the produced TNTA occurred.

Acknowledgments

The authors would like to thank LP3M Institut Teknologi Indonesia and Directorate General of Higher Education (DGHE), Indonesian Ministry of National Education for the financial support of this research (Hibah Bersaing grant no. 025/K3/KM/SPK/2013).

References

1. R.P. Antony, T. Mathews, C. Ramesh, M. Murugesan, A. Dasgupta, S. Dhara, S. Dash and A.K. Tyagi: *Int. J. Hydrogen Energy* Vol. 37 (2012), p. 8268
2. V.M. Daskalaki and D.I. Kondarides: *Catal. Today* Vol. 144 (2009), p. 75
3. N. Luo, Z. Jiang, H. Shi, F. Cao, T. Xiao and P.P. Edwards: *Int. J. Hydrogen Energy* Vol. 34 (2009), p. 125
4. Ratnawati, J. Gunlazuardi, E.L. Dewi and Slamet: *Int. J. Hydrogen Energy* Vol. 39 (2014), p. 16927
5. Slamet, D. Tristantini, Valentina, and M. Ibadurrohman: *Int. J. Energy. Res.* Vol. 37 (2013), p. 1372
6. A.E.R. Muhamed and S. Rohani: *Energy Environ. Sci.* Vol. 4 (2011), p. 1065
7. S.K. Mohapatra, M. Misra, V.K. Mahajam and K.S. Raja: *J. Catal.* Vol. 246 (2007), p. 362
8. L. Huang, F. Peng, H. Yu, H. Wang, J. Yang and Z. Li: *Mat. Res. Bull.* Vol 25 (2010), p. 200
9. Ratnawati, J. Gunlazuardi and Slamet: *Mater.Chem.Phys.* In Press <http://dx.doi.org/10.1016/j.matchemphys.2015.04.013> Vol.xxx (2015), p. 1
10. F.M.B. Hasan, H. Nanjo, S. Venkatachalam, M. Kanakubo and T. Ebina: *J. Power Sources* Vol. 195 (2010), p. 5889
11. H. Wu and Z. Zhang: *Int. J. Hydrogen Energy* Vol. 36 (2011), p. 1348
12. Y.W. Wen and R.C. Bo: *Int. J. Photoenergy* (2013), <http://dx.doi.org/10.1155/2013/348171>. Article ID 34871
13. P. Panagiotopoulou, E.E. Karamerou and D.I. Kondarides: *Catal. Today* Vol. 200 (2013), p. 91

Synthesis of TiO₂ Nanotube Arrays by Sonication Aided Anodization and Its Application for Hydrogen Generation from Aqueous Glycerol Solution

ORIGINALITY REPORT

9%

SIMILARITY INDEX

2%

INTERNET SOURCES

10%

PUBLICATIONS

1%

STUDENT PAPERS

PRIMARY SOURCES

- 1 Slamet, , Dewi Tristantini, Valentina, and Muhammad Ibadurrohman. "Photocatalytic hydrogen production from glycerol-water mixture over Pt-N-TiO₂ nanotube photocatalyst : PHOTOCATALYTIC H₂ PRODUCTION OVER Pt-N-TiO₂ NANOTUBES", International Journal of Energy Research, 2012.
Publication 1%
- 2 Ahmed El Ruby Mohamed, Sohrab Rohani. "Modified TiO₂ nanotube arrays (TNTAs): progressive strategies towards visible light responsive photoanode, a review", Energy & Environmental Science, 2011
Publication 1%
- 3 tesisred.net
Internet Source 1%
- 4 Tuany N.S. Trindade, Luciana A. Silva. "Cd-doped SnO₂ /CdS heterostructures for 1%

efficient application in photocatalytic reforming of glycerol to produce hydrogen under visible light irradiation", *Journal of Alloys and Compounds*, 2018

Publication

5

Marcos de Oliveira Melo, Luciana Almeida Silva. "Visible light-induced hydrogen production from glycerol aqueous solution on hybrid Pt–CdS–TiO₂ photocatalysts", *Journal of Photochemistry and Photobiology A: Chemistry*, 2011

Publication

1 %

6

Bruno Ribeiro, Ruben Offoiach, Stefano Rossetti, Elisa Salatin, Maria Lekka, Lorenzo Fedrizzi. "On Growth and Morphology of TiO₂ Nanotubes on CP-Ti by Anodic Oxidation in Ethylene Glycol Electrolyte: Influence of Electrolyte Aging and Anodization Parameters", *Materials*, 2022

Publication

1 %

7

Hye Won Jeong, Kyu Jun Park, Yiseul Park, Dong Suk Han, Hyunwoong Park. "Exploring the photoelectrocatalytic behavior of free-standing TiO₂ nanotube arrays on transparent conductive oxide electrodes: Irradiation direction vs. alignment direction", *Catalysis Today*, 2019

Publication

1 %

8

Maria Dalcin Fornari, Ana, Mariele Brambilla de Araujo, Cesar Bergamin Duarte, Giovanna Machado, Sérgio R. Teixeira, and Daniel Eduardo Weibel. "Photocatalytic reforming of aqueous formaldehyde with hydrogen generation over TiO₂ nanotubes loaded with Pt or Au nanoparticles", International Journal of Hydrogen Energy, 2016.

Publication

1 %

9

www.fulbrighter.org

Internet Source

<1 %

10

www.scientific.net

Internet Source

<1 %

11

Crawford, G.A.. "Tailoring TiO₂ nanotube growth during anodic oxidation by crystallographic orientation of Ti", Scripta Materialia, 200905

Publication

<1 %

12

Rajendra P. Panmand, Yogesh A. Sethi, Sunil R. Kadam, Mohaseen S. Tamboli et al. " Self-assembled hierarchical nanostructures of Bi WO for hydrogen production and dye degradation under solar light ", CrystEngComm, 2015

Publication

<1 %

13

"Photocatalytic Performance of CdS/(Pt-TiO₂)-Pumice for E. Coli Disinfection in Drinking

<1 %

Water", International Journal of Innovative Technology and Exploring Engineering, 2020

Publication

Exclude quotes Off

Exclude matches Off

Exclude bibliography On

Synthesis of TiO₂ Nanotube Arrays by Sonication Aided Anodization and Its Application for Hydrogen Generation from Aqueous Glycerol Solution

GRADEMARK REPORT

FINAL GRADE

/0

GENERAL COMMENTS

Instructor

PAGE 1

PAGE 2

PAGE 3

PAGE 4
