TiO$_2$ Nanotube Array Prepared by Anodization in Aqueous Electrolyte Containing Sodium Carboxyl Methyl Cellulose

L N M Z Saputri and J Gunlazuardi

Department of Chemistry, Mathematics and Natural Sciences, Universitas Indonesia, Depok 16424, Indonesia

jarnuzi@ui.ac.id

Abstract. TiO$_2$ nanotubes arrays (TNTAs) were produced on titanium foil by electro oxidation (anodization) based on aqueous electrolyte containing sodium carboxyl methylcellulose (Na-CMC) at various concentration and the applied anodization potential. In aqueous electrolyte, the concentration of Na-CMC showed significant influence in the formation of TiO$_2$ nanotubes. While little effect from the anodization potential was observed. The TNTAs, with very good nanotubes array morphology and photocurrent generation was successfully obtained under aqueous electrolyte containing 0.5% NH$_4$F and 2% Na-CMC. This obtained TNTAs films has slightly different inner tube diameter when prepared under different anodization voltages, these are 52 ± 4.08, 80 ± 3.48, and 79 ± 4.01 nm respected to 15, 20, 25 V applied potential, respectively. The best photocatalytic activity of TNTAs was observed on the TNTAs film that was prepared under 20 V, whereas this TNTAs film has biggest porosity (41.14 %) and smallest space depletion layer (4.34 nm) compare to other prepared TNTAs film. This result confirms that, narrower of the depletion layer, the separation of the charge on the surface of TNTAs and electrolytes will increase, thus the efficiency of photo conversion increases. Preparation of TNAs by anodization in aqueous electrolyte containing Na-CMC can be an alternative way that meet the environmentally friendly nature, in contrast to those current common way which is using an organic electrolyte.

1. Introduction

TiO$_2$ semiconductor have been widely used as photoelectrodes in water splitting application due to its high chemical and mechanical stability, strong catalytic activity, low price, and environmentally friendly nature. However, it has the energy conversion efficiency of photons into hydrogen in water splitting due to recombination-generation of electrons and holes, the rapid occurrence of back reactions (the combination of H$_2$ and O$_2$ into water) [1]. One way to overcome this problem is by engineering of the TiO$_2$ architecture into 1-dimensional structure such as nanorod [2], nanotubes [3], and nanowire [4]. Among the various morphological uniqueness of TiO$_2$, the highly organized TiO$_2$ nanotubes array attract may attentions due to its 1-D channel feature, which may provide excellent photon and chemical penetration to its active surfaces. The TNTAs are more vertically oriented and are able to form integrated surfaces due to they have a large surface area and have one-dimensional channels for charge transport, thereby recombining of electrons and holes can be minimized [5]. However, among these preparation methods, electrochemical oxidation (anodization) has been carried out, with a quite great success, since it was first introduced by Zwilling (1999) [6].

In the early development, they used aqueous solution electrolyte containing F$, but the obtained nanotubes were poorly organized and only had a few hundred nanometers in length. Later on,
researchers used an organic electrolyte containing fluoride ion and small amount of water, which gave a highly ordered nanotubes with a micrometer length [7]. Currently, most reported anodization methods in preparing TiO₂ nanotube films were using electrolyte containing ethylene glycol, fluoride ion, and small amount of water. Because of the excellent characteristics of nanotubes based on organic electrolyte mentioned above, but due to more consideration to environmentally friendly processes, many researchers have been investigating deeper studies on this matter. The use of organic electrolytes is more expensive and less environmentally friendly than aqueous electrolytes.

Recent report reveal that researchers had the opportunity to develop the preparation method of TNTAs in aqueous electrolytes, which produced a well organized and highly ordered nanotubes. Ocampo et al. (2019) reported the used of sodium carboxymethylcellulose (Na-CMC), in the aqueous electrolyte, resulting more controllable viscous electrolyte [8]. The advantages of Na-CMC such as low price, non-toxic and environmentally friendly nature [9]. It was found that the higher the viscosity of the electrolyte the larger the interpore distance and the lower the oxide growth rate. Therefore, in this study, an attempt to obtain more efficiently preparation method and provide more discussion about how the variation Na-CMC concentration and anodization potential affect the diameter and porosity of nanotubes. In large porosity can ensure a much shorter hole diffusion path toward wall surface and accelerate ion migration in the tube to enhance the PEC water splitting efficiency of the TNTAs. A relationship of TiO₂ nanotubes morphologies and its photocatalytic activity of TNTAs, in term of generated photocurrent will also be discussed.

2. Experimental

2.1. Preparation of TNTAs

The preparation of TNTAs was conducted according to work of Ocampo et al., 2019 [8]. The Ti foil (4 cm x 1.5 cm x 0.02 cm) was first mechanically polished with sand papers 1500 and 1000 grits then sonicated with acetone and ethanol solution for 10 minutes, respectively, then rinsed with distilled water, and dried. The anodization was carried out in a two-electrode configuration, where Ti foil acts as an anode and stainless-steel foil as a cathode. The distance between the anode and the cathode was 1.5 cm. The anodization was prepared in an aqueous electrolyte solution containing sodium carboxymethylcellulose (CMC), at concentration variation of 0.5%, 1%, and 2%, and 0.5% NH₃F, while the initial pH of the solution was maintained at pH=5, which was adjusted by the addition of H₃PO₄. The electro oxidation potentials were varied between 10-25 V for 2 hours. When the anodizing process completed, the sample was washed with distilled water and dried in the air. The sample was then calcined at 450°C.

2.2. Characterization of the TNTAs

The morphology of TNTAs films were characterized by field emission scanning microscopy (FESEM) analysis. While, the photo electrochemical characterizations were conducted in a quartz-glass container equipped with a three electrodes system, namely the working electrodes (TNTAs), reference electrodes (Ag/AgCl), and platinum counter electrodes, in 0.1 M Na₂SO₄ electrolytes. The photo electrode performance was carried out by measuring photocurrent vs potential bias by the linear sweep voltammetry method.

3. Result and discussion

3.1. Anodization of TiO₂ nanotubes (TNTAs)

a. Various CMC concentration

In stage I, the process begins with an instant increase in current density then rapidly decrease (S₁) from 7.2 mA/cm² to 2.67 mA/cm² in 170 seconds [Fig.1(a)-1% CMC], 7.67 mA/cm² to 3.83 mA/cm² in 170 seconds [Fig.1(a)-1.5% CMC], and 7.33 mA/cm² to 4.17 mA/cm² in 110 seconds [Fig.1(a)-2% CMC], which was occurred in the anodizing process in aqueous electrolyte containing F⁻, and CMC at concentrations of 1%, 1.5%, and 2%, respectively. Decreasing in current density indicated the formation of a TiO₂ oxide layer as a boundary layer [10] which caused the inhibition of ion and electron flow,
therefore the current and potential between the titanium metal and electrolyte decreased. It was also said when the pore nucleation occurred and the barrier layer continued to grow until reached the \(J_{\text{min}}\) value \cite{11}. In the stage II, there is increasing current density from 2.67 mA/cm\(^2\) to 2.83 mA/cm\(^2\) in 180 seconds \[\text{Fig.1(a)}\] 1% CMC, 3.83 mA/cm\(^2\) to 4.50 mA/cm\(^2\) in 180 seconds \[\text{Fig.1(a)}\] 1.5% CMC, and 4.17 mA/cm\(^2\) to 5.17 mA/cm\(^2\) in 240 seconds \[\text{Fig.1(a)}\] 2% CMC, that occurred in anodization process in aqueous electrolyte containing F\(^-\), and CMC at concentration of 1%, 1.5%, and 2%, respectively. Increasing in current due to small holes were formed as a result of breaking Ti and O bonds by an electric field that produce complex [TiF\(_6\)\(^2-\)].

In stage III, the equilibrium was maintained as the anodizing time increases while the current decreases slightly due to changes pore depth in the tubes. This process produced nanotubes that grow vertically. The slope of the curve indicates the beginning of a new stage (S\(_{\text{III}}\)) in the process of nanotube formation, where nanotubes begin to grow along with this process. Apolinaro et al. \cite{11} defined nucleation time as: \(t_n = t_{\text{III}} - t_{\text{II}}\), where \(t_{\text{III}}\) and \(t_{\text{II}}\) are the time to reach S\(_{\text{III}}\) and S\(_{\text{II}}\), respectively. According to his work, nucleation time is directly related to the level of ordering and uniformity of nanotubes, thus, the higher the nucleation time can produce better tubes. Referring to Table 1, the \(t_n\) obtained is in agreement with the observed results in Figures 1(b), that are 730 and 1150 seconds, which was achieved in an electrolyte containing 1.5% and 2% Na-CMC. While as shown in Table 1 and Figure 1(b), at Na-CMC concentration of 1%, the \(t_n\) was about 610 seconds, and the related nanotubes film was less uniformity and regularity. Although, the results show a little bit differences, but it is clearly that the tubes array was observed in the film, which was processed with 2% Na-CMC [Fig.1(b)].

![Figure 1](image1.png)

\textbf{Figure 1.} (a) Current density profile and (b) SEM images show morphologies of TNTAs prepared by anodization in aqueous electrolyte containing 0.5% NH\(_4\)F and Na-CMC at various concentrations, these were 1%, 1.5%, 2% at 20 V applied potential.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
Aqueous electrolyte in various CMC concentration (%) & \(t_1\) (s) & \(t_{\text{II}}\) (s) & \(t_{\text{III}}\) (s) & \(t_n\) (s) \\
\hline
1 & 170 & 180 & 780 & 610 \\
1.5 & 170 & 180 & 900 & 730 \\
2 & 110 & 240 & 1200 & 1150 \\
\hline
\end{tabular}
\caption{Times of different stages observed during anodization}
\end{table}

\textit{b. Various potential anodization}
Profiles of current density during the anodizing process (0.5% NH4F, 2% CMC in aqueous electrolyte), with the potential variations of 10, 15, 20, and 25 V, are shown almost the same pattern (Figure 2(a)). The current density was increasing along with increasing of anodization potential. Higher anodizing potential increased the driving force for ionic transport through the boundary layer at the bottom of the pore (Ti/TiO2 interface) to the Ti metal, this process lead to increases the diameter and length of the nanotubes [12]. However, the current density profile at 25 V voltage did not show decreasing profile (S1) and increasing profile (S2) of current density that indicated that the tubes have not yet been formed or organized. This phenomenon was supported by the results of the calculation of the inner diameter of TNTAs by 52 ± 4.08 nm, 80 ± 3.48 nm, and 79 ± 4.01 nm at voltage of 15, 20, and 25 V where decreasing in inner diameter of TNTAs at 25V. Figure 2(b) shown the SEM morphology of TNTAs with potential anodizing variations. The SEM of TNTAs anodized at 10 V do not show the pores (Figure 2(b)-10V), while for those that was being anodized at 15-25 V clearly show the tubular structures (Figure 2(b) at 15-25 V). Higher anodizing potential increases the migration of O2- ions towards the metal substrate Ti and Ti4+ ions towards the electrolyte, therefore the oxidation process rate was faster and the formed oxide layer was thicker [13].

![Figure 2.](image)

**Figure 2.** (a) Current density and (b) SEM images show morphology of TNTAs, prepared by anodization in aqueous containing 0.5%NH4F and 2% Na-CMC at various anodization potentials: (a) 10 V (b) 15 V (c) 20 V (d) 25 V

### 3.2. The relation of morphological synthesis and photocatalytic activity of TNTAs

The porosity parameters that affected by the wall thickness and the inner diameter of the tubes can be calculated according to the Equation 1:

\[
P = 1 - 2\pi W(W + D)/(\sqrt[3]{2}(D + 2W)^2)
\]

where W is the wall thickness and D is the diameter of the tubes.

### Table 2. Wall thickness, inner diameter, and porosity of prepared TNTAs film.

| Sample Anodization Conditions | Wall Thickness, W (nm) | Inner diameter, D (nm) | Porosity (%) |
|------------------------------|------------------------|------------------------|--------------|
| 0.5% NH4F, 2% CMC, 15 V      | 29.07                  | 56.08                  | 31.21        |
| 0.5% NH4F, 2% CMC,20 V       | 28.75                  | 83.48                  | 41.14        |
| 0.5% NH4F, 2% CMC, 25 V      | 40.59                  | 83.01                  | 35.54        |
According to Suzhen Liang et al. the porosity are parameters that play a role in determining photocatalytic activity in which the efficiency of photoconversion increases with increasing porosity values [14]. Based on the calculation results obtained, the widest porosity is 41.14%, which achieved when it as anodized in 0.5% NH4F, 2% CMC, at 20 V.

3.3. Photoelectrochemical behavior of TNTAs

A photoelectrochemical testing is needed to study the properties of semiconductor-electrolyte interfaces, especially the properties of TiO2 in electrolytes. The photo electrochemical technique that provide photocurrent vs potential profile can be applied to get insight of a meaningfully photo electrocatalytic properties. The photo current vs bias potential profile obtained, i.e. flat band and steady state potential, can be applied to deduce the space charge layer depletion of the TiO2 nanotubes electrode (Figure 3). The space charge layer produced, at the semiconductor-electrolyte interface, may play an important role, due to it is the site of the charge separation process. The space charge layer is the place for electron charge in the semiconductor system in contact with the electrolyte. The space charge layer can be obtained from Equation 2:

\[
d_{sc} = \sqrt{\frac{2\varepsilon\varepsilon_0(U - U_{fb})}{qN_D}}
\]  

where \(\varepsilon\) is dielectric constant, \(\varepsilon_0 = 8.854 \times 10^{-12} \text{ F/m}\) vacuum dielectric constant, \(U\) is bias potential, \(U_{fb}\) is flat-band potential, \(q = 1.602 \times 10^{-19} \text{ C}\), and \(N_D\) is donor density. The value of \(\varepsilon\) and \(N_D\) are 85 and 6x10^{19} \text{ cm}^{-3}, respectively.

Table 3. Flat band & steady state potentials, and space charge layer of prepared TNTAs

| Anodization Conditions | Potential flat band, \(U_{fb}\) | Potential steady state, \(U\) | Space charge layer, \(d_{sc}\) (nm) |
|------------------------|-------------------------------|------------------------|-------------------------------|
| 0.5% NH4F, 1% CMC, 20 V | -0.97                         | -0.806                 | 5.04                          |
| 0.5% NH4F, 1.5% CMC, 20 V | -0.98                         | -0.834                 | 4.75                          |
| 0.5% NH4F, 2% CMC, 20 V | -0.99                         | -0.868                 | 4.34                          |
| 0.5% NH4F, 2% CMC, 10 V | -0.96                         | -0.578                 | 7.69                          |
| 0.5% NH4F, 2% CMC, 15 V | -0.954                        | -0.826                 | 4.45                          |
| 0.5% NH4F, 2% CMC, 25 V | -0.986                        | -0.834                 | 4.85                          |

**Figure 3.** Photocurrent density produced by prepared TNTAs by anodization in aqueous electrolyte containing 0.5% NH4F and Na-CMC at (a) various Na-CMC concentration and (b) various anodization potential from the TNTAs prepared with 2% Na-CMC in electrolyte.
The TNTAs space charge value for each treatment variation were shown in Table 3. The space charge layer was considered as the area where the electron charge in the semiconductor will interact with the electrolyte solution. The value of the space charge layer was inversely proportional to the value of the resulting photocurrent. To obtain TNTAs with high photocatalyst activity, a small space charge layer is needed due to the small width of the depletion layer, thus separation of charge on the surface of TNTAs and electrolytes will increase [15]. Based on the calculation employing Equation 2, the obtained smallest space charge layer was 4.34 nm which was achieved at anodization condition with 0.5% NH₄F TNTAs, 2% CMC, 20 V.

4. Conclusion
TiO₂ nanotubes arrays (TNTAs) film was successfully produced on to titanium metal surface by anodization in an aqueous electrolyte containing fluoride ion and sodium carboxyl-methylcellulose (CMC). The addition of CMC in aqueous electrolyte may control the fluoride ion diffusion, thus maintaining the balance of oxide formation and its dissolution, hence provide regular and uniform nanotube array. At low Na-CMC concentration (1%) the obtained tubular structures were less regular, on the other hand at higher Na-CMC concentration the good uniformity and regularity nanotubes array were observed, where under current investigation 2% Na-CMC gave the best result. The inner diameter of the nano tubes were depend on the bias potential applied during anodization, whereas at 15, 20, and 25 V the observed inner diameters were 52 ± 4.08, 80 ± 3.48, and 79 ± 4.01 nm respectively. The best photocatalytic activity, in term of photocurrent produced, was obtained by the TNTAs film, which was prepared under aqueous electrolyte and bias potential condition of 0.5% NH₄F, 2% CMC, and 20 V, and this TNTAs showed best porosity (41.1%) and smallest depletion layer (4.34 nm) compare the other TNTAs film. This result confirmed that, more narrow of the depletion layer, the separation of the charge on the surface of TNTAs and electrolytes will increase, thus the efficiency of photoconversion increases.

Acknowledgment
This work is financially supported by Indonesia Endowment Fund for Education, Ministry of Finance of The Republic of Indonesia (Saputri), and PDUPT-RISTEKDIKTI research grant.

References
[1] Dholam R, Patel N, Adami M, Miotella A 2008 Int. J. Hydrogen Energy 33 6896-903
[2] Chen X and Samuel S M 2007 Chem. Rev 107 2891-2956
[3] Gopal M K, Shankar K, Paulose M, Varghese O K, and Grimes C A 2006 Nano Lett. 6 215-218
[4] Ming X, Da P, Wu H, Zhao D, and Zheng G 2012 Nano Lett. 12 1503-1508
[5] Sun Y, Yan K P 2014 Int. J. Hydrogen Energy 39 11368-11375
[6] Zwilling V, Darque-Ceretti E, Boulty-Forveille David D, Perrin M Y, Aucouturier M 1999 Surf. Interface Anal. 27 629-637
[7] Shankar K, Mor G K, Prakasham H E, Yoriya S, Paulose M, Varghese O K 2007 Nanotechnology 18 06570.
[8] Ocampo R A and Felix E E 2019 App. Surf. Sci. 469 994-1006
[9] Wong T W, Ramli N A 2014 Carbohydr. Polym 112 367-375
[10] Indira K, Mudali U K, Nishimura T, Rajendran N 2015 J. Bio-Tribo-Corrosion 1:28.
[11] Apolinario A, Quiterio P, Sousa C T, Ventura J, Sousa J B, Andrade L 2015 J. Phys. Chem. Lett. 6 845-851
[12] Zhang Q, Wang L, Feng J, Xu H, and Yan W 2014 Phys. Chem. Chem. Phys. 16 23431-23439
[13] Allam N K, and El-Sayed M A 2010 J. Phys. Chem. C 114 12024-12029
[14] Liang S, He Jingfu, Sun Z, Liu Q, Jiang Y, Cheng H, He Bo, Xie Z, and Wei S 2012 J. Phys. Chem. C. 116 9049-9053
[15] Wojciech J, Ste, pniowski, Marcin M., Malgorzata N., Marta M-D. Electrochimica Acta 211 453-460