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REVIEW ARTICLE

LATEST PROGRESS ON THE INFLUENCING FACTORS AFFECTING THE FORMATION OF TiO_2 NANOTUBES (TNTs) IN ELECTROCHEMICAL ANODIZATION- A MINIREVIEW

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ABSTRACT

TiO_2 nanotubes (TNTs) have drawn special attention for their wide range of applications in a variety of fields. In comparison to other TiO_2 nanostructures, it is attracted much due to its high surface area and low fabrication cost. By using the electrochemical anodization approach, highly ordered TNT arrays can be produced with minimum cost compared to other synthesized methods. The nanotubes of the desired diameter, length and wall thickness can be tailored by adjusting anodization parameters. Here in this article, the effects of anodization parameters including type of electrolytes, electrolyte concentration, pH, temperature, aging, anodization voltage, time and type of electrodes on tube formation, tube diameters, length, thickness, organization, and formation mechanisms are reviewed. The collection methods of as-produced TNTs from Ti substrate also summarized in this review. Finally, the article concludes by outlining potential future research scope and challenges.

KEYWORDS

Anodic Oxidation, Synthesis, Titania Nanotubes, Influencing Factors, Peeling Off

1. INTRODUCTION

In recent years, a wide range of research works are going on to find out new materials and tailoring the properties of existing materials for the application in numerous fields. Nanomaterials are crucial for modern technologies to achieve improved performance. TiO_2 nanomaterials have received a lot of attention since Honda and Fujishima first reported using it to oxidize water in 1972 since it can be modified into various structures for applications in diverse fields (Kang et al., 2019; Jafari et al., 2020; Arun et al., 2022). TiO_2 in the form of nanoparticles (NPs), nanowires (NWs), nanorods (NRs) and nanotubes (NTs) structures are being employed in various fields (Prakash et al., 2021; Reghunath et al., 2021). Among the one-dimensional (1D) hierarchal structures of TiO_2, TiO_2 nanotubes (TNTs) attracted much attention and have been extensively utilized in a variety of fields, as shown in Figure 1 (Lee et al., 2014; Ge et al., 2016; Noman et al., 2019; Reghunath et al., 2021; Hossen et al., 2022a). Compared to other 1D nanomaterials, nanotubes have double the surface area per unit volume due to their hollow structure (Li and Yu, 2019). Since nanotubes have a large surface area, more electron donors can be incorporated, enhancing solar photon absorption and charge transfer in solar cells (Ghartavol et al., 2019). The tube shape morphology of TNT leads to a directional charge transfer pathway, as the diameter and length increase, the recombination rate will decrease when utilized as a photocatalyst in CO_2 reduction and H_2 evaluation (Zubair et al., 2018; Xue et al., 2022; Hossen et al, 2022b).

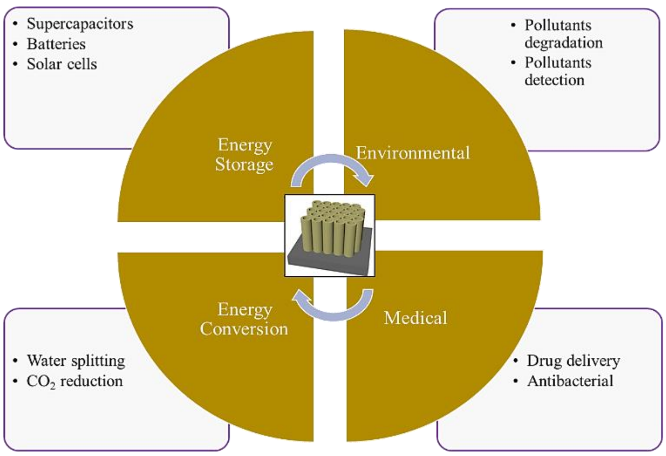

Figure 1: Applications of TNTs in various fields

There are several methods available to synthesize TNTs namely sol-gel method, hydrothermal method, template synthesis, sono-electrochemical and electrochemical anodization (Montakhab et al., 2020; Kouao et al., 2022). Electrochemical anodization has been extensively used in recent years to produce well-organized nanotubular patterns due to its simplicity in the formulation and cost-effective preparation (Saqib et al., 2016;

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Mohammadi et al., 2020; Puga et al., 2022). The key benefit of this method is that it allows for the production of nanotubes with the desired morphology (Patil et al., 2017; Puga et al., 2022). The anodization parameters, such as electrolyte composition, pH, temperature, aging, anodization voltage and duration, influence the morphological parameters, such as nanotube length, diameter, wall thickness, and self-organization (Indira et al., 2015; Puga et al., 2022; Ribeiro et al., 2021). As the interest in TNTs has grown, remarkable research works have been published on the influences of the individual anodization parameters on the morphology of nanotubes (Lai & Sreekantan, 2012; Mazierski et al., 2016; Robinson and Félix, 2018; Mohan et al., 2020; Alijani et al., 2021; Gulati et al., 2022; Hou et al., 2022). However, to the best of our knowledge, an extremely limited number of studies have been performed to review the overall effects of crucial parameters on the morphology of TNTs. The objective of this review is to summarize the latest progress on influencing factors affecting the formation of TNTs during the electrochemical anodization process. This review also presents the basic preparation and detachment procedure of TNTs in the electrochemical anodization method.

2. Fundamentals of Electrochemical Anodization For The Development of TNTs

Electrochemical anodization method provides a low-cost way to synthesize TNTs among other methods (soi-gel, template assisted, hydrothermal, sono-electrochemical and micro-wave irradiation) (Indira et al., 2015; Abbas et al., 2019; Kouao et al., 2022). This method is widely utilized because of its controllable, strong adherent strength, achievability in tailoring the size and form of the nanotube (NT) arrays to the necessary dimensions, and capability to fulfill the demands of specific applications (Abbas et al., 2019; Tesler et al., 2020). The process of developing nanotubes is relatively simple. Figure 2 shows the schematic diagram of typical two electrodes anodization device for development of TNT layers.

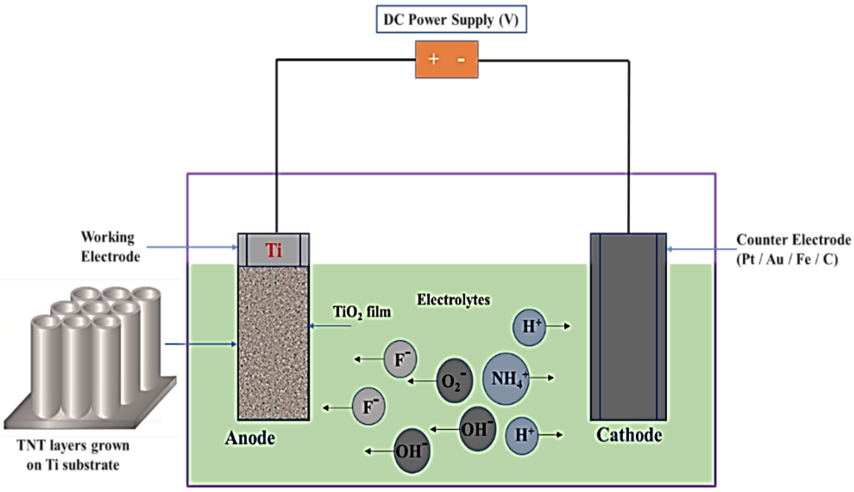

Figure 2: Schematic illustration of typical two electrodes anodization device for formation of TNT layers

During the electrochemical anodization process both electricity and chemistry have been utilized to form the oxide layer on Ti substrate. The working electrode and counter electrode are submerged in an aqueous electrolyte solution. When DC power supply is applied, water and electrolyte molecules split into oxidizing and reducing ions. The electrical potential forces the oxidizing ions to the titanium surface, which causes an oxide layer to develop on the surface of the Ti employed as the anode. Three main processes must take place in order to form the tubular array: the first is the field-assisted oxidation of Ti metal, which results in the formation of TiO_2 and an oxide layer on its surface; the second is the field-assisted dissolution of Ti metal ions in the electrolyte; and the third is the surface etching formed by the chemical dissolution of Ti (Abbas et al., 2019). The formation of TiO_2 nanotube layers on Ti largely depends on the anodization voltage and time (Mazierski et al., 2016; Puga et al., 2022). When oxidation and dissolution are in balance, the corrosion pits expand continuously into nanopores or nanotubes with a vertical symmetry. Since anodized nanotubes are amorphous, crystalline structure must be developed by annealing the samples in an environment of air, oxygen, or nitrogen at 300–500 °C with a gradual heating and cooling rate (1–5 °C/min) (Liu et al., 2019; Puga et al., 2022). TNTs can be developed in any of the crystalline forms of TiO_2 depending on the annealing temperature (Fang et al., 2011). To get TNTs with the required morphology, control of the anodization parameters is crucial.

3. Influencing Factors For TNTs Formation in Electrochemical Anodization

In recent years, great attention has been received to modify the morphology of TNT for wide range of applications. The formation of TNT in terms of quantity and quality such as pore size, length, and wall thickness depend on various factors including electrolytes type, concentration, pH, temperature, aging, anodization voltage, time, and type of electrodes as shown in Figure 3. The following sections present brief description regarding the influence of aforementioned anodization parameters on the development of TNT.

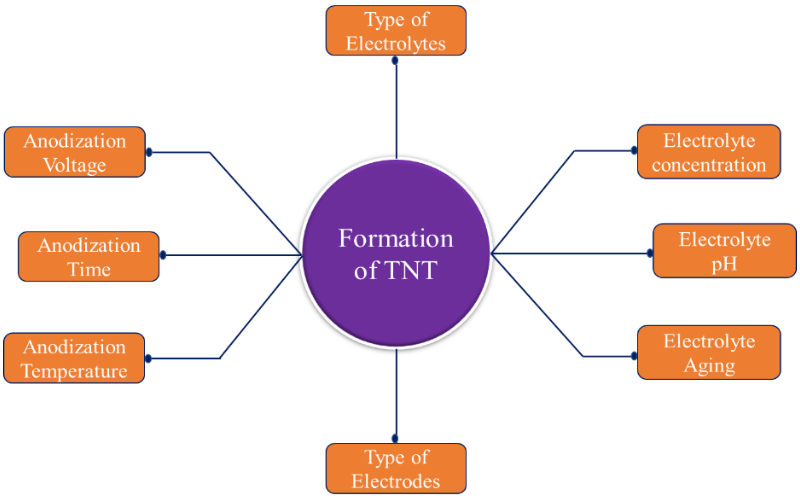

Figure 3: Factors influencing the formation of TNTs

3.1 Type of Electrolytes

The morphology of TNT is significantly influenced by the type of electrolytes employed during the anodization process. It is widely recognized that different electrolytes can yield distinct structural configurations under the same conditions (Puga et al., 2022). TNT can be formed by anodizing fluoride-containing electrolytes such as NH_4F/CH_3COOH, H_2SO_4/HF, Na_2HPO_4/NaF, and so on. For the manufacture of TNT, two main types of electrolytes have been used: organic (or neutral) and aqueous electrolytes. When anodization occurs in a high-water content, it is referred to as aqueous electrolytes, whereas when it occurs in a low oxygen/water content, it is treated as organic electrolytes.

The effects of organic solvents during anodization on the morphology and tube-to-tube spacing of TiO_2 nanotubes were investigated (Niu et al., 2020). They employed electrolytes that include fluoride, such as glycerol, diethylene glycol (DEG), and ethylene glycol (EG). The results showed that in the EG electrolyte, close-packed nanotubes were formed, but in the DEG electrolyte, spaced nanotubes were formed. In another study, under identical anodization conditions investigated two types of electrolytes EG and polyethylene glycol (PEG) and reported that the PEG-produced nanotubes were much shorter (330.4 nm) than the EG-produced ones (2.40 µm) (Dumitriu et al., 2013). Using an aqueous electrolyte made up of carboxymethylcellulose (CMC) and NaF, synthesized TiO_2 nanotubes on curved titanium surfaces (Ocampo and Echeverría, 2021). They observed the length of nanotubes on curved titanium surfaces was shorter than in flat titanium surfaces under the same anodizing conditions.

Robinson Aguirre & Félix Echeverría evaluated the effect of several fluoride ion sources (HF, NaF, and NH_4F) on the morphology of TiO_2 nanotubes while keeping the other anodization parameters constant (Robinson and Félix, 2018). They revealed that the thickness of the nanotubes formed in NaF and NH_4F solutions was roughly two times that of the HF electrolyte. The possible mechanism of TiO_2 formation in fluoride-containing electrolytes is shown in Figure 4. One of the key attributes of F^- to form water-soluble $[TiF_6]^{2-}$ complexes, which efficiently produce a thin oxide layer at the bottom of the tube by etching the oxide layer (Puga et al., 2022). The chemical dissolution of produced TiO_2 is also aided by the formation of Ti^{4+} ions upon their arrival at the oxide-electrolyte interface. The small ionic radius of F^- is ideal for moving into the TiO_2 lattice and competing with the mobility of O^{2-} via the bottom oxide layer (Puga et al., 2022; Zheng et al., 2022).

$$Ti + 2H_2O \rightarrow TiO_2 + 4H^+ + 4e^- \quad (1)$$
$$TiO_2 + 6F^- + 2H^+ \rightarrow [TiF_6]^{2-} + H_2O \quad (2)$$
$$2H_2O \leftrightarrow 4H^+ + 2O^{2-} \quad (3)$$
$$2H^+ + 4e^- \rightarrow H_2 \quad (4)$$
$$Ti^{4+} + O^{2-} \rightarrow TiO_2 \quad (5)$$

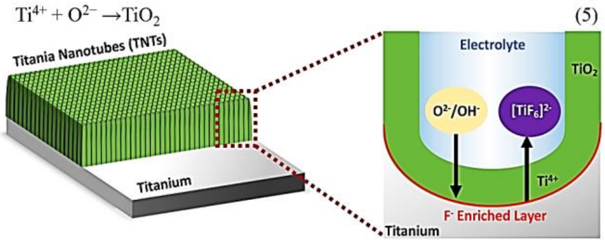

Figure 4: Possible mechanism of TNTs formation in fluoride containing electrolyte, reproduced (Gulati et al., 2022).

The formation of TNT is also greatly influenced by the use of additives in electrolytes during the anodization process (So et al., 2012; Song et al., 2019). Aguirre Ocampo & Echeverría Echeverría (2019) used carboxymethylcellulose (CMC) as an additive in aqueous electrolyte to examine the nanotube morphology. Due to the addition of CMC, well-organized nanotubes were formed with a maximum length 5.85 µm and diameter 100 nm at an applied voltage 20 V. In a recent study, TNT with a high aspect ratio was obtained within quickest time by using lactic acid (LA) as an additive in the organic electrolyte ($NH_4F/H_2O/EG$) (Alijani et al., 2021). Higher potential anodization is attained by LA, which inhibits the dielectric breakdown. The resulting TNT layers had an average thickness and diameter of around 80 µm and 170 nm after 15 minutes of anodization at 160 V, respectively.

3.2 Electrolyte Concentration

The nanotube morphology is affected by the concentration of electrolytes as like as the type of electrolytes. Well-organized TNT can be produced by varying the electrolyte concentration and keeping other parameters constant. For instance, Aguirre Ocampo & Echeverría Echeverría (2019) used two different concentrations of NaF (0.25 and 0.50 wt.%) to make nanostructures while keeping the other anodization parameters the same. The nanotubes synthesized with 0.50 wt.% did not show a dense layer covering them; consequently, this concentration leads to the formation of clean nanotubes without oxide coatings or particles covering them. Furthermore, the nanotubes made with 0.50 wt.% exhibited a better degree of organization than those made with 0.25 wt.%. a group researchers reported that in between 0.1M to o.15M concentration of NH_4F, tube formation was well organized and compacted (Omidvar et al., 2011). However, the surface density of nanotubes began to decline around 0.2M and completely scattered at 0.3M. The diameter of nanotube is significantly influenced by the contents of electrolytes used. A group researchers investigated the effect of electrolyte content on TiO_2 nanotube diameter (Ozkan et al., 2018). They used a composition of DEG, HF and NH_4F electrolyte containing several amounts of water from 6 wt.% to 26 wt.%. When water was added to the electrolyte at a concentration of 6 to 26 wt.%, the outer diameter of the nanotubes was increased from 147 to 185 nm. In another study, they described a well-ordered organization of nanotubular arrays with a layer thickness of 250 nm using a low-concentrated NH_4F electrolyte (≤ 3 M) (Tesler et al., 2020). TNT arrays produced in 1M NH_4F electrolyte showed tightly packed U-shaped nanotubular structures with a mean wall thickness of roughly 12 nm, which is twice as thin as at 3M NH_4F concentration.

3.3 Electrolyte pH

The pH of the electrolyte is critical for the formation of high-aspect ratio nanotubes, and it can influence the self-organization pattern of TNT. The pH value of the electrolyte varies during anodization due to the gradual increase in hydrolysis product at the working electrode which developed acidic environment. To adjust to an acidic environment, the rate of TiO_2 dissolution try to be increased. Thus, providing a more protective barrier against the dissolution along the tube mouth leads to longer nanotube formation. It has been reported that the length of nanotubes varied from 380 nm to 6 µm, while the diameter of the nanotubes varied from 30 to 110 nm due to the electrolyte pH and anodization voltage (Paulose et al., 2006). A group researchers showed that nanotube lengths ranging from ~0.7 to 2.5 µm was formed within pH value 3 to 7 (Sreekantan et al., 2009). The pore diameter varies significantly depending on the pH difference (Indira et al., 2015). The thickness of nanotubes is also related to the pH dependency of the oxide dissolution rate, which is substantially larger at low pH than at higher pH. Only a few nanotubes were seen surrounded by an oxide layer at pH 5 and 0.5 wt.% CMC (Aguirre and Echeverría, 2019). However, at pH 4, well-structured nanotube structures were detected. The organization of TNTs, on the other hand, decreased when employing the same CMC content with a pH value of 1.5.

3.4 Electrolyte Aging

Among the various influencing factors, electrolyte aging is one of the major influencing factors that lead to enhanced ordering and stability of TiO_2 nanotubes (Gulati et al., 2022; Guo et al., 2021; Suhadolnik et al., 2020). A group researchers investigated the effect of electrolyte aging on TiO_2 electrochemical anodization and addressed the nanostructure characteristics briefly (Gulati et al., 2022). Ti was anodized for 6 hours at 60 V in an EG-based electrolyte, followed by anodization for 0, 24, 72, and 114 h (same electrolyte) for up to 20 days. The formation of barrier layer on fresh and aged electrolytes can be easily shown in Figure 7. Electrolyte samples aged during 24 and 72 h had a homogenous surface morphology, whereas those aged 0 and 114 h had a heterogeneous surface morphology. A group researchers reported that the length of TiO_2 nanotubes reduced as the electrolyte aged due to its lower conductivity (Suhadolnik et al., 2020). The effect of electrolyte aging has been extensively studied and they have also mentioned with the increasing usage of the electrolyte results in lower conductivity (Ribeiro et al., 2021; 2022). Results showed that electrolyte usage between 12 to 148 h exhibited well-defined open-top nanotubular structures.

3.5 Anodization Temperature

It is apparent that the anodizing temperature is one of the most fundamental factors in the NT formation process. It is well-established that anodization temperature is crucial for developing TNTs in an ordered orientation (Fleischer et al., 2018; Indira et al., 2015). In a study reported that TNT arrays with wall thickness ranging from 12.5 nm to 37.5 nm were achieved while maintaining other parameters unchanged only by tailoring the anodization temperature from 10 to 80 °C (Lai and Sreekantan, 2012). A group of researchers evaluated the influence of electrolyte temperature on TNT formation at 5, 25, and 60 °C while maintaining all other parameters constant (20 V, 0.5 wt.% CMC and 0.5 wt.% NaF) (Aguirre and Echeverría, 2019a). They reported that at room temperature (25 °C), the optimum equilibrium between oxide dissolution and formation was attained. A group researchers anodized Ti-6Al-7Nb for 1 hour at 30 V in an electrolyte containing 1M H_2SO_4 and 0.08M HF at 5, 10, 25, 30, 50, and 70 °C (Mohan et al., 2020). In samples anodized at 30, 50, and 70 °C, they identified a regular and vertically aligned tube structure. On the other hand, reported that closely packed TNTs formation achieved temperatures beyond 100 °C (Tesler et al., 2020). The formation of well-organized TNTs layers at higher anodization temperatures can be attributed to faster rates of oxidization and dissolution.

3.6 Anodization Voltage

Table 1: Effect of anodization voltage and time on morphology of TNTs

State of Ti	Counter electrode	Applied voltage (V)	Time (h)	Tube length (µm)	Inner diameter (nm)	Wall thickness (nm)	Main solvent	Electrolyte	Reference
Ti foil (15×20× 0.25 mm)	Pt	30	1	-	36.66	-	EG	0.25 wt% NH_4F + 2 vol% H_2O	Qin et al. (2015)
		40	1	3.9	56.19	-			
		50	1	-	82.97	-			
		60	1	-	86.68	-			
		40	0.5	2.3	-	-			
		40	1.5	6.0	-	-			
Ti foil (15×20× 0.20 mm)	Ti	60	0.5	1.41	98.23	52.43	EG	0.4 wt% NH_4F + 5 mL H_2O	Chernozem et al. (2016)
		60	4	6.27	155.95	32.78			
		30	0.5	0.91	52.96	50.70			
Ti foil	Pt	20	1	0.8	48	6	EG	0.09 M NH_4F + 2 vol% H_2O	Mazierski et al. (2016)
		30	1	1.7	59	6			
		40	1	2.2	66	6			
		50	1	2.7	60	14			
		40	0.5	1.6	90	6			
		40	2	3.8	55	11.5			
Ti foil (0.1 mm thick)	Pt	30	0.5	0.5	103	12	DEG	4 wt% HF + 0.3 wt% NH_4F + 7 wt% H_2O	Ozkan et al. (2018)
		30	4	1.2	152	19			
		30	24	1.6	172	13			
		10	4	-	52	-			
		20	4	-	108	-			
		40	4	-	202	-			
Unalloyed Ti plate (20×20× 1 mm)	Pt	10	20	-	55.92	-	Water	0.5 wt% NaF + 0.5 wt% CMC	Ocampo & Echeverría, (2019a)
		15	20	-	63.62	-			
		20	20	4.76	88.60	-			
		20	5	2.83	-	-			
		20	3	1.89	-	-			
Ti6Al4V alloy (4 mm thick, 30 mm diameter)	Pt	20	0.5	-	-	-	EG	0.5% wt. NH_4F + 2.5 vol% H_2O	Ribeiro et al. (2021)
		40	0.5	-	-	-			
		60	0.5	-	55	-			
		80	0.5	-	118	-			
		100	0.5	-	160	-			
		20	1	-	28	-			
		40	1	-	75	-			
		60	1	-	108	-			
		80	1	-	130	-			
		100	1	-	165	-			
		20	2	-	42	-			
		40	2	-	88	-			
		60	2	-	96	-			
CP-Ti alloy (4 mm thick, 30 mm diameter)	Pt	20	3	-	55	-	EG	0.5% wt. NH_4F + 2.5 vol% H_2O	Ribeiro et al. (2022)
		20	6	-	60	-			
		20	9	-	67	-			
		40	3	-	95	-			
		40	6	-	108	-			
		40	9	-	127	-			
		60	3	-	125	-			
		60	6	-	158	-			
		60	9	-	197	-			

The morphology of TNTs is significantly influenced by the most important anodization parameters e.g., applied voltage and time, as illustrated in Table 1. The applied voltage greatly influences the diameter, interpore distance, film thickness, and organization of tubes. For instance, reported well-organized nanotube layers with big-diameter NTs integrated into small-diameter tube layers at an optimum applied voltage of 30 V (Ozkan et al., 2018). According to some study, the exterior NT diameter and thickness grew constantly as the applied voltage was increased from 10V to 40V (Tesler et al., 2020). It is worth mentioning that beyond certain applied voltage nanotubes morphology could be highly irregular due to substantial bubble formation (Tesler et al., 2020; Ribeiro et al., 2021). The influence of the applied voltage difference over the nanotube diameter is well-known, and related findings have been obtained by several authors in both aqueous and organic-based electrolyte compositions (Qin et al., 2015; Chernozem et al., 2016; Mazierski et al., 2016; Ozkan et al., 2018; Ocampo and Echeverría, 2019a; Tesler et al., 2020; Ribeiro et al., 2021; Ribeiro et al., 2022). According to some study, when the applied voltage was increased, the inner diameter of the nanotube increased linearly (Ribeiro et al., 2021; 2022).

3.7 Anodization Time

Nanotube length, thickness and degree of self-organization are greatly influenced by the anodization time. Table 1 shows that increasing the anodization time results in a notable increase in the length of nanotubes. In a recent study, some researchers found a strong correlation between nanotube growth and film thickness with anodization time (Hou et al., 2022). A certain time is required to form TNTs with desired morphology. The minimum time required to produce uniform and well-organized TNTs is most commonly 30 min (Ozkan et al., 2018; Ribeiro et al., 2021). With the addition of an additive to the electrolyte, highly ordered TNT with a high aspect ratio can be formed within a short anodization time. For instance, produced TNT layers with higher aspect ratio nearly 450 only 15 min of optimized anodization time with the addition of lactic acid in the electrolyte as additive (Alijani et al., 2021).

Generally, nanotubes formed with higher voltages and longer anodization time are more uniform and longer as compared to nanotubes formed with lower voltages and shorter anodization time. A group of researchers found that increasing the applied voltage difference and the anodization time resulted in a nearly linear increase in the uniformity and diameter of nanotubes (Ribeiro et al., 2021). However, after a certain period of anodization, the morphology of nanotubes may not be improved (Ozkan et al., 2018; Yi et al., 2019). A group of researchers found that the morphology of nanotubes improved significantly up to 4 h of anodization, while the morphology of nanotubes did not change much beyond that. They also observed that the wall thickness of nanotubes decreased with the increasing anodization time (1h to 4h), while the inter-tube distances remain virtually unchanged.

3.8 Type of Electrodes

In addition to the aforementioned factors, the type of electrodes utilized in the anodization process has also a significant impact on TNT formation. Ti substrate used as a working electrode is an important part of anodization as TNT layers grow on it. Till to date, TNT layers have been attempted to be synthesized on several Ti substrates, including Ti alloy, Ti wire, Ti foil, Ti sheet, and Ti mesh (Galstyan et al., 2022). The most common Ti substrate for anodization is Ti foil, which typically has a thickness between 100 and 1000 µm. The property of counter electrodes greatly influenced the shape and size of nanotubes. For the development of TNT, the most typically employed counter electrodes are Pt, Ni, Fe, Co, Cu, C, and Sn. The influence of counter electrodes on the physical properties of TNTs is depicted in Table 2. For the development of TNT, used a wide range of CEs, including Ni, Pd, Pt, Fe, Co, Cu, Ta, W, C, and Sn (Allam and Grimes, 2008). They pointed out that the cathode's over potential has a considerable impact on the dissolution kinetics of anode Ti, as well as the activity of the electrolyte and the morphology of the formed TNT. The cathode materials are arranged in the following order based on their stability in aqueous electrolytes: Pt > Pd > C > Ta > Al > Sn > Cu > Co > Fe> Ni > W. A group of researchers investigated the characteristics of TiO_2 nanotube arrays using low-cost cathode materials (charcoal, graphite, and iron) (Joseph et al., 2017). Results showed that the Ti cathode material provided arrays with a maximum tube length of 153 µm, whilst the cost-effective cathode materials yielded approximately 100 µm long nanotubes for an anodization duration of 48 h.

Table 2: Influence of counter electrodes on physical properties of TNTs

State of Ti	Counter electrode		Length (µm)	Diameter (nm)	Time (h)	Voltage (V)	Main solvent	Electrolyte	Reference
Ti foil	Transition metals	Platinum (Pt)	152	–	48	60	EG	0.35 wt% NH_4F + 2 vol% H_2O.	Joseph et al. (2017)
		Titanium (Ti)	153						
		Iron (Fe)	56						
	Non-transition metals	Graphite (Gr)	98	–					
		Charcoal (Chr)	108						
Ti foil	Pt group metals	Platinum (Pt)	1.20	143	10	20	Water	0.2M NH_4F + 0.1M H_3PO_4	Allam & Grimes, (2008)
		Nickel (Ni)	1.44	134					
		Palladium (Pd)	1.52	105					
	Non-Pt group metals	Iron (Fe)	2.47	99					
		Cobalt (Co)	1.90	135					
		Copper (Cu)	1.27	81					
		Tantalum (Ta)	1.18	140					
		Tungsten (W)	0.69	91					
	Non-transition metals	Carbon (C)	1.30	143					
		Aluminum (Al)	0.59	96					
		Tin (Sn)	1.22	147					

4. Collection of As-anodized TNTs from Ti Substrate

The use of TNTs in powder form has been a hot topic for the past few decades in many applications. TNTs in the powder form can be achievable by hydrothermal method without any further treatment. However, producing TNTs with the desired morphology using the hydrothermal approach is not possible and this is also time-consuming method (Abbas et al., 2019; Bjelajac et al., 2020). Due to the several advantages mentioned before, electrochemical anodization method is being utilized for TNTs production. To use as-produced TNTs via electrochemical anodization in powder form need to detach from the Ti substrate. This is a challenging task to peel off TNTs from the Ti substrate without disturbing the as-produced morphology. There are some techniques available to detach TNTs from the Ti substrate including ultrasonication, rapid breakdown anodization, N_2-stream blowing and mechanical bending.

The anodized Ti foil is typically placed into an ultrasonic bath for sonication that contains a 1:4 (v/v) mixture of water (H_2O) and ethanol (C_2H_5OH) before being subjected to ultrasonic agitation. When the entire film became bright during the ultrasonication, the sample was removed from the solution right away and rinsed with C_2H_5OH. These procedures enhanced the imperfections between the bottoms of TiO_2 nanotubes and Ti foil and made it possible for TiO_2 nanotube arrays to separate. After rinsing with DI water and drying in atmosphere or nitrogen stream, the TNT film would detach from the substrate. This technique was successfully adopted (Chen et al., 2011; Liu et al., 2012; Zhang et al., 2014; Montakhab et al., 2020). N_2- stream blowing method not only provides uniform, oriented, and smooth substrates for subsequent anodization, however, it

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also serves to safeguard against any mechanical damage to the substrates (Ali et al., 2011).

After soaking the Ti substrate in methanol (CH_3OH), N_2 blowing makes it easy to detach the TNT layer. The TNT layer is detached, leaving a Ti foil with a honeycomb-like patterned surface that can be employed for the second anodization phase under the same circumstances as the first anodization and then undergo the same detachment procedure as illustrated in Figure 5. Mechanical bending of Ti foil is also used for detaching the TNT layer after rinsing extensively with DI water and CH_3OH. The thin barrier layer of TiO_2 that had been developed during anodization between the TiO_2 layer and Ti foil eventually delaminated as a result of the subsequent evaporation of CH_3OH (Liu et al., 2012). This method creates mechanical damage to foil and is applicable if the foil thickness is less.

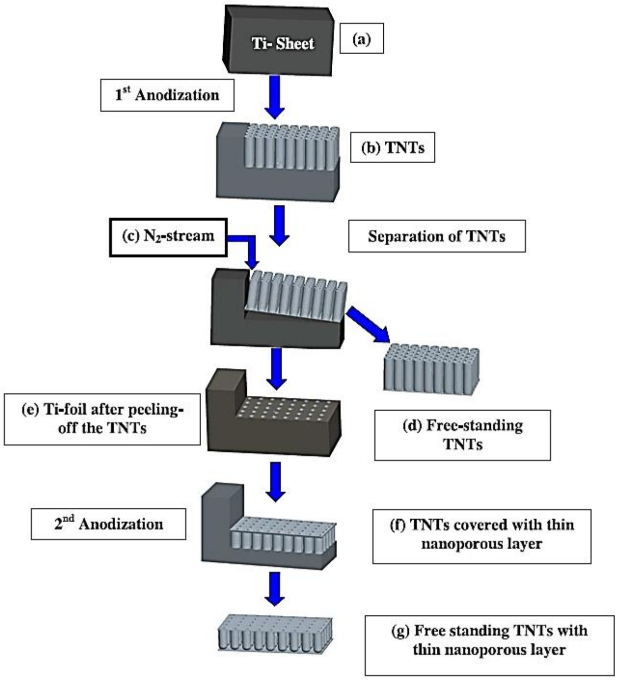

Figure 5: Detachment process of TNT from Ti substrate, adopted from Ali et al. (2011)

The rapid breakdown anodization process is regarded as the simplest and most cost-effective way to produce TNT in powder form since it provides high yield using the same anodization configuration (Abbas et al., 2019; Galstyan et al., 2022). The chemical oxidation and dissolving of the metal substrates are primarily responsible for the development of TNT in powder form. Cl^- ions rather than F^- ions are typically employed in the electrolyte (e.g., $HClO_4$) for this approach (Lin et al., 2015; Ali and Hannula, 2017). When potential voltage is applied, ions are transported via the dissolution process; Ti^{4+} cations move in the direction of the electrolyte solution and produce a thick oxide layer at the metal/oxide interface as a result of the oxidation process (Abbas et al., 2019). The anodic oxidation subsequently tends to stop as the electrolyte impedance is increased. Following the localized breakdown of the oxide barrier, the Cl^- ions begin to dissolve the metal oxide layer and develop pores (Ali et al., 2018). The white TNT layer separates from the substrate and subsequently disintegrates into powder form in the electrolyte. The TNT layer separated from the substrate due to the mechanical stress developed at the Ti/TiO_2 interface (Lin et al., 2015; Abbas et al., 2019). The produced NT powder is then extracted by centrifugation and dried overnight in oven. After that to get crystalline TNTs, the oven-dried powder is generally annealed in the air at 450°C for at least two hours.

5. Conclusion

The paper briefly summarizes recent advances regarding the electrochemical anodization method with a detailed focus on influencing parameters that alter the morphology of as-prepared TNTs. To produce uniform ordered TNTs with the desired diameter, length and wall thickness is a great deal for applications in a wide range of fields. The desired morphology of TNTs can be produced by employing suitable electrolytes with adjusting concentration, pH, temperature, aging, anodization voltage and time during the anodization process. The size, thickness and material properties of utilized working and counter electrodes also have a substantial influence on the formation of TNTs. In general, electrolyte concentration and temperature had a significant impact on the organization of tubes, while anodization voltage and time had a great influence on nanotube length and diameter. After the formation of the TNTs layer on the Ti substrate, the collection of TNTs for further use is a challenging task. The simplest technique used to date for separating the TNTs layer from the Ti substrate is ultrasonication. Great advances have been done in controlling the morphology of TNTs during the past few decades, but now focus should be on establishing a systematical and reproducible recipe for controlling the nanotube diameter, length and wall thickness with precise alteration of anodization parameters. Meta-analysis considering so far published research on anodization parameters for nanotube diameter, length and wall thickness can be handy. There is still some sort of challenges for peeling off TNTs from Ti substrate without disturbing as-anodized morphology. Attention should be given on future research to produce TNTs with desired morphology in bulk amounts to meet the increasing applications in a variety of fields.

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References

Abbas, W.A., Abdullah, I.H., Ali, B.A., Ahmed, N., Mohamed, A.M., Rezk, M.Y., Ismail, N., Mohamed, M.A., and Allam, N.K., 2019. Recent advances in the use of TiO2 nanotube powder in biological, environmental, and energy applications. Nanoscale Advances, 1 (8), Pp. 2801–2816. https://doi.org/10.1039/c9na00339h

Aguirre Ocampo, R., and Echeverría Echeverría, F., 2019. Effect of the anodization parameters on TiO 2 nanotubes characteristics produced in aqueous electrolytes with CMC. Applied Surface Science, 469, Pp. 994–1006. https://doi.org/10.1016/j.apsusc.2018.11.097

Ali, G., Yoo, S.H., Kum, J.M., Kim, Y.N., and Cho, S.O., 2011. A novel route to large-scale and robust free-standing TiO2 nanotube membranes based on N2 gas blowing combined with methanol wetting. Nanotechnology, 22 (24). https://doi.org/10.1088/0957-4484/22/24/245602

Ali, S., and Hannula, S.P., 2017. Titania nanotube powders obtained by rapid breakdown anodization in perchloric acid electrolytes. Journal of Solid-State Chemistry, 249, Pp. 189–198. https://doi.org/10.1016/j.jssc.2017.03.007

Ali, S., Orell, O., Kanerva, M., and Hannula, S.P., 2018. Effect of Morphology and Crystal Structure on the Thermal Conductivity of Titania Nanotubes. Nanoscale Research Letters, 13. https://doi.org/10.1186/s11671-018-2613-3

Alijani, M., Sopha, H., Ng, S., and Macak, J.M., 2021. High aspect ratio TiO2 nanotube layers obtained in a very short anodization time. Electrochimica Acta, 376, 138080. https://doi.org/10.1016/j.electacta.2021.138080

Allam, N.K., and Grimes, C.A., 2008. Effect of cathode material on the morphology and photoelectrochemical properties of vertically oriented TiO2 nanotube arrays. Solar Energy Materials and Solar Cells, 92 (11), Pp. 1468–1475. https://doi.org/10.1016/j.solmat.2008.06.007

Arun, J., Nachiappan, S., Rangarajan, G., Alagappan, R.P., Gopinath, K.P., and Lichtfouse, E., 2022. Synthesis and application of titanium dioxide photocatalysis for energy, decontamination and viral disinfection: a review. Environmental Chemistry Letters. https://doi.org/10.1007/s10311-022-01503-z

Bjelajac, A., Petrović, R., Vujancevic, J., Veltruska, K., Matolin, V., Siketic, Z., Provatas, G., Jaksic, M., Stan, G. E., Socol, G., Mihailescu, I.N., and Janaćković, D., 2020. Sn-doped TiO2 nanotubular thin film for photocatalytic degradation of methyl orange dye. Journal of Physics and Chemistry of Solids, 147 (June), Pp. 1–8. https://doi.org/10.1016/j.jpcs.2020.109609

Chen, B., Lu, K., and Tian, Z., 2011. Effects of titania nanotube distance and arrangement during focused ion beam guided anodization. Journal of Materials Chemistry, 21 (24), Pp. 8835–8840. https://doi.org/10.1039/c1jm11083g

Chernozem, R.V., Surmeneva, M.A., and Surmenev, R.A., 2016. Influence of Anodization Time and Voltage on the Parameters of TiO2 Nanotubes. IOP Conference Series: Materials Science and Engineering, 116 (1). https://doi.org/10.1088/1757-899X/116/1/012025

Dumitriu, C., Pirvu, C., and Demetrescu, I., 2013. The Electrochemical Formation and Shielding Mechanism of TiO 2 Nanotubes in Organic Electrolytes with Different Viscosity. Journal of The Electrochemical Society, 160 (2), Pp. G55–G60. https://doi.org/10.1149/2.035302jes

Fang, D., Luo, Z., Huang, K., and Lagoudas, D.C., 2011. Effect of heat treatment on morphology, crystalline structure and photocatalysis properties of TiO 2 nanotubes on Ti substrate and freestanding membrane. Applied Surface Science, 257 (15), Pp. 6451–6461. https://doi.org/10.1016/j.apsusc.2011.02.037

Fleischer, C., Chatzitakis, A., and Norby, T., 2018. Intrinsic photoelectrocatalytic activity in oriented, photonic TiO2 nanotubes. Materials Science in Semiconductor Processing, 88, Pp. 186–191. https://doi.org/10.1016/j.mssp.2018.08.009

Galstyan, V., Macak, J.M., and Djenizian, T., 2022. Anodic TiO2 nanotubes: A promising material for energy conversion and storage. Applied Materials Today, 29, Pp. 101613. https://doi.org/10.1016/j.apmt.2022.101613

Ge, M., Cao, C., Huang, J., Li, S., Chen, Z., Zhang, K.Q., Al-Deyab, S.S., and Lai, Y., 2016. A review of one-dimensional TiO2 nanostructured materials for environmental and energy applications. Journal of Materials Chemistry A, 4 (18), Pp. 6772–6801. https://doi.org/10.1039/c5ta09323f

Ghartavol, H.M., Mohammadi, M.R., Afshar, A., and Li, Y., 2019. On the assessment of incorporation of CNT-TiO2 core-shell structures into nanoparticle TiO2 photoanodes in dye-sensitized solar cells. Photochemical and Photobiological Sciences, 18 (7), Pp. 1840–1850. https://doi.org/10.1039/c9pp00100j

Gulati, K., Martinez, R.D.O., Czerwiński, M., and Michalska-Domańska, M., 2022. Understanding the influence of electrolyte aging in electrochemical anodization of titanium. Advances in Colloid and Interface Science, 302, Pp. 1–10. https://doi.org/10.1016/j.cis.2022.102615

Guo, T., Oztug, N.A.K., Han, P., Ivanovski, S., and Gulati, K., 2021. Old is gold: Electrolyte aging influences the topography, chemistry, and bioactivity of anodized TiO2 nanopores. ACS Applied Materials and Interfaces, 13 (7), Pp. 7897–7912. https://doi.org/10.1021/acsami.0c19569

Hossen, M.A., Solayman, H.M., Leong, K.H., Sim, L.C., Yaacof, N., Abd Aziz, A., Lihua, W., Monir, M.U., 2022a. Recent progress in TiO2-Based photocatalysts for conversion of CO2 to hydrocarbon fuels: A systematic review. Results in Engineering, 16(November), 100795. https://doi.org/10.1016/j.rineng.2022.100795

Hossen, M.A., Solayman, H.M., Leong, K.H., Sim, L.C., Yaacof, N., Abd Aziz, A., Lihua, W., Munir, M.U., 2022b. A Comprehensive Review on Advances in TiO2 Nanotube (TNT)-Based Photocatalytic CO2 Reduction to Value-Added Products. Energies, 15 (22), Pp. 8751. https://doi.org/https://doi.org/10.3390/en15228751

Hou, X., Lund, P.D., and Li, Y., 2022. Controlling anodization time to monitor film thickness, phase composition and crystal orientation during anodic growth of TiO2 nanotubes. Electrochemistry Communications, 134, Pp. 107168. https://doi.org/10.1016/j.elecom.2021.107168

Indira, K., Mudali, U.K., Nishimura, T., and Rajendran, N., 2015. A Review on TiO2 Nanotubes: Influence of Anodization Parameters, Formation Mechanism, Properties, Corrosion Behavior, and Biomedical Applications. Journal of Bio- and Tribo-Corrosion, 1 (4). https://doi.org/10.1007/s40735-015-0024-x

Jafari, S., Mahyad, B., Hashemzadeh, H., Janfaza, S., Gholikhani, T., and Tayebi, L., 2020. Biomedical Applications of TiO 2 Nanostructures: Recent Advances. International Journal of Nanomedicine, 15, Pp. 3447–3470. https://doi.org/10.2147/IJN.S249441

Joseph, S., Melvin Boby, S.J., Theresa Nathan, D.M.G., and Sagayaraj, P., 2017. Investigation on the role of cost-effective cathode materials for fabrication of efficient DSSCs with TiNT/TiO2 nanocomposite photoanodes. Solar Energy Materials and Solar Cells, 165, Pp. 72–81. https://doi.org/10.1016/j.solmat.2017.02.038

Kang, X., Liu, S., Dai, Z., He, Y., Song, X., and Tan, Z., 2019. Titanium dioxide: From engineering to applications. In Catalysts, 9 (2). https://doi.org/10.3390/catal9020191

Kouao, D.S., Grochowska, K., and Siuzdak, K., 2022. The Anodization of Thin Titania Layers as a Facile Process towards Semitransparent and Ordered Electrode Material. Nanomaterials, 12 (7). https://doi.org/10.3390/nano12071131

Lai, C.W., and Sreekantan, S., 2012. Photoelectrochemical performance of smooth TiO 2 nanotube arrays: Effect of anodization temperature and cleaning methods. International Journal of Photoenergy. https://doi.org/10.1155/2012/356943

Lee, K., Mazare, A., and Schmuki, P., 2014. One-dimensional titanium dioxide nanomaterials: Nanotubes. Chemical Reviews, 114 (19), Pp. 9385–9454. https://doi.org/10.1021/cr500061m

Li, H.H., and Yu, S.H., 2019. Recent Advances on Controlled Synthesis and Engineering of Hollow Alloyed Nanotubes for Electrocatalysis. Advanced Materials, 31 (38), Pp. 1–23. https://doi.org/10.1002/adma.201803503

Lin, J., Liu, X., Zhu, S., Liu, Y., and Chen, X., 2015. Anatase TiO2 nanotube powder film with high crystallinity for enhanced photocatalytic performance. Nanoscale Research Letters, 10 (1), Pp. 0–5. https://doi.org/10.1186/s11671-015-0814-6

Liu, G., Wang, K., Hoivik, N., and Jakobsen, H., 2012. Progress on free-standing and flow-through TiO 2 nanotube membranes. Solar Energy Materials and Solar Cells, 98, Pp. 24–38. https://doi.org/10.1016/j.solmat.2011.11.004

Liu, X., Carvalho, P., Getz, M.N., Norby, T., and Chatzitakis, A., 2019. Black Anatase TiO2 Nanotubes with Tunable Orientation for High Performance Supercapacitors. Journal of Physical Chemistry C, 123 (36), Pp. 21931–21940. https://doi.org/10.1021/acs.jpcc.9b05070

Mazierski, P., Nischk, M., Gołkowska, M., Lisowski, W., Gazda, M., Winiarski, M.J., Klimczuk, T., and Zaleska-Medynska, A., 2016. Photocatalytic activity of nitrogen doped TiO2 nanotubes prepared by anodic oxidation: The effect of applied voltage, anodization time and amount of nitrogen dopant. Applied Catalysis B: Environmental, 196, Pp. 77–88. https://doi.org/10.1016/j.apcatb.2016.05.006

Mohammadi, I., Zeraatpisheh, F., Ashiri, E., and Abdi, K., 2020. Solvothermal synthesis of g-C3N4 and ZnO nanoparticles on TiO2 nanotube as photoanode in DSSC. International Journal of Hydrogen Energy, 45 (38), Pp. 18831–18839. https://doi.org/10.1016/j.ijhydene.2020.04.277

Mohan, L., Dennis, C., Padmapriya, N., Anandan, C., and Rajendran, N., 2020. Effect of Electrolyte Temperature and Anodization Time on Formation of TiO2 Nanotubes for Biomedical Applications. Materials Today Communications, 23, Pp. 101103. https://doi.org/10.1016/j.mtcomm.2020.101103

Montakhab, E., Rashchi, F., and Sheibani, S., 2020. Modification and photocatalytic activity of open channel TiO2 nanotubes array synthesized by anodization process. Applied Surface Science, 534, Pp. 147581. https://doi.org/10.1016/j.apsusc.2020.147581

Niu, D., Zhou, Q., Zhu, X., Feng, X., Chen, S., Wang, A., and Song, Y., 2020.

Formation of TiO2 nanopetal architectures originated from anodic titanium oxide nanotubes. Chemical Physics Letters, 759, Pp. 137950. https://doi.org/10.1016/j.cplett.2020.137950

Noman, M.T., Ashraf, M.A., Ali, A., 2019. Synthesis and applications of nano-TiO 2 : a review. Environmental Science and Pollution Research, 26 (4), Pp. 3262–3291. https://doi.org/10.1007/s11356-018-3884-z

Ocampo, R.A., and Echeverría, F.E., 2021. TiO2 nanotubes are produced on curved titanium surfaces using aqueous electrolytes with carboxymethyl cellulose. Physica E: Low-Dimensional Systems and Nanostructures, 125, Pp. 2–5. https://doi.org/10.1016/j.physe.2020.114391

Omidvar, H., Goodarzi, S., Seif, A., and Azadmehr, A.R., 2011. Influence of anodization parameters on the morphology of TiO2 nanotube arrays. Superlattices and Microstructures, 50 (1), Pp. 26–39. https://doi.org/10.1016/j.spmi.2011.04.006

Ozkan, S., Mazare, A., and Schmuki, P., 2018. Critical parameters and factors in the formation of spaced TiO2 nanotubes by self-organizing anodization. Electrochemical Acta, 268, Pp. 435–447. https://doi.org/10.1016/j.electacta.2018.02.120

Patil, J.V., Mali, S.S., Hong, C.K., Kim, J.H., and Patil, P.S., 2017. Structural, morphological, and wettability study of electrochemically anodized 1D TiO2 nanotube arrays. Applied Physics A: Materials Science and Processing, 123 (10), Pp. 1–8. https://doi.org/10.1007/s00339-017-1197-6

Paulose, M., Varghese, O.K., Mor, G.K., Grimes, C.A., and Ong, K.G., 2006. Unprecedented ultra-high hydrogen gas sensitivity in undoped titania nanotubes. Nanotechnology, 17 (2), Pp. 398–402. https://doi.org/10.1088/0957-4484/17/2/009

Prakash, J., Samriti, Kumar, A., Dai, H., Janegitz, B.C., Krishnan, V., Swart, H.C., and Sun, S., 2021. Novel rare earth metal–doped one-dimensional TiO2 nanostructures: Fundamentals and multifunctional applications. Materials Today Sustainability, 13, 100066. https://doi.org/10.1016/j.mtsust.2021.100066

Puga, M.L., Venturini, J., ten Caten, C.S., Bergmann, C.P., 2022. Influencing parameters in the electrochemical anodization of TiO2 nanotubes: Systematic review and meta-analysis. Ceramics International, https://doi.org/10.1016/j.ceramint.2022.04.059

Qin, L., Chen, Q., Lan, R., Jiang, R., Quan, X., Xu, B., Zhang, F., and Jia, Y., 2015. Effect of anodization parameters on morphology and photocatalysis properties of TiO2 nanotube arrays. Journal of Materials Science and Technology, 31 (10), Pp. 1059–1064. https://doi.org/10.1016/j.jmst.2015.07.012

Reghunath, S., Pinheiro, D., KR, S.D., 2021. A review of hierarchical nanostructures of TiO2: Advances and applications. Applied Surface Science Advances, 3, Pp. 100063. https://doi.org/10.1016/j.apsadv.2021.100063

Ribeiro, B., Offoiach, R., Rahimi, E., Salatin, E., Lekka, M., and Fedrizzi, L., 2021. On growth and morphology of tio2 nanotubes on ti6al4v by anodic oxidation in ethylene glycol electrolyte: Influence of microstructure and anodization parameters. Materials, 14 (10). https://doi.org/10.3390/ma14102540

Ribeiro, B., Ruben, O., Stefano, R., Elisa, S., Maria, L., 2022. On Growth and Morphology of TiO2 Nanotubes on CP-Ti by Anodic Oxidation in Ethylene Glycol Electrolyte: Influence of Electrolyte Aging and Anodization Parameters. Materials, 15 (09). https://doi.org/https://doi.org/10.3390/ma15093338

Robinson, A.O., and Félix, E.E., 2018. Effects of fluoride source on the characteristics of titanium dioxide nanotubes. Applied Surface Science, 445, Pp. 308–319. https://doi.org/10.1016/j.apsusc.2018.03.139

Saqib, M., Lai, J., Zhao, J., Li, S., and Xu, G., 2016. Bipolar Electrochemical Approach with a Thin Layer of Supporting Electrolyte towards the Growth of Self-Organizing TiO2 Nanotubes. Chem. Electro. Chem., 3 (3), Pp. 360–365. https://doi.org/10.1002/celc.201500182

So, S., Lee, K., Schmuki, P., 2012. Ultrafast growth of highly ordered anodic TiO 2 nanotubes in lactic acid electrolytes. Journal of the American Chemical Society, 134 (28), Pp. 11316–11318. https://doi.org/10.1021/ja301892g

Song, E., Kim, Y.T., Choi, J., 2019. Anion additives in rapid breakdown anodization for nonmetal doped TiO2 nanotube powders. Electrochemistry Communications, 109, Pp. 106-610. https://doi.org/10.1016/j.elecom.2019.106610

Sreekantan, S., Lockman, Z., Hazan, R., Tasbihi, M., Tong, L.K., and Mohamed, A.R., 2009. Influence of electrolyte pH on TiO2 nanotube formation by Ti anodization. Journal of Alloys and Compounds, 485 (1–2), Pp. 478–483. https://doi.org/10.1016/j.jallcom.2009.05.152

Suhadolnik, L., Marinko, Ž., Ponikvar-Svet, M., Tavčar, G., Kovač, J., and Čeh, M., 2020. Influence of Anodization-Electrolyte Aging on the Photocatalytic Activity of TiO2 Nanotube Arrays. Journal of Physical Chemistry C, 124 (7), Pp. 4073–4080. https://doi.org/10.1021/acs.jpcc.9b09522

Tesler, A.B., Altomare, M., Schmuki, P., 2020. Morphology and Optical Properties of Highly Ordered TiO2Nanotubes Grown in NH4F/ o-H3PO4Electrolytes in View of Light-Harvesting and Catalytic Applications. ACS Applied Nano Materials, 3 (11), Pp. 10646–10658. https://doi.org/10.1021/acsanm.0c01859

Xue, J., Jiang, S., Lei, C., Chang, H., Gao, J., Liu, X., Li, Q., and Shen, Q., 2022. Construction of multi-homojunction TiO 2 nanotubes for boosting photocatalytic hydrogen evolution by steering photogenerated charge transfer.

Yi, Z., Zeng, Y., Wu, H., Chen, X., Fan, Y., Yang, H., Tang, Y., Yi, Y., Wang, J., and Wu, P., 2019. Synthesis, surface properties, crystal structure and dye-sensitized solar cell performance of TiO2 nanotube arrays anodized under different parameters. Results in Physics, 15, Pp. 102-609. https://doi.org/10.1016/j.rinp.2019.102609

Zhang, J., Li, S., Ding, H., Li, Q., Wang, B., Wang, X., and Wang, H., 2014. Transfer and assembly of large area TiO2 nanotube arrays onto conductive glass for dye sensitized solar cells. Journal of Power Sources, 247, Pp. 807–812. https://doi.org/10.1016/j.jpowsour.2013.08.124

Zheng, X., Li, Y., You, W., Lei, G., Cao, Y., Zhang, Y., and Jiang, L., 2022. Construction of Fe-doped TiO2−x ultrathin nanosheets with rich oxygen vacancies for highly efficient oxidation of H2S. Chemical Engineering Journal, 430 (P2), Pp. 132-917. https://doi.org/10.1016/j.cej.2021.132917

Zubair, M., Kim, H., Razzaq, A., Grimes, C.A., In, S.I., 2018. Solar spectrum photocatalytic conversion of CO2 to CH4 utilizing TiO2 nanotube arrays embedded with graphene quantum dots. Journal of CO2 Utilization, 26, Pp. 70–79. https://doi.org/10.1016/j.jcou.2018.04.004