Synthesis of TiO$_2$ Nanotube Arrays by Sonication Aided Anodization and Its Application for Hydrogen Generation from Aqueous Glycerol Solution

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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 µ m 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 TiO$_2$ 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 H$_2$ [2,3]. Furthermore, glycerol can serve as a hole scavenger/an electron donor that can increase the H$_2$ generation [3,4]. The amounts of H$_2$ 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 Eg. 1 [2,3,4]:

$$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2 \qquad (1)$$
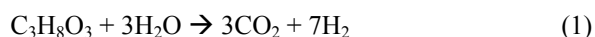
TiO$_2$ is the most suitable photocatalyst due to its photo-stability, photo-corrosion resistance, nontoxicity, availability and relatively cheap [3,5]. Morphology modifications to increase surface area and the addition of non-metal doping to enhance photo-responsive to solar spectra have been developed to minimize the drawbacks of TiO$_2$ [4,5,6]. Anodic oxidation of Ti foil produces TNTA that have larger surface area and provide superior electron – hole separation compared to the TiO$_2$ 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 NH$_4$F 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% H$_2$/Ar atmosphere at 500 ^{o}C for 3 h resulted in C, N, and F incorporation (as doping) in the TNTA [4,9]. Carbon was supplied by thermal

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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 an 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.
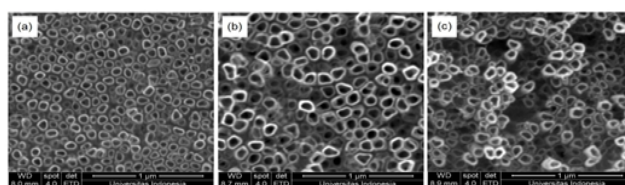

Figure 1. Top view FESEM image of (a) TNTA-U10, (b) TNTA-U30 and (c) TNTA-U60
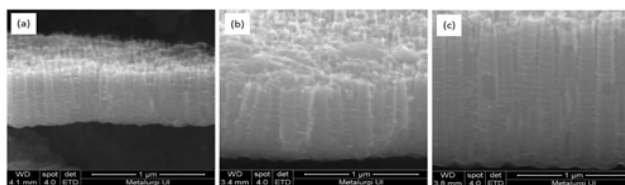

Figure 2. Cross view FESEM image of (a) TNTA-U10, (b) TNTA-U30 and (c) TNTA-U60.

**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

[a]average inner diameter,
[b]average wall thickness,
[c]average 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]

$$Ti + 2H_2O \rightarrow TiO_2 + 4H^+ + 4e^-. \qquad (2)$$
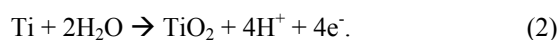
The mechanism of tube formation (chemical dissolution of TiO$_2$ film) due to F$^-$ ion is presented by the reaction that can be seen in Eq. 3 [6,8,12]

$$TiO_2 + 6F^- + 4H^+ \rightarrow [TiF_6]^{2-} + 2H_2O. \quad (3)$$
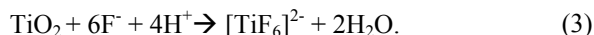
The two above processes determine the morphology and the growth rate of TNTA and it is influenced by water content in the electrolyte solution, applied voltage, temperature, electrolyte composition, concentration of fluoride, mode of agitation, anodization time, etc. [6]. In this study, the variation 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 $[TiF_6]^{2-}$ 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 H$_2$/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 H$_2$.
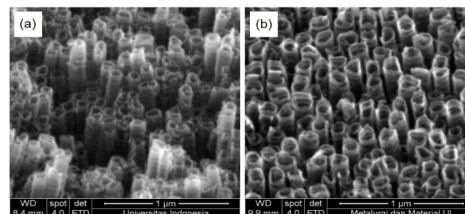

Figure 3. FESEM top view image with angle 45o of (a) TNTA-U60 and (b) TNTA-M60.

Photocatalytic hydrogen generation. Fig. 4 shows the effect anodization time toward the tube length of TNTA and H$_2$ production.
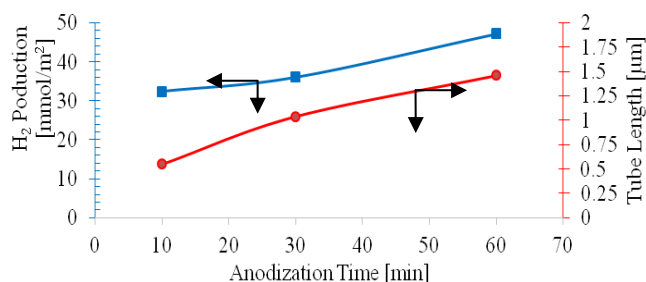

Figure 4. Effect of anodization time on the tube length of TNTA and H2 production.

The hydrogen generation for the 10; 30 and 60 min irradiation time were 32,43; 36,07 and 47,22 mmol/m^2 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 H$_2$ generation since TNTA can absorb more photon that result in higher photocatalytic reaction rate. Compare to the TNTA-M60 (produces 29.5 mmol H$_2$/m^2 photocatalyst), the TNTA-U60 provided more H$_2$ generation (produces 47.22 mmol H$_2$/m^2 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 TiO$_2$ to produce H$_2$ and CO$_2$ 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 TiO$_2$ and chemical dissolution of formed TiO$_2$ 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 H_2 production, indicate that reducing band gap energy of the produced TNTA occurred.

Acknowledgments

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