

In-situ Generation of Radicals in Photocatalytic Reactor with TiO₂ Nanotube Plate

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ABSTRACT

A photocatalytic reactor employing TiO₂ nanotubes grown on Ti plate was designed and operated. In order to synthesize TiO₂ nanotubes on a Ti plate, self-organized oxide nanotube layers were grown by anodization in a glycerol based electrolyte. The ultimate conditions for the synthesis of the TiO₂ nanotube array on the Ti plate were investigated by comparing the morphology, length, and inner diameter of the nanotubes. They were significantly affected by the applied anodic voltage, anodization time, and composition of the electrolyte such as the water and fluoride ion concentration. The photocatalytic reactor used in this study consisted of two parallel and closely spaced TiO₂ nanotube plates. The plates were squares while a UV lamp was inserted perpendicularly to them. OH radical generation in the photocatalytic reactor was monitored by using a probe compound, para-chlorobenzoate (pCBA). The longer the nanotubes, the higher the steady state OH radical concentration.

Keywords: OH radical, photocatalytic reactor, TiO₂ nanotube, anodization

1. INTRODUCTION

In recent years, photocatalytic oxidation processes have shown great potential as a low-cost, environmental friendly treatment technology in the water and wastewater industry [1, 2]. This oxidation technology has been widely demonstrated to have the ability to remove persistent organic compounds and microorganisms in water [3, 4]. The rationale for this advanced oxidation technology is based on the in-situ generation of highly reactive transitory species (i.e. OH[•], H₂O₂, O₂[•], O₃) for oxidation of refractory organic compounds and disinfection of water pathogens. For photocatalysis, semiconductor catalysts (TiO₂, ZnO, Fe₂O₃, CdS, GaP, and ZnS) have demonstrated their efficiency in degrading a wide range of refractory compounds or mineralizing them into carbon dioxide and water [5, 6].

Recent researches have moved toward the use of nanostructures of TiO₂ such as nanotubes. The unique properties of the high aspect ratio of TiO₂ nanotubes include a large surface area, high cation exchangeability, high catalytic activity, easier separation, and recyclability [7]. These advantages make nanotubes attractive for industrial-scale applications. TiO₂ nanotubes with an ordered arrangement and high aspect ratio can be produced by using the electrochemical anodization method. Basically, TiO₂ nanotubes grow on the surface of the anode of titanium foils or thin sheets. However, it was reported that TiO₂ nanotube grown on titanium foils or thin sheets can be easily peel-off from under lying Ti substrate. Ali et al. [8] tried to fabricate

nano-porous structures on Ti foils using two-step anodizing method. TiO₂ nanotubes covered with a few nanometer thin nano-porous layer was produced when the first and the second anodization was carried out in the same electrolyte. However, the second-step anodization was conducted in a more viscous electrolyte and for longer anodization time when compared to the first one.

In this study, TiO₂ nanotubes were grown on the surface of titanium plate instead of foils or thin sheets by using electrochemical anodization. The dimensions of nanotubes formed can be controlled by applying different electrolyte compositions, applied voltages, pH levels, and anodizing durations. The factors affecting the dimensions of nanotubes grown on the titanium plate were investigated. In order to test the photocatalytic activity, the Ti plate with TiO₂ nanotubes was installed in parallel and closely spaced in a photocatalytic reactor. OH radical generation was monitored when titanium plates with different nanotube dimensions were installed in the photocatalytic reactor.

2. MATERIALS AND METHODS

2.1 Electrochemical synthesis of TiO₂ nanotube array on Ti plate

A Ti plate (99.5% purity, 1 mm thick) was cut into pieces with dimensions of 2.5 cm × 3 cm. Before anodization, the Ti plate was degreased by ultrasonication in a mixture of acetone and ethanol for 10 min, followed by washing with DI water and drying at room temperature. Electrochemical anodization was carried out in a two-electrode cell using a power source (AMETEK XG150-10), where the Ti plate was used as the anode and a platinum mesh was used as the counter electrode. The anodizing process was carried out under a voltage from 30 to 80 V in electrolyte. A glycerol solution containing ammonium fluoride (0.1- 0.5 wt%) was used as the electrolyte. H₂O addition was varied from 1 to 5 vol%. The anodization was performed in a bath controlled at room temperature. After a certain period of anodization (5~20 h), the Ti plate was immediately washed with DI water and subsequently dried. To induce the crystalline phase, the anodized Ti plate was annealed at temperatures from 300 to 600 °C in air for 3 hours.

2.2 Photocatalytic reactor with TiO₂ nanotubes

The photocatalytic reactor (4 × 4 × 4 cm) consists of a number of parallel and closely spaced TiO₂ nanotube plates. The TiO₂ nanotube plates are squares while the UV lamp is inserted perpendicularly to them. Figure 1 shows the photocatalytic reactor with one LED lamp (Sankyo Denki G8T5, 8W) emitting

UV (253 nm) light and a square configuration. Two TiO₂ nanotube plates (4 × 4 cm) were spaced 2 cm apart in the photocatalytic reactor. The intensity of light was 44 mW cm⁻². The photocatalytic experiments were carried out in a batch mode and at room temperature (approximately 22 °C). The sample was taken from the top of the reactor.

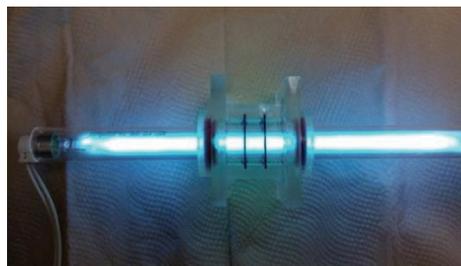


Figure 1. Schematic diagram of photocatalytic reactor

2.3 OH radical monitoring in the photocatalytic reactor

To determine the concentration of OH radicals, an experimental approach using an OH radical probe compound was adopted in this study. The method is based on the measurement of a probe compound, which reacts rapidly with OH radicals. The selected probe compound is para-chlorobenzoate (*p*CBA), which reacts with OH radicals with a second-order rate coefficient $k_{(OH, pCBA)} = 5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ [9]. Prior to each experiment, *p*CBA was added to the photocatalytic reactor to yield a concentration of 0.5 μM. The probe compound, *p*CBA, was measured by HPLC (Younglin, Korea). A C18 reverse phase column (XTerra Rp-18 reverse-phase column (5 μm, 150 mm × 2.1 mm) was used with a UV detector (Gilson Co., 151 UV/VIS, USA) at 230 nm to measure the *p*CBA concentration. The concentration of the *in situ* probe compound was monitored by HPLC (using a 55% methanol, 45% 10 mM H₃PO₄ buffer eluent (pH 2) at 1 mL/min and UV-detection at 234 nm) as described previously [9].

3. RESULTS AND DISCUSSION

3.1 Electrochemical synthesis of TiO₂ nanotube array on Ti plate

During electrochemical synthesis, the crucial key factors to achieve an arrangement of nanotubes are the applied anodic voltage, anodization time, and composition of electrolyte. In order to find the ultimate conditions for the synthesis of TiO₂ nanotube arrays, the effect of the applied voltage was investigated while keeping the composition of electrolyte constant. Experiments were performed in a non-aqueous electrolyte solution containing 0.2 wt% NH₄F and 2 vol% H₂O in ethylene glycerol. Applied voltages were kept at 30, 40, 50, 60, 70, and 80 V for 15 hours. Current–time curves during the first 5 minutes of anodization are shown in Fig. 2. At the beginning of anodization, the current decreases with time. During the first drop of current density, a perforated and porous oxide layer is formed, and finally the current density drops to a steady value while a self-organization process creates a highly

ordered oxide structure [9]. At 30 V, the current decreases, stays at zero for 200 seconds, and then increases to a steady value. When the applied voltage increases to 50 V, the current decreases not to zero but to a steady value. The current transient curves were also reported in NH₄F-containing electrolyte during anodization [10]. In that work it was observed that the current dropped slowly in the initial phase and then rose again after the initial decay. This finding was ascribed to the dissolution of the electrochemically formed TiO₂ as soluble hexafluorotitanium complexes [TiF₆]²⁻, which go into solution. In NH₄F-free electrolyte, however, the extended anodization resulted in a steady-state value that represented leakage through a compact oxide layer. In this electrolyte, non-porous structures were observed on the surface.

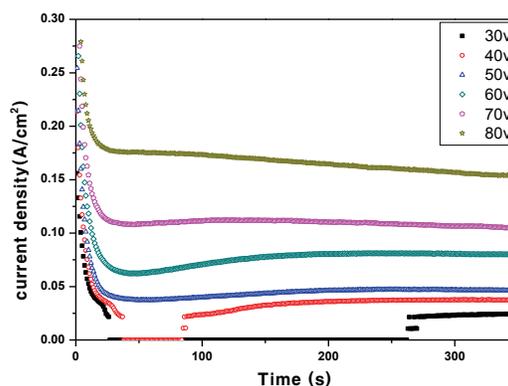


Figure 2. Current–time curve obtained during the first 5 minutes of anodization of titanium plate in glycerol electrolyte containing 0.2 wt% NH₄F and 2 vol% H₂O at different applied anodic voltages

Figure 3 shows the morphology of self-ordered TiO₂ nanotube arrays prepared at different applied voltages. Nanotube structures were dominant on the surface when the voltage was raised to 30 V and the inner diameter of the tube was 79 nm. An increase of the applied voltage produced larger nanotubes and increased the surface density and length of the nanotube array. Table 1 shows that the thickness of the oxide layer continues to increase with increasing anodizing voltage. Prakasam et al. [11], who also examined nanotube formation in ethylene glycol (EG)-based electrolytes, reported that, with an anodization time of 17 hours in EG electrolyte containing 0.3 wt% NH₄F and 2 vol% H₂O, the higher the anodizing voltage (20–65 V), the longer the resulting nanotube length (5–105 μm). Table 1 summarizes our observations at different applied voltages ranging from 30 to 80 V. The resulting nanotube array lengths were found to increase from 7.5 to 84.7 μm during 15 hours of anodization. As the applied voltage increases, the inner diameter of the nanotubes is also shown to increase from 79 to 178 nm.

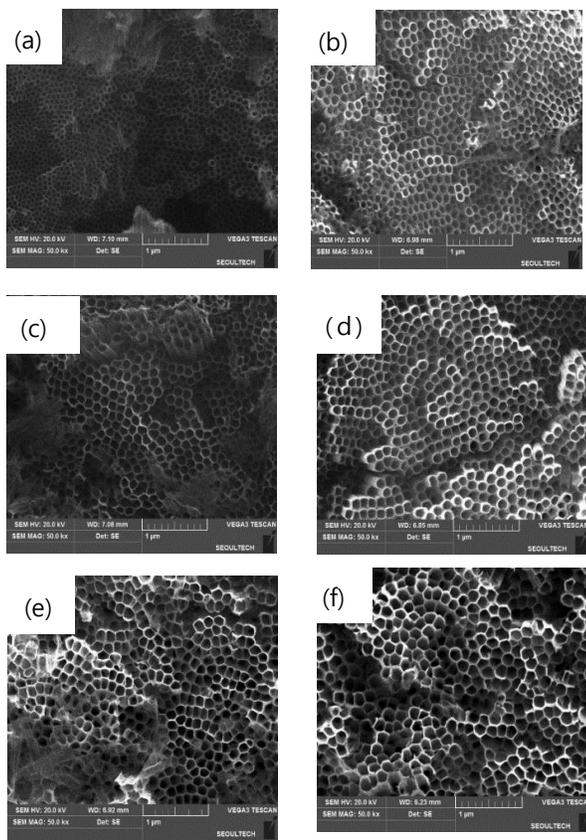


Figure 3. SEM images showing topology of a Ti plate sample anodized in an electrolyte comprised of 0.2 wt% NH₄F and 2 vol% H₂O in ethylene glycol: (a) 30 V, (b) 40 V, (c) 50 V, (d) 60 V, (e) 70 V, and (f) 80 V.

Table 1. Summary of length and inner diameter of TiO₂ nanotubes obtained at different applied anodic voltages after 15 hours of anodization in an electrolyte containing 0.2 wt% NH₄F and 2 vol% H₂O

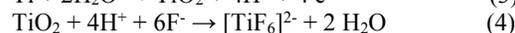
Voltage	Nanotube length (μm)	Inner diameter (nm)
30	7.5	79
40	10.9	110
50	18.3	120
60	40.1	136
70	52.3	167
80	84.7	178

Anodization time is an important factor in controlling the TiO₂ nanotubes to obtain desirable characteristics. However, relevant reports on the effect of anodization time on the properties are quite few. Table 2 summarizes our observations on the nanotube length and inner diameter during different anodization times. Up to 20 hours of anodization, the nanotube length and inner diameter increase with increases in anodization time.

Table 2. Nanotube length and inner diameter obtained after different anodization durations in an electrolyte containing 2 vol% H₂O and 0.2 wt% NH₄F with an applied anodic voltage of 60 V

Anodization time (hr)	Nanotube length (μm)	Inner diameter (nm)
5	22.2	80
10	30.5	120
15	41.7	140
20	62.4	144

The composition of electrolyte is also an important factor and is involved in achieving an arrangement of nanotubes. According to the literature, the most widely accepted formation mechanism of TiO₂ nanotubes during electrochemical anodization involves several steps. At the initial stage of anodization, a dense TiO₂ layer is formed on the titanium surface by field-assisted oxidation via reaction. Ion migration occurs within the metal/metal oxide interface under the applied electric field. Titanium ions can dissolve and react with oxygen ions (O₂⁻) or hydroxyl ions (OH⁻) provided by water to form TiO₂ or titanium hydroxide, respectively. In the next stage, the titanium metal and oxide layer, which is in contact with the electrolyte, is etched by F⁻ ions through chemical dissolution to form soluble hexafluorotitanium complex. The localized dissolution of oxide results in the formation of tiny pits on the oxide layer, which gradually grow into bigger pores with increasing anodization time. The formation of nanotubes can be expressed in terms of the following chemical reaction in the case of titanium:



From the chemical reaction, it can be inferred that ammonium fluoride and water are involved in the formation of TiO₂ nanotubes. In order to find the optimum composition of electrolyte, the concentration of ammonium fluoride was changed from 0.1 to 0.5 wt% in ethylene glycol solution containing 2 vol% H₂O, and anodizing experiments were performed at 60 V for 15 h. Table 3 summarizes our observations of nanotube length and inner diameter obtained at different NH₄F concentrations in an electrolyte containing 2 vol% H₂O and an applied voltage of 60 V during 15 h of anodization. At a low concentration of NH₄F, that is, 0.1 wt%, the surface density of nanotubes was relatively low, but at a higher concentration, that is, > 0.2 wt%, the surface density of nanotubes gradually increased. The inner diameter of the resulting nanotube arrays increases with increasing NH₄F concentration. Ghicov et al. [10] showed that in an acidic electrolyte containing NH₄F, the size of nanotubes increased with increasing NH₄F concentration.

Another series of experiments was conducted to find the effect of the water volume in the electrolyte. The water volume was changed from 1 to 5 vol% in ethylene glycol containing 0.2 wt% NH₄F, and anodizing experiments were performed at 60 V for 15 h. Table 4 summarizes our observations of nanotube

length and inner diameter at different water volumes ranging from 1 to 5 vol%. The resulting nanotube array lengths were found to be longest at 2 vol% water for the same anodization duration. There is no change in the inner diameter of nanotubes at different H₂O volumes.

Table 3. Nanotube length and inner diameter obtained at different NH₄F concentrations in an electrolyte containing 2 vol% H₂O during 5 hours of anodization with an applied anodic voltage of 60 V.

NH ₄ F (wt%)	Tube length	Inner diameter (nm)
0.1	36.8	104
0.2	44.6	130
0.3	39.2	150
0.4	36.0	160
0.5	30.2	170

Table 4 Length and inner diameter of TiO₂ nanotubes obtained at different water volumes in glycerol electrolyte containing 0.2 wt% NH₄F during 15 hours of anodization

Water (vol%)	Nanotube length (μm)	Inner diameter (nm)
1	14.8	125
2	37.0	115
3	33.1	125
4	28.1	130
5	12.5	135

3.2 OH radical generation in the photocatalytic reactor with TiO₂ nanotube plates

The photocatalytic reactor with TiO₂ nanotube plates was operated in batch mode. In order to find out the effect of nanotube length on degradation of *p*CBA in the photocatalytic reactor, nanotubes were grown in ethylene glycerol containing 0.2 wt% NH₄F and 1 – 5 vol% H₂O by anodization at 60 V and annealed at temperature of 400 °C. The observed degradation rate constant (k_{exp}) of *p*CBA can be obtained from the slope of the semi-log plot of *p*CBA degradation as shown in Fig. 6. The *p*CBA degradation data obtained at each TiO₂ nanotube length were within the 95% confidence interval, indicating the existence of a steady-state condition for OH radical formation. The steady-state OH radical concentration ($[·OH]_{ss}$) formed at different nanotube lengths is shown in Fig. 4. This observation can be explained on the basis of the hypothesis that longer nanotubes produce more OH radicals. It is evident from the literature that photocurrent is drastically increased upon annealing of TiO₂ nanotubes. It has been deduced that, for the as-formed nanotubes, most of the photocurrent is generated in the bottom of the tubes and the tube wall contribution is negligible. The amorphous structure provides a high number of defects, leading to a high carrier recombination rate. By conversion to anatase, the tube walls are activated and contribute to the photocurrent. Therefore the tube length has a strong effect on the overall photo-response. The longer the nanotubes, the higher the total light absorption. This might lead to the production of more OH radicals.

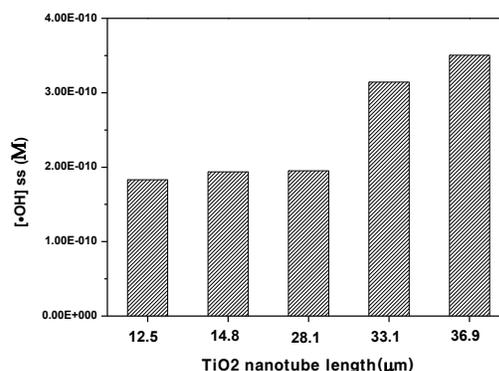


Figure 4. Effect of TiO₂ nanotube length on steady state OH radical concentration formed in the photocatalytic reactor with TiO₂ nanotube plate (annealing temperature: 400 °C, anodization voltage: 60V)

4. CONCLUSIONS

Well-aligned TiO₂ nanotube arrays on Ti plates were prepared using the electrochemical method for use in a photoreactor for water treatment. During the electrochemical synthesis of TiO₂ nanotube arrays it was observed that the morphology, length, and inner diameter of the nanotube array were influenced by the electrolyte composition, applied anodic voltage, and anodizing time. The length and inner diameter of the nanotube array increase with anodization potential between 30 and 80 V. The nanotube length and inner diameter can be controlled by the anodization time. In the photocatalytic reactor with a TiO₂ nanotube array plate, the longer the nanotube, the higher the steady-state OH radical concentration formed.

REFERENCES

- [1] C. C. Wong, W. Chu, Chemosphere, 50, 981–987, 2003.
- [2] T. Intgens, F. Salehi, R. Hochstrat, T. Melin, Water Sci. Technol. 57, 99–107, 2008.
- [3] D. Bamba, P. Atheba, D. Robert, A. Trokourey, B. Dongui, Chem. Lett., 6, 163–167, 2008.
- [4] A. K. Benabbou, Z. Derriche, C. Felix, P. Lejeune, C. Guillard, Appl. Catal. B: Environ., 76, 257–263, 2007
- [5] N. C. Meng, J. Bo, W.K. Christopher, S. Chris, Water Res., 44, 2997–3027, 2010
- [6] S. Malato, P. Fernandez-Ibanez, M. I. Maldonado, J. Blanco, W. Gernjak, Catal. Today, 147, 1–59, 2009.
- [7] Y. L. Pang, S. Lim, H. C. Ong, W. T. Chong, Appl. Catal. A: Gen., 481, 127–142, 2014.
- [8] G. Ali, C. Chen, S. H. Yoo, J. M. Kum, S. O. Cho, Nanoscale Research Letters, 6, 332–341, 2011.
- [9] M. S. Elovitz, U. von Gunten, H. P. Kaiser, Ozone Sci. Eng., 22, 123–50, 2000.
- [10] A. Ghicov, H. Tsuchiya, J. M. Macak, P. Schmuki, Commun., 7, 505–509, 2005.
- [11] H. Prakasam, K. Shankar, M. Paulose, O. Varghese, C. Grimes, J. Phys. Chem., 111, 7235–7241, 2007.