

Photocatalytic Decomposition of Glycerol Solution on TiO₂ Nanotube Arrays (TNNTA) doped with C and N to Produce Hydrogen

by Ratnawati Ratnawati

Submission date: 05-Feb-2023 09:11AM (UTC+0500)

Submission ID: 2006451326

File name: 1c.._ICMSET2016-pdfs_25.pdf (751.54K)

Word count: 2813

Character count: 14030

Photocatalytic Decomposition of Glycerol Solution on TiO₂ Nanotube Arrays (TNTA) doped with C and N to Produce Hydrogen

Ratnawati^{1,a}, Jarnuzi Gunlazuardi^{2,b}, Slamet^{3,c}

¹Department of Chemical Engineering, Institut Teknologi Indonesia, Tangerang Selatan 15320, Indonesia, Tel.: +62-21-7561092, fax: +62-21-7561092

³Department of Chemistry, Faculty of Mathematics and Sciences, Universitas Indonesia, Depok 16424, Indonesia, Tel.: +62-21-7270027, fax: +62-21-7863432

²Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia, Depok 16424, Indonesia, Tel.: +62-21-7863518, fax: +62-21-7863515

^arnwt63@yahoo.co.id, ^bjarnuzi@ui.ac.id, ^cslamet@che.ui.ac.id

Keywords: Anodic oxidation, TNTA, Photocatalytic, Hydrogen

Abstract. Carbon and Nitrogen-doped TNTA were synthesized by in-situ anodic oxidation of Ti using glycerol containing NH₄F followed by annealing with 20% H₂/Argon at 500 °C. Variation water content in the electrolyte solution (25 and 37.5 v%) and time of anodic oxidation (1, 2, 4 and 6 h) that influence the morphology of TNTA and H₂ produced was examined. At water content 37.5 v% in the electrolyte solution, FESEM results indicated that the disorder with not vertically oriented of the tube were observed. For water content 25 v%, TNTA with average inner diameters of 81 to 105 nm, wall thicknesses from 15 to 27 nm and lengths from 882 to 1705 nm were synthesized for 1-6 h anodization. Morphology of TNTA such as well developed, vertically oriented, ordered and long could influence photon absorption and, therefore, influence the accumulative H₂ production. The result indicated that the average inner diameter of the tubes increase as anodic oxidation time increased up to 6 h, on the other hand, the tube length reached the maximum at 4 h anodic oxidation. TNTA that anodized for 2 h, water content in the electrolyte solution 25 v% with average tube length 1570 nm showed the highest accumulative H₂ production (47 mmol/m²photocatalyst).

Introduction

Depletion of fossil fuel source and pollution from combustion of fossil fuel are problems faced by modern society and it must be solved. Hydrogen, a renewable energy, is a potential alternative to solve those problems since combustion of H₂ also does not cause the environmental problem. Water splitting with the photocatalytic process using solar photon and TiO₂ semiconductor that generated hydrogen is an attractive process. When TiO₂ illuminated by the photon, photo excited electrons in conduction band can split water to generate H₂. In this photo-splitting, TiO₂ has suitable valence and conduction band position for reduction of H⁺ and oxidation of OH⁻ [1]. Enhancement of H₂ production can be performed by addition of glycerol solution (the by-product of the biodiesel industry that now has limited demand in the market) [2] and it renewable and sustainable source for H₂ generation. Glycerol can act as sacrificial agents in water splitting and as the H₂ source [2]. As a result, enhancement of H₂ generation and waste minimization could be done simultaneously.

The most promising photocatalyst is TiO₂ since it is nontoxic, relatively inexpensive and its photostability [3]. Unfortunately, the use of TiO₂ has several constraints such as visible light inactive (its wide band gap i.e. 3.2 eV for the anatase and 3.0 eV for rutile phase), limited surface area and electron-hole recombination [1]. As a result, its application efficiency in solar light is still poor since UV portion accounts for only about 5%, meanwhile visible light accounts for about 45% in solar spectra [4]. Synthesis of TiO₂ nanotube arrays (TNTA) by in situ anodic oxidation of Ti foil using glycerol containing NH₄F as electrolyte solution and followed by annealing at 500 °C is one of the modifications strategies as it provides a larger surface area, gives better performance in charge transport than other morphologies. Moreover, not only longer TNTA can be obtained, but

22 also may lead to the incorporation of C, N, in the lattice of TNTA that result in lowering band gap [5,6]. This is because glycerol and NH_4F that available in the electrolyte solution can act as precursors [5,6]. The morphology of TNTA can be design by some variations such as voltage, pH, time, water content in the electrolyte solution, mode of agitation and flour ion (F^-) concentration [5].

In this present study, the effect of water content in the electrolyte solution and anodic oxidation time in the synthesis of TNTA was investigated. The characterization of TNTA is performed using FESEM/EDAX and photocurrent density measurement. The photo-activity of TNTA under visible light illumination in generating H_2 from glycerol solution was also discussed.

Experimental

Preparation and characterization of TNTA. Titanium sheet (0.3 mm thick, 99.6% purity) were anodized to produce TNTA. A constant potential of 30 V was set using DC power supply (Escord 6030SD) for 1; 2; 4; and 6 h under magnetically stirring at 28 °C. The water content in the glycerol electrolyte solution containing NH_4F was also varied (25 and 37.5 v%). Annealing with 20% H_2/Argon at 500 °C to induce crystallization was performed with the heating rate 9.2 °C min^{-1} , held 3 h and cooled naturally and to room temperature. More details of anodic oxidation had been described previously [6]. The surface morphology of TNTA was examined using an FESEM (FEI-Inspect F50). To determine the elements that present in the TNTA, energy dispersive X-ray spectroscopy (EDAX) is attached to the FESEM. Photocurrent density of TNTA was measured with photoelectrocatalytic reactor with a standard three-electrode configuration that connected to the computer-controlled potentiostat (e-DAQ/e-corder 401) [6].

1 **Photocatalyst test for hydrogen generation.** Photocatalytic H_2 generation experiments were carried out in a 500 ml Pyrex glass reactor equipped with a mercury lamp of Philips HPL-N 250 W/542 E40 HG ISL as a photon source (17% of UV and 83% of visible light), thermocouple, and magnetic stirrer. All TNTA (3 cm x 3 cm) were underwent photocatalytic reaction for producing H_2 from glycerol solution (the mixture of 180 ml water and 20 ml of glycerol). The photo reactor system was put inside a reflector box and the reactions were performed for 4 h irradiation as shown in Fig. as previously reported [6]. Before the commencement of the study, the reactor was purged with argon to complete removal of the O_2 atmosphere from the reactor for 1 h. The H_2 generated was analyzed every 30 min with on-line sampling using Shimadzu Gas Chromatograph (GC 2014) that equipped with molecular sieve column (MS Hydrogen 5A, 80-100 mesh) for H_2 and CO_2 Porapak N column, Thermal Conductivity Detector (TCD) to record the signal/peak of H_2/CO_2 produced and an injection valve. High purity argon (99.99%) is used as a carrier gas at 50 cm^3/min .

Result and Discussion

8 **FESEM/EDAX analysis.** Fig. 1 shows the FESEM image of TNTA obtained as a function of water content in the electrolyte solution. It is clear that, at water content 37.5 v%, the TNTA obtained was disorder and damaged. The effect of the anodic oxidation time on the tube diameter and length is presented in Table 1.

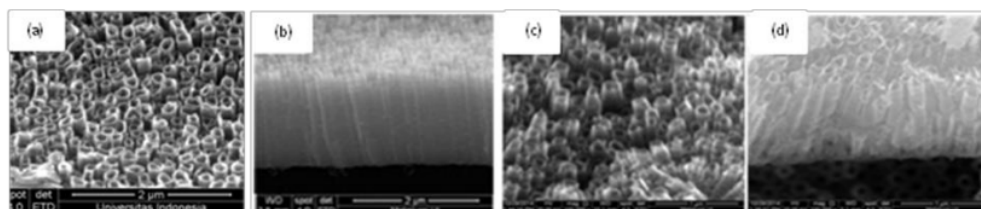


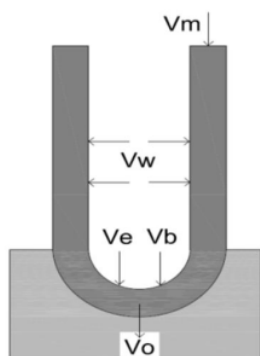
Fig 1. Top view with angle 45° and cross view FESEM image of TNTA obtained by anodic oxidation for 2 h at water content of 25 v% (a and b) and 37.5 v% (c and d).

Table 1. The Dimension of the tube as a function of anodic oxidation time at 25 v% water content.

Time, min	Di ^a [nm]	t ^b [nm]	L ^c [μm]	Tube growth rate(dL/dt), [μm/min]
1	80,6 (55-120)	15,2 (10-19)	0,882	0,015
2	96 (74-120)	27 (15-33)	1,570	0,013
4	98 (90-156)	23 (13-30)	1,705	0,007
6	105 (91-150)	20 (15-28)	1,663	0,005

Di^a = average inner diameter, t^b = average thickness, L^c = average length. In the brackets is range value

From Table 1 it clearly shows that the inner diameters of the TNTA increase as anodic oxidation time increase across 1-6 h since the dissolution of TNTA in the inner tube wall increase. On the other hand, the tube lengths increase from 1-4 h anodic oxidation time (882 nm to 1705 nm) and then decreased up to 1663 nm for 6 h anodic oxidation time. The formation mechanism of the TNTA from Ti can be explained as presented in Fig. 2 [5, 7].



The anodic oxidation of Ti to form TiO₂ is



The formation of small pits or pores due to the dissolution of TiO₂ formed by H⁺ and F⁻ ions (from NH₄F) given by the reaction:

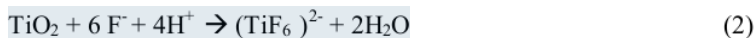


Fig. 2. The mechanism of anodic oxidation of Ti to produce TNTA

Firstly, Ti surface is oxidized to form TiO₂ layer according to the (Eq. 1) and followed by dissolution of TiO₂ (electric field-assisted dissolution, Ve), therefore, tube-like TiO₂ layer was obtained. Ti and TiO₂ are also chemically dissolved since the availability of fluoride and acidic environment according to (Eq. 2) and it happens at the entire porous surface. The dissolution of the TNTA in the bottom (Vb) and in the tube wall (Vw) resulted in the longer the tube length and wider the inner diameter. However, the dissolution in the mouth (Vm) resulted in the shorter the tube length. In the first hour, the formation of the TNTA (Vo) is in fast speed, therefore around 0.9 μm length of TNTA was achieved (Table 1). With increasing the time of anodic oxidation, the oxidation (Vo) and dissolution (Ve + Vb - Vm) rates slowed down (due to high electric resistance by the thicker oxide layer and long diffusion of F⁻ to the bottom of the tube) and finally caused the formation and dissolution of the TNTA reached equilibrium. The decreasing of the tube length (at 6 h anodization) occurs when the total dissolution rate (Ve + Vb - Vm) was little faster than the oxidation rate (Vo). The result indicated that the maximum length of the TNTA was reached at 4 h anodic oxidation and hereafter the equilibrium was achieved and in the long run the decreasing the tube length occurs. As presented in Table 1, the rate of tube formation decreasing along with the increasing the time and these results agree with the mechanism of the tube growth rate. In this study, until 6 h anodic oxidation, the inner diameter increased (resulted from the dissolution to the wall) but at 4 and 6 h anodic oxidation, part of the tube started to collapse (not vertically oriented). This

phenomenon also reported by some researchers [7,8]. They found that collapse and decrease of the tube length occur with increasing the time of anodic oxidation at 40°C and without magnetically stirring. The un-uniform in the tube length and collapse of the TNTA with increasing the time is predicted by the longer time of magnetically stirring during the anodic oxidation.

The tube dimension is a result of the competition of the oxidation and dissolution of the TNTA, and therefore any variation such as water content and anodic oxidation time affect these processes [7,8]. The water content in the electrolyte solution is a significant factor in the formation of TNTA according to the (Eq. 1) [4,6,7] and the formation of small pits or pores due to H⁺ and F⁻ ions as can be seen in (Eq. 2). At higher water content (37.5 v%), 2 h anodic oxidation, the tube length, diameter and the tube wall were 1622, 117, and 24 nm respectively. At higher water content, the chemical dissolution of TNTA occurred at a faster rate. As a result, the TNTA formed were disordered, damaged and not vertically oriented as presented in Fig. 1 (c) and (d). This phenomenon is in agreement with the results reported by Yu Wang et al. [8] with anodic oxidation process in the glycerol electrolyte at 30 V, 2 h, pH of 6 and 40 °C at 20 and 40 wt% water content.

At lower water content in the organic electrolyte alleviate the availability of oxygen in the oxidation reaction and results in thinner oxide barrier layers beneath the TNTA as presented by (Eq. 1). Moreover, it also inhibits chemical dissolution of TNTA according to (Eq. 2). Chemical dissolution occurs at the bottom of the tube, entire tube wall and the top of the tube. As a result, lower water content provides shorter inner diameter and tube length. A similar result is also presented by Muhamed et al. [5]. Furthermore, at lower water content (25%), the viscosity of electrolyte solution is relatively higher than at 37.5 v%, and therefore, the mobility/diffusion of O₂⁻ and F⁻ ions are inhibited [5]. As a consequence, the oxidation rate (Eq. 1) and chemical dissolution rate (Eq. 2) decreases, which results in smaller diameters and shorter tube lengths. Although shorter, the TNTA produced by 25 v% water content produced the current density (0.086 mA/m²) higher compare to the one with 37.5 v% (0.070 mA/m²). This is because TNTA produced with 37.5 v% water content have morphology disordered and some of them broken and, therefore, limited photon absorption occurs. The EDAX analysis of TNTA synthesized in glycerol electrolyte solution containing NH₄F with 25 v% water content shows that Ti, O, N, C, F were obtained and N, C were doped in the TNTA (FTIR analysis) that reduced the band gap energy until 2.7 eV (Uv-Vis DRS analysis).

Photocatalyst test for hydrogen generation. Fig. 3 presents accumulative H₂ generation for 4 h. (mmol/m² of TNTA) and the tube length as a function of anodic oxidation time.

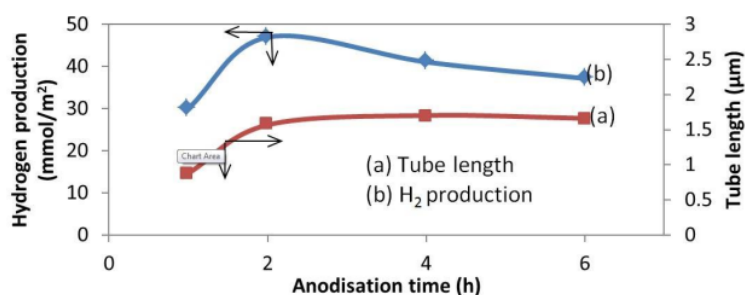


Fig. 3. Accumulative H₂ production and the tube length as a function of anodic oxidation time

Photocatalytic H₂ production from glycerol solution consists of two distinct mechanisms that are water splitting (at glycerol concentration of 0%) and photo-reforming of glycerol [9]. These two reactions take place simultaneously according to the overall reaction as follows [2,9]:



Introducing glycerol in the reactant could improve H₂ generation as it acts as sacrificial agents/hole scavenger that able to reduce the electron-hole recombination and as hydrogen source that undergoes oxidation reaction [2,6,9]. From Fig. 3, it is obvious that the hydrogen generation has the linear correlation with the tube length and the morphology since they proportional to photon absorption and therefore comparable with the H₂ production. In this study, CO₂ also generated and it gave evidence that the photo reforming glycerol taken place. Moreover, the TNTA obtained also performed a positive response to the visible light meant that reduction of band gap energy happened. Similar result also reported by other researchers when they synthesized TNTA via anodization using ethylene glycol as electrolyte solution [10].

Summary

The longer the anodic oxidation time up to 6 h the bigger the inner diameter of TNTA. However, tube length was found maximum in 4 h anodic oxidation. Partially disorder and not vertically of the tube obtained start from 4 h anodic oxidation. The difference of the TNTA morphology due to the competition of the oxidation reaction of Ti to TiO₂ and chemical dissolution of formed TiO₂ that is influenced by water content and time in anodic oxidation. In relation to H₂ production, it was concluded that TNTA synthesized in 2 h anodic oxidation, 25 v% water content showed well-ordered, long, vertically oriented of the tube with highest photocatalytic H₂ production.

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. Hydrog. Energy* Vol. 37 (2012), p. 8268
- [2] V.M. Daskalaki and D.I. Kondarides: *Catal. Today* Vol. 144 (2009), p. 75
- [3] Y. R. Smith, B. Sarma, S. K. Mohanty and M. Misra: *Int. J. Hydrog. Energy* Vol. 38 (2013), p.2062
- [4] S.K. Mohapatra, M. Misra, V.K. Mahajan and K. S. Raja: *J. Phys. Chem. C: Vol. 111* (2007), p. 8677
- [5] A.E.R. Muhamed and S. Rohani: *Energy Environ. Sci.* Vol. 4 (2011), p. 1065
- [6] Ratnawati, J. Gunlazuardi, E.L. Dewi and Slamet: *Int. J. Hydrog. Energy* Vol. 39 (2014), p. 16927
- [7] L. Huang, F. Peng, H. Yu, H. Wang, J. Yang and Z. Li: *Mater. Res. Bull.* Vol. 45 (2010), p. 200
- [8] Y.W. Wen and R.C. Bo: *Int. J. Photoenergy* (2013), p.1 <http://dx.doi.org/10.1155/2013/348171>. Article ID 34871
- [9] Slamet, D. Tristantini, Valentina and M. Ibadurrohman: *Int. J. Energy. Res.* Vol. 37 (2013), p. 1372
- [10] S.K. Mohapatra, M. Misra, V.K. Mahajan and K. S. Raja: *J. Catal.* Vol. 246 (2007), p. 362

Photocatalytic Decomposition of Glycerol Solution on TiO₂ Nanotube Arrays (TNTA) doped with C and N to Produce Hydrogen

ORIGINALITY REPORT

15%

SIMILARITY INDEX

8%

INTERNET SOURCES

12%

PUBLICATIONS

0%

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 3%

- 2** zh.scientific.net
Internet Source 2%

- 3** pubs.rsc.org
Internet Source 1%

- 4** 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%

5	pubhtml5.com Internet Source	1 %
6	www.orientjchem.org Internet Source	1 %
7	Slamet, Raudina. "Degradation of 2,4,6-Trichlorophenol and hydrogen production simultaneously by TiO ₂ nanotubes/graphene composite", AIP Publishing, 2017 Publication	1 %
8	core.ac.uk Internet Source	1 %
9	www.mdpi.com Internet Source	1 %
10	Hamed Eskandarloo, Mazdak Hashempour, Antonello Vincenzo, Silvia Franz et al. "High-temperature stable anatase-type TiO ₂ nanotube arrays: A study of the structure-activity relationship", Applied Catalysis B: Environmental, 2016 Publication	1 %
11	Shinde, Pravin S., Jin Woo Park, Mahadeo A. Mahadik, Jungho Ryu, Jung Hee Park, Young-Joo Yi, and Jum Suk Jang. "Fabrication of efficient CdS nanoflowers-decorated TiO ₂ nanotubes array heterojunction photoanode by a novel synthetic approach for solar	<1 %

hydrogen production", International Journal of Hydrogen Energy, 2016.

Publication

12

Susanta K. Mohapatra, Narasimharao Kondamudi, Subarna Banerjee, Mano Misra. " Functionalization of Self-Organized TiO Nanotubes with Pd Nanoparticles for Photocatalytic Decomposition of Dyes under Solar Light Illumination ", Langmuir, 2008

Publication

<1 %

13

www.scientific.net

Internet Source

<1 %

14

Kang, Q.. "A ternary hybrid CdS/PtTiO² nanotube structure for photoelectrocatalytic bactericidal effects on Escherichia Coli", Biomaterials, 201004

Publication

<1 %

15

link.springer.com

Internet Source

<1 %

16

www.amrita.edu

Internet Source

<1 %

17

Ampelli, Claudio, Gabriele Centi, Rosalba Passalacqua, and Siglinda Perathoner. "Synthesis of solar fuels by a novel photoelectrocatalytic approach", Energy & Environmental Science, 2010.

Publication

<1 %

18

Hamid Omidvar, Saba Goodarzi, Ahmad Seif, Amir R. Azadmehr. "Influence of anodization parameters on the morphology of TiO₂ nanotube arrays", Superlattices and Microstructures, 2011

Publication

<1 %

19

Liu, Y.. "Preparation of short, robust and highly ordered TiO₂ nanotube arrays and their applications as electrode", Applied Catalysis B, Environmental, 20091109

Publication

<1 %

20

iopscience.iop.org

Internet Source

<1 %

21

www.ncbi.nlm.nih.gov

Internet Source

<1 %

22

Kamel Eid, Mostafa H Sliem, Aboubakr M Abdullah. "Tailoring the Defects of Sub-100 nm Multipodal Titanium Nitride/Oxynitride Nanotubes for Efficient Water Splitting Performance", Nanoscale Advances, 2021

Publication

<1 %

23

Zhu, W.. "An efficient approach to control the morphology and the adhesion properties of anodized TiO₂ nanotube arrays for improved photoconversion efficiency", Electrochimica Acta, 20110215

Publication

<1 %

Exclude quotes Off

Exclude matches Off

Exclude bibliography On

Photocatalytic Decomposition of Glycerol Solution on TiO₂ Nanotube Arrays (TNTA) doped with C and N to Produce Hydrogen

GRADEMARK REPORT

FINAL GRADE

/0

GENERAL COMMENTS

Instructor

PAGE 1

PAGE 2

PAGE 3

PAGE 4

PAGE 5
