Photo-electrochemical properties of TiO$_2$ nanotube arrays: effect of different polishing method of Ti substrate prior to anodization in fluoride-H$_2$O$_2$-containing electrolyte

H Budiman$^{1,2}$, R Wibowo$^1$, O Zuas$^2$, J Gunlazuardi$^1$

$^1$Department of Chemistry, Faculty of Mathematic and Natural Science, Universitas Indonesia, Depok, 1640, Indonesia
$^2$Gas Analysis Laboratory, Metrology in Chemistry Research Group, Research Center for Metrology-Indonesian Institute of Science (RCM-LIPI), Tangerang Selatan, 15314, Indonesia

E-mail: jarnuzi@ui.ac.id

Abstract. The comparison of two pre-treatment methods, such as mechanical polishing and chemical polishing, prior to anodization of titanium surface in the ethylene glycol based electrolyte containing H$_2$O$_2$, were carried out to investigate their effects on photo-electrochemical property of produced highly ordered TiO$_2$ nanotube arrays (HOTNAs). The Ti-chemical polishing was conducted in electrolyte containing H$_2$O$_2$ (0.6% H$_2$O$_2$/1.4% H$_2$O). The prepared HOTNAs were characterized by FT-IR, UV-Vis DRS and SEM. The obtained FTIR spectrum, showed vibration band at 1100 and 425 cm$^{-1}$, give strong indication on the existent of a -Ti-O-Ti- network. While from UV-Vis DRS spectra, the band gap of the fabricated HOTNAs were found in the range of 3.10-3.22 eV, which are characteristics for anatase phase. In addition, obtained SEM image indicates the existence of quite good ordered nanotube arrays morphology. Linear sweep voltammetry (LSV) measurement showed that the steady state photocurrent density of HOTNAs fabricated by Ti-chemical polishing were greater than that of prepared by Ti-mechanical polishing. The increasing of H$_2$O$_2$ content in electrolyte (1.5% H$_2$O$_2$/3.5% H$_2$O) affected to the enhancement of steady state photocurrent density of HOTNAs. Thus pre-treatment of the Ti foils using chemical polish method does enhance its photo-electrochemical property.

1. Introduction
Highly Ordered TiO$_2$ nanotube arrays (HOTNAs) fabricated by electrochemical anodization (ECA) method has become great attention due to the ECA may produce HOTNAs with distinctive properties, such as high specific surface area, high electron mobility or quantum confinement effect, and high mechanical strength[1, 2]. With such distinctive properties, therefore, the HOTNAs have been widely used in many areas of applications including photocatalytic oxidation for degradation of organic pollutants[3], gas sensor[4], dye-sensitized solar cells[5], hydrogen generation by water photo catalysis (photo-splitting water)[6], photocatalytic reduction of CO$_2$[7] and biomedical-related application[8, 9].

In the ECA method, the formation of nanotube has been considerably affected by the initial surface conditions of Titanium (Ti) foils substrate [1]. A direct use of commercial Ti foils for the fabrication of HOTNAs without any pre-treatment (neither polishing nor cleaning) causes some disordered morphology on the top of nano array, lead to the formation of unexpected morphologies such as nanograin, collapsed, or bundled nanotube [1, 8]. Thus, in order to enhance the properties of HOTNAs, the formation nanotube with unexpected morphologies should be avoided [8]. Some studies related to the
effect of polishing on the growth of anodic TiO$_2$ nanotube have been previously reported [1, 8, 10,11] and most of the prepared HOTNAs were fabricated by anodization using ethylene glycol containing H$_2$O electrolyte. Meanwhile, Shibu and Sagayaraj reported that H$_2$O was found as powerful of oxidizing agent to rapidly anodic growth of TiO$_2$ nanotube. Thus, H$_2$O can be used as a better alternative for replacing H$_2$O in the anodization process [12].

To the best of our knowledge, no study has been reported regarding the effect of polishing method of Ti foil on the formation and photoelectrochemical of HOTNAs prepared in the ethylene glycol based electrolyte containing H$_2$O$_2$. Therefore, in this work, two methods for the surface pre-treatment of Ti foils including mechanical polishing (using abrasive paper) and chemical polishing (immersing in the acid mixture) were used prior to anodization using ethylene glycol based electrolyte containing H$_2$O$_2$ in the preparation of HOTNAs. In addition, their effects on photo-electrochemical properties of prepared HOTNAs were investigated. The prepared HOTNAs characterized by Fourier transform infrared (FTIR), UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS), and Scanning Electron Microscope (SEM).

2. Experimental Methods

2.1 Surface pre-treatment of Ti foil

The HOTNAs were fabricated by ECA of titanium foil (99.6% purity, Baoji Jinheng Metal Material Co) with a thickness of 0.3 mm. The Ti foils were cut into pieces with dimension of 35 mm x 10 mm. Before anodization, the Ti foils were first pre-treated by polishing to obtain an appropriate brittle, roughness, reflective and smooth surface. Two different methods of polishing of Ti foils were performed and compared in this study i.e., mechanical and chemical polishing. In the mechanical polishing (MP), Ti foils were polished using silica carbide paper (1500 cc, 2000cc). The Ti foils were then degreased by sonication sequentially in acetone, ethanol and deionized water for 10 minutes each and followed by drying in the air. For the chemical polishing (CP), Ti foils treated by mechanical polishing were immersed in a mixture acid solution of HF (40%, Merck) , HNO$_3$ (65%, Merck) and deionized water with 1:3:6 of volume ratio for 2 minutes[13]. Finally, the Ti foils were rinsed in deionized water and dried in air.

2.2 Fabrication of highly ordered titania nanotube arrays (HOTNAs)

The ECA was carried out in a two-electrode system with the Ti foil as an anode and the platinum foil (99.99% purity, Shanghai Chong Xin Electric Alloy Co) having the same dimension as that of Ti foil as a cathode. The distance between two electrodes was 15 mm. The pre-treated Ti foils were immersed (with exposed area of 1cm$^2$) in an electrolyte solution consisting of 0.3 wt% NH$_4$F (Merck) and the various concentration of H$_2$O$_2$ (30%, Merck) in 20 mL ethylene glycol. All of anodization were conducted at room temperature (approximately 23°C). A regulated direct current (DC) power supply (Kenwood Trio PR653) was employed as the voltage source to drive anodization at a constant potential of 30 V for 90 min. In addition, a controlled electrometer (Agilent model U1241) was connected in series with DC power supply to monitor generated current during anodization. The as-anodized samples were washed with deionized water and dried by the gently streaming of pure nitrogen gas. The as-prepared samples were HOTNAs with amorphous phase. In order to transform the HOTNAs into anatase phase, as-prepared samples were annealed at 450 °C for 2 h under atmospheric condition with heating and cooling rates 5 °C/min. The prepared HOTNAs produced from mechanical polished and chemical polished Ti foil were denoted as HOTNAs -MP and HOTNAs -CP, respectively.

2.3 Characterization of HOTNAs

To analyze the functional groups in the HOTNAs, Fourier Transform Infrared (FTIR) analysis (Shimadzu IR Prestige-21) was conducted by scanning the wavenumber in the range of 400-4000 cm$^{-1}$. Diffuse reflectance UV-Vis adsorption spectra were recorded using a spectrophotometer (Shimadzu, 2450 type) at wavelength ranging from 200 to 900 nm with fine BaSO$_4$ powder as reference. The
morphologies of TNTAs were examined by field emission scanning electron microscope (FESEM, JEOL JIB-4610F) at accelerating voltage of 15 kV.

2.4 Photoelectrochemical performance of HOTNAs
Photoelectrochemical (PEC) response of HOTNAs were investigated using a three-electrode electrochemical system consisting of quartz cell (height: 50 mm, diameter: 30 mm), and three electrode configuration with HOTNAs as a working electrode, Ag/AgCl (3 M KCl) electrode as reference electrode, and Pt foil as a counter electrode. The working electrode with an irradiated area 10 mm x 10 mm was immersed in 0.1 M NaNO₃ as supporting electrolyte. All three electrodes in the cell were connected to a electrochemical workstation (eDAQ, model ED401) to control the potentials of the photoelectrode and record all generated photocurrent. The photocurrent was measured under irradiation from UV (11 W UV lamp/black light, GNB model, 365 nm) and visible source light (75 W tungsten lamp, 350-800 nm). Linear sweep voltammetry was conducted with a voltage scan speed 100 mV s⁻¹ ranging from -1.0 to 1.0 V.

3. Results and Discussion

3.1 Physical appearance of pre-treated Ti foil
The difference of between untreated Ti and pre-treated Ti foil using mechanical (MP) and chemical polishing (CP) method can be visually observed, as can be seen in Figure 1.A. Chemical polished Ti foil had a smoother with mirror-like surface than mechanical polished Ti foil, as shown in Figure 1.A. In addition, Figure 1.A shows that untreated Ti foil had a duller surface than pre-treated Ti foil indicating the presence of adhesive layer of native TiO₂ on the Ti foil surface[14, 15].

3.2 Mechanism of TiO₂ nanotube formation
In order to get better understanding the formation mechanism of TiO₂ nanotube array, the current density versus time transient curve during the anodization process was plotted [16, 17] and the result, is shown in Figure 1.B. As it can be seen from Figure 1.B.d, the formation of TiO₂ nanotube characteristically involves three stages of the anodization process; I) the formation of a high resistance compact TiO₂ barrier layer, II) the formation of irregular nanopores penetrating to the TiO₂ layer, and III) the steady state growth of nanotube [12, 16, 18, 19].

![Figure 1](image_url)

Figure 1. (A) Visual appearance of untreated (a) and pre-treated Ti foil: mechanical polished (b), chemical polished (c); (B) Anodizing current time density-time plot recorded during anodization of Ti foils (different pre-treatment, chemical polish: CP and mechanical polish: MP) at 30 V for 90 minutes in electrolyte with different of H₂O₂ content. The inset is magnification view in range 0-1000 s
3.3 Effect of pre-treated Ti foil in the formation of HOTNAs by anodization

Figure 1.B shows a typical curve of the HOTNAs formation obtained from anodization of pretreated Ti foil by mechanical and chemical polishing. Region II (stage for the transformation of compact layer into porous layer) in the curve of formation of HOTNAs-MP was not clearly observed when anodization was performed using the EG electrolyte with the 0.6% H2O2/1.4% H2O content, as depicted in Figure 1.B.a. However, region II in the curve of HOTNAs-MP was obviously formed when the concentration H2O2/H2O in EG electrolyte was increased into 1.5% /3.5%, as described in Figure 1.B.b. These phenomena occurred might be due to the mechanical polishing pre-treatment was not able to entirely remove the native oxide (TiO2) film on the surface of Ti foil. As reported by Liu et al., titanium metal and its alloy are commonly encapsulated by a native oxide film of TiO2 [15]. This native oxide film of TiO2 is a protective and stable layer (thickness in the 3-10 nm range) on the surface of Ti foil that probably interfere the anodization process [14]. The presence of native oxide film of TiO2 on the surface of Ti foil is due to the nature of the native incipient-air-formed oxide film resulted by the exposure of Ti foil to the ambient environment [20].

In contrast to the curve of formation of HOTNAs-MP, region II can be visibly observed in the formation of HOTNAs-CP by anodization in electrolyte containing 0.6% H2O2/1.4% H2O or 1.5% H2O2/3.5% H2O, as shown in Figure 1.B.c and 1.B.d, respectively. It indicates that the process of the formation porous layer did not inhibited by the presence of native oxide film on Ti foil surface. In other words, native protective oxide film was completely removed from the surface of Ti foil by the chemical polishing pre-treatment. Some authors reported that the chemical polishing can renew the Ti foil surface by removing the adhesion layer of native oxide and generate smoother of the Ti foil surface [21, 22]. The smooth surface of Ti foil leads to producing of a better mechanical strength of TiO2 nanotube preventing the detachment of TiO2 nanotube film from the Ti substrate [22]. Moreover, as it can be seen in Figure 2, steady state of anodizing current density for the formation of HOTNAs-CP (Figure 1.B.c-d) was found to be higher than HOTNAs-MP (Figure 1.B.a-b). The higher anodizing current density was probably attributed by the formation of porous layer in HOTNAs-CP with larger of surface area than HOTNAs-MP. In addition, the higher current density indicates that a higher rate of chemical dissolution of TiO2 layer was occurred due to the formation of HO2- in anodization of Ti foil using electrolyte containing H2O2 [23].

3.4 SEM image of HOTNAs

The morphologies structure of prepared HOTNAs-1.2% H2O2/ 2.8% H2O-CP was described in Figure 2. As can be seen from Figure 2, a quite good highly ordered of TiO2 nanotube was formed in HOTNAs-1.2% H2O2/ 2.8% H2O-CP. The TiO2 nanotube had diameter, length, and wall thickness about 38.518 nm, 4.824 µm, and 16.296 nm, respectively, as shown in Figure 2. In addition, the pit holes (circle-dashed line) were also formed on the top of nanotubes layer with diameter 0.472 µm, as illustrated in Figure 2.a.

Figure 2. FESEM images of HOTNAs prepared by anodization Ti-CP in 1.2% H2O2/ 2.8% H2O +0.3% NH4F in ethylene glycol at 30 V for 90 minutes, a) surface view, b) cross section view.
3.5 FTIR analysis of HOTNAs
The existence of TiO$_2$ was confirmed by analysis of the functional groups in the HOTNAs sample using FTIR. FTIR spectra of amorphous HOTNAs is illustrated in Figure 3.h. The amorphous HOTNAs show FTIR peaks at 1620-1630 cm$^{-1}$ and 3100-3600 cm$^{-1}$ which correspond to the bending and stretching mode of hydroxyl groups, respectively. In particular, the broad peaks at ~3300 cm$^{-1}$ and the sharper bands at 1650 cm$^{-1}$ correspond to the OH stretching and the OH bending of free water, respectively. The FTIR peaks in the 3400-3600 cm$^{-1}$ region is assigned to –OH groups that is weakly attached to uncoordinated of Ti surface sites[24, 25], as depicted in Figure 3. After annealing process of as-prepared HOTNAs at 450ºC for 2 hours, the broad peaks at 3000-3700 cm$^{-1}$ (corresponding to Ti-OH) was disappeared and the peaks at 1100 and 425 cm$^{-1}$ that correspond to the vibration peaks of Ti-O-Ti were arisen, as illustrated in Figure 3. b-g.

![FTIR Spectra](image)

**Figure 3.** FTIR spectra of, a) Ti foil, b) 2% H$_2$O-MP, c) (0.6% H$_2$O$_2$/1.4% H$_2$O)-MP, d) (1.5% H$_2$O$_2$/3.5% H$_2$O)-MP, e) 2% H$_2$O-CP, f) (0.6% H$_2$O$_2$/1.4% H$_2$O)-CP, g) (1.5% H$_2$O$_2$/3.5% H$_2$O)-CP, h) As-prepared HOTNAs (amorphous)

In addition, FTIR spectra of as-prepared HOTNAs show the peak at 2840-3000 cm$^{-1}$ corresponding to alkyl –CH$_2$ and CH stretching that originate from EG residues [24]. The presence of carbon in as-prepared HOTNAs were also confirmed by the appearance of FTIR peaks at 1050 cm$^{-1}$, 1350 cm$^{-1}$ and 1450 cm$^{-1}$, as shown in Figure 3, which were assigned to the C-O stretching and C-H bending from EG electrolyte. These FTIR peaks demonstrate that carbonaceous species of the electrolyte are incorporated into HOTNAs [25]. The FTIR peaks for carbon functional groups cannot be observed in the annealed HOTNAs because the carbon residue from EG was completely decomposed at 450ºC.

3.6 UV-Vis DRS analysis of HOTNAs
A UV-Vis DRS analysis was carried out to investigate the optical bandgap of HOTNAs. The UV-VIS DRS spectra in Figure 4.A shows that the reflected light intensity enhanced in the region 300-400 nm. The increasing of reflectance intensity suggests the decreasing of light intensity adsorbed by TiO$_2$ material. Figure 4.A describes that as-prepared HOTNAs had the maximum absorbance in the UV region at $\lambda = 328$ nm.
From UV-VIS DRS spectra, the bandgap energy of HOTNAs were calculated using the Kubelka-Munk function and Tauc plots, as shown in Figure 4.A and 4.B. The calculated band gap energy for as-prepared HOTNAs was found to be 3.28 eV that is a typical bandgap value for amorphous TiO$_2$ in the range 3.2-3.5 eV[2]. The calculated of bandgap energy for annealed HOTNAs were 3.11 eV (HOTNAs-CP; 1.2%H$_2$O/2.8% H$_2$O$_2$), and 2.72 eV (HOTNAs-MP; 0.6% H$_2$O/ 1.4% H$_2$O). These bandgaps energy for annealed HOTNAs were shifted to smaller value (< 3.2 eV) compared with the as-prepared HOTNAs. It confirms that the amorphous HOTNAs was transformed to crystal phase after annealing.

3.7 Photoelectrochemical properties of HOTNAs

From the analysis by LSV measurement technique, photocurrent responses as a function of applied potentials (I-V curve) for HOTNAs-MP and –CP fabricated by anodization using electrolyte were evaluated under no illumination and illumination condition (UV, and visible light), as depicted in Figure 5. The photocurrent density describes the amount of excitation electrons (from valence to conduction band) that transport from working electrode (TiO$_2$ photoanode) to counter electrode (Pt) when the photoanode is illuminated with light (UV or visible). As it can be seen in Figure 5, the photocurrent of HOTNAs under dark condition and visible light illumination was approximately 0.09 mA/cm$^2$. This insignificant of photocurrent indicates that under dark condition and visible light illumination the HOTNAs was inactive and no photoreaction was occurred, implying that no photo-induced electron was produced. In the other hand, the photocurrent greatly improved when the voltage was increased from -0.5 to 1 V under UV light illumination. This phenomenon suggests that HOTNAs is a good photoresponse semiconductor for the transfer and decay of photo-induced electrons through the sample [17].

Figure 4. A) UV-visible DRS spectra, B) the corresponding Tauc plots for HOTNAs prepared from different pre-treated Ti foil and anodization using electrolyte with H$_2$O$_2$ content

Figure 5. Curve I-V (under illumination of UV light) of HOTNAs prepared from different pre-treated Ti foil and anodization using electrolyte with H$_2$O$_2$ content
The steady state of photocurrents density produced from the photoelectrochemical performance of HOTNAs can be observed in Figure 5. As can be seen in the Figure 5, photocurrent responses of HOTNAs-CP (0.6% H₂O₂/ 1.4% H₂O:0.382 mA/cm²; 1.5% H₂O₂/ 3.5% H₂O: 0.447 mA/cm²) were greater than HOTNAs-MP (0.6% H₂O₂/ 1.4% H₂O:0.327 mA/cm²; 1.5% H₂O₂/ 3.5% H₂O: 0.337 mA/cm²). It suggests that the chemical polishing on Ti foil lead the formation of highly ordered nanotube structure with the higher surface area. This higher surface area provided the greater of effective surface site of HOTNAs to adsorb UV-light for generating photo-induced electron/hole. In accord with the findings of Xing et al., the HOTNAs with a top porous layer and regular underneath nanotubes produced by using chemical polished Ti foil had better photoelectrochemical properties [11]. In addition, the enhancement of photocurrent response of HOTNAs were also occurred when the concentration H₂O₂ in electrolyte was increased from 0.6% H₂O₂/ 1.4% H₂O into 1.5% H₂O₂/ 3.5% H₂O, as can be observed in Figure 5. This improvement of photoelectrochemical performance of HOTNAs was probably happened in anodization using electrolyte with H₂O₂ due to the presence of H₂O₂ stimulating the faster formation of nanotube. The existence of H₂O₂ in electrolyte might triggered the formation of greater amount nanotube and longer structure of nanotube that lead more effective the adsorption of UV light by HOTNAs.

4. Conclusion
From this study, it can be concluded that a high steady state anodizing currents (SSAC) value can be obtained by using chemical polish method on Ti foil and EG electrolyte with H₂O₂ content when preparation of HOTNAs. In addition, the photoelectrochemical performance of the HOTNAS can be improved not only by pre-treating the Ti foils using chemical polishing method, but also by increasing the concentration of H₂O₂ in EG electrolyte used for the anodization process.

5. Acknowledgement
Authors would express the most gratitude to Hibah Tugas Akhir Doktor Universitas Indonesia (TADOK-UI 2018) and Sainstek 2018 grants from Ministry of Research Technology and Higher Education that support for funding this research.

6. References
[1] K. Lu, Z. Tian, and J. A. Geldmeier, 2011, Electrochim. Acta, vol. 56, pp. 6014–20.
[2] P. Roy, S. Berger, and P. Schmuki, 2011, Angew.Chem. International Edition, vol. 50, pp. 2904–39.
[3] A. B. Aritonang, H. Surahman, Y. K. Krisnandi, and J. Gunlazuardi, 2017, Mater. Sci. Eng., no. 012005, pp. 0–10.
[4] V. Galstyan, E. Comini, F. Gaglia, A. Vomiero, L. Borgese, E. Bontempi, and G. Sberveglieri, 2012, Nanotechnology, vol. 23, p. 235706.
[5] D. Kim, K. Lee, P. Roy, B. I. Birajdar, and E. Spiecker, 2009, Angew.Chem. International Edition, vol. 48, pp. 9326–29.
[6] H. Surahman, Y. K. Krisnandi, and J. Gunlazuardi, 2017, Int. J. ChemTech Res., vol. 10, no. 2, pp. 32–39.
[7] O. Zuaa, Y. K. Krisnandi, W. Wibowo, J. S. Kim, and J. Gunlazuardi, 2014, Adv. Mater.Res., vol. 896, pp. 134–140.
[8] K. F. Albertin, A. Tavares, and I. Pereyra, 2013, Appl.Phys. Lett., vol. 284, pp. 772–779.
[9] G. G. Bessegato, M. Valnice, and B. Zanoni, 2014, Modern Electrochemical Methods in Nano, Surface and Corrosion Science, In Tech.
[10] J. M. Macak, M. Jarosova, H. Sotha, 2016, J. Surf. Sci., vol. 371, no. 0001, pp. 1–18.
[11] J. Xing, H. Li, Z. Xia, J. Chen, Y. Zhang, and L. Zhong, 2014, Electrochim. Acta, vol. 134, pp. 242–8.
[12] S. Joseph and P. Sagayaraj, 2015, N. J. Chem.,
[13] R. Ratnawati, J. Gunlazuardi, and S. Slamet, 2015, Mater. Chem. and Phys., vol. 160, pp. 111–118.
[14] F. Variola, J. Yi, L. Richert, J. D. Wuest, F. Rosei, and A. Nanci, 2008, *Biomaterials*, vol. 29, pp. 1285–98.

[15] X. Liu, P. K. Chu, and C. Ding, 2010, *Mater. Sci.and Eng. R*, vol. 70, pp. 275–302.

[16] J. Song, M. Zheng, B. Zhang, Q. Li, F. Wang, L. Ma, and Y. Li, 2017, *Nano Micro Lett.*, vol. 9, no. 13, pp. 1–11.

[17] C. W. Lai and S. Sreekantan, 2011, *J. Nanomater.*, vol. 2011, pp. 1–7.

[18] Y. R. Smith, R. S. Ray, K. Carlson, B. Sarma, and M. Misra, 2013, *Materials*, vol. 6, pp. 2892–2957.

[19] R. Jin, M. Liao, T. Lin, S. Zhang, X. Shen, Y. Song, and X. Zhu, 2017, *Mater. Res. Exp.*, vol. 4, no. 6

[20] E. McCafferty and J. P. Wightman, 1999, *Appl. Surf. Sci.*, vol. 143, pp. 92–100.

[21] S. Chen, M. Liao, P. Yang, S. Yan, R. Jin, and X. Zhu, 2016, *RSC Adv.*, vol. 6, pp. 84309–84318.

[22] S. Zhang, Y. Li, P. Xu, and K. Liang, 2017, *Int. J. Electrochem. Sci.*, vol. 12, pp. 10714–10725.

[23] S. Sreekantan, C. Wei, and Z. Lockman, 2011, *J. Electrochem. Soc.*, vol. 158, no. 12, pp. 397–402.

[24] S. So, F. Riboni, I. Hwang, D. Paul, J. Hammond, O. Tomanec, R. Zboril, D. R. Sadoway, and P. Schmuki, 2017, *Electrochim. Acta*, vol. 231, pp. 721–31.

[25] G. Ali, H. J. Kim, J. J. Kim, and S. O. Cho, 2014, *nanoscale*, vol. 6, pp. 3632–37.