Factor Affecting Geometry of TiO$_2$ Nanotube Arrays (TNAs) in Aqueous and Organic Electrolyte

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Abstract

TiO$_2$ nanotube arrays (TNA) have attracted scientific interest due to the combination of functional material properties with controllable nanostructure. Superior properties of TNA, including vectorial pathway of $e^-$ transport, minimized $e^-$ recombination, and high specific surface area render them as the most promising candidate for environment remediation, energy conversion and biocompatibility applications. The superior properties and efficacy of the TNA in various applications influenced by structural characteristics such as pore size, length and wall thickness. Therefore in this chapter the effect of various electrochemical parameters such as applied voltage, anodization time, electrolyte composition on the formation of controlled dimension of TNA in aqueous and organic electrolytes are reviewed.

Keywords: TiO$_2$ nanotube arrays (TNA), anodization, electrochemical parameters, aqueous electrolyte, organic electrolytes

1. Introduction

Within the last decade, nanoscale and nanostructured metal oxide materials have strongly influenced numerous fields in science and technology. Among the various nanostructured oxide materials, TiO$_2$ nanotube arrays (TNA) have received special attention due to its enhanced properties, cost-effective fabrication and higher surface-to-volume ratio [1]. TNA offers unique properties and a high functionality for various applications such as photocatalysis [2, 3], solar cell [4–6], biomedical [7, 8], and sensors [9, 10]. Their performance in various applications significantly determined by geometry, shape, and morphology of nanostructures [11]. In this concern, a
defined arrangement and a vertical and homogeneous alignment over the entire substrate sur-
face, based on the self-organized anodic oxidation is pursued. Electrochemical anodization is
widely used because of its controllable, reproducible results and simplicity of the process. The
feasibility to tune the size and shape of nanotubular arrays to the desired dimensions and
meeting the demands of specific applications by means of controlled anodic oxidation of the
metal substrate have widen the application of TNA. Furthermore, it is a cost-effective method
and the tubes prepared via this method have good adherent strength.

2. Factor affecting geometry and composition of TNA

The anodic growth of self-organized tubular structure is well known as the equilibrium
reaction between electrochemical oxidation at the metal/electrolyte interface and chemical
dissolution at the oxide/electrolyte interface [12, 13]. The structural characteristics of the nano-
tube arrays can be controlled through various synthesis parameters, including applied poten-
tial [14–16], anodization time [14, 17, 18], electrolyte type and chemical composition [12, 13,
19]. Therefore, this section provides a comprehensive review on the influence of aforemen-
tioned parameters on the formation of TNA.

2.1. TNA synthesis using aqueous electrolytes

Gong and co-workers [20] first obtained self-organized, highly-uniform TNA by anodizing
Ti in aqueous electrolyte containing 0.5 wt% HF under applied potential of 10–20 V. The pore size
increased with increasing applied potential while the nanotube length was dependent on the
anodization time. Titanium undergoes electrochemical oxidation process as follow: Ti + 2H₂O →
TiO₂ + 4H⁺ (Reaction 1) and chemical dissolution process: TiO₂ + 6HF → [TiF₆]²⁻ +2H₂O + 2H⁺
(Reaction 2) to form nantubular structure. However, the length of nanotubes was limited to a
maximum of ~500 nm, due to the restriction imposed by high chemical dissolution of formed oxide
by strong acidity of HF aqueous electrolyte, c.a., pH < 2 [14, 21]. The chemical dissolution of the
formed oxide is determined by the F⁻ concentration and the pH value of the solution (Reaction 2).
The model proposed by Macak and co-workers suggest that F⁻ and H⁺ are attracted toward the
pore bottom during anodization (Figure 1a), followed by establishment of pH profile as in
(Figure 1b). The variation in pH profile triggers different degree of dissolution rate along the tube
inner surface (Figure 1c).

This work directly leads to the use of buffer solution as electrolyte to control pH and increase
the length of nanotube produced. Reaction 2 permits the dissolution reaction and become the
core foundation of field-assisted dissolution model. Since then, many authors have adapted
the dissolution process into their research framework such that field-assisted dissolution
model is gradually established for TNA anodization [22–24].

Large number of F⁻ and H⁺ ions in HF aqueous electrolyte dominates high chemical dissolu-
tion and thus hinders the equilibrium growth of the nanotube arrays [12]. Beranek et al. [25]
found that the incorporation of low concentration of HF aqueous electrolyte with acetic acid
(H₂SO₄) addition could reduce the chemical dissolution, and thus allows the formation of porous TiO₂ with improved structural morphologies. This basis was later used to obtain TNA with well-defined tubular structure over applied potential range of 10–25 V [14]. The nanotube length and pore diameter increased linearly with increasing applied potential. In summary, the structural morphologies of anodic growth oxides can be controlled by the acidity of electrolyte [26].

Macak et al. [12] investigated the influence of the electrolyte acidity on the growth of nanotube arrays using HF, potassium fluoride (KF) and sodium fluoride (NaF) as F⁻ sources. TNA with ~280 nm long and ~40 nm pore diameter were formed in strong acidity (pH < 1) HF aqueous electrolyte after 2 h of anodization at 10 V. The increase in the pH value of electrolyte to 1.3 and 2.8 by using KF and NaF instead of HF resulted in the formation of TNA with the nanotube length of ~320 and 590 nm, respectively. TNA with a maximum length of 1.5 μm were achieved at 25 V. Moreover, the nanotube length is proportional to the anodization time, and thus resulted in the formation of nanotube arrays with length of ~800 nm, ~1.8 μm and ~2.3 μm after exposure for 20, 60 and 90 h in electrolyte with pH of 3.8. It is interesting to note that the acidity of electrolyte plays an essential role for the growth of long nanotube arrays instead of
the anodization time. The increase of pH value from 3.8 to 4.5 resulted in significant increase in the nanotube length from ~800 nm to ~4.4 μm after anodization at 10 V for 20 h.

The significance of the pH value of an electrolyte on the growth of TNA was proven by Bauer et al. [27]. Self-organized TNA was successfully formed in 1 M H$_3$PO$_4$ containing 0.3 wt% HF over applied potential range from 1 V to 25 V. Weak acidity of H$_3$PO$_4$ governs the local acidification during pore growth, and thus allowed the control of nanotube geometry over wide range of applied potential [12]. In 2007, Allam and Grimes [28] demonstrated an alternative method to fabricate TNA using hydrochloride (HCl) instead of fluoride-containing electrolyte. The anodization in 3 M HCl aqueous electrolyte at 20 V for 20 min allowed the formation of TNA with the nanotube length of ~600 nm. However, high chemical dissolution of aqueous electrolytes still remains as significant restriction in achieving long nanotubes with smooth walls. This limitation of forming long TNA in aqueous electrolyte has extended the use organic electrolyte to reduce the chemical dissolution process.

2.2. TNA synthesis using organic electrolytes

An organic electrolyte is known as efficient solvent in anodic fabrication of highly-ordered self-organized porous alumina (Al$_2$O$_3$) at high applied potential, c.a., 100 V [29, 30]. The incorporation of organic component from the electrolyte into anodic oxide film is known to lower the relative permittivity of oxide and increase its dielectric breakdown potential [18], thereby allowing the anodic growth of oxide film under wide range of applied potential [13, 31].

2.2.1. Dimethyl sulfoxide (DMSO)

Ruan et al. [19] demonstrated the anodic growth of TNA in fluorinated dimethyl sulfoxide (DMSO) and ethanol (EtOH) mixture. Well-aligned TNA with 2.3 μm in length were formed by anodization in 1:1 DMSO and EtOH mixture containing 4 wt% HF at 20 V for 70 h. DMSO is a dipolar aprotic solvent. Unlike protic solvents, aprotic solvents do not have a hydrogen atom directly bonded to an electronegative atom, such as oxygen or nitrogen. DMSO has a very weak ability to donate protons (hydrogen bond donation) and it is more basic than water, implying that DMSO has a protophilic nature [21]. DMSO accepts the hydrogen proton from HF and thus allows the formation of long nanotubes by the reduction of the chemical dissolution. However, the donation of oxygen in organic electrolyte is more difficult than aqueous electrolyte, and thus limited the nanotube length even after long anodization time. Discrete nanotube arrays obtained in 1:1 DMSO and EtOH mixture exhibited fourfold higher photocurrent density as compared to that formed in aqueous electrolyte [20]. This reveals the potential of organic electrolyte for the formation of long TNA for superior photoelectrochemical properties. The nanotube length was later increased up to 93 μm by anodization in DMSO containing 2 wt% HF at 60 V for 70 h refer to Figure 2a-d [13, 15].

To enhance the oxidation rate in organic electrolyte, water usually serves as a source of O$_2^-$ and hydroxyl ion; OH$^-$ [13, 15]. Several authors reported that small amount of water addition could improve the adhesion between the nanotube and underlying oxide barrier layer. This facilitates the growth of long nanotubes [32, 33]. Large amount of water addition however
decreased the viscosity of electrolyte [3, 34], leading to high chemical dissolution by the higher diffusion rate of reactant ions [35]. The minimum amount of water less than 5 wt% limits the chemical dissolution and thus allows the nanotube to grow deeply into the metal without significant loss at the pore mouth. Besides, thinner barrier layer in such condition allows greater ionic conduction and faster movement of the metal/oxide interface into the metal, thus producing long TNA [13, 32].

The significance of anodization parameters, including applied potential, $F^-\text{ concentration}$, water content and anodization time on the structural characteristics of TNA were extensively investigated by Yoriya et al. [33] and the finding are presented in Figure 3a-e. Higher applied potentials provide a greater driving force for both electronic and ionic conduction and thus allow the growth of long nanotube arrays. A maximum length of TNA of 101 $\mu m$ was achieved by anodic growth in DMSO containing 2 wt% HF at 60 V for 70 h.

Figure 3b reveals that 2 wt% HF concentration allowed the formation of longest nanotube at both 40 and 60 V. HF concentration higher than 2% greatly increases the chemical dissolution, and thus reduces nanotube length. Furthermore, chemical dissolution is relatively lower than electrochemical oxidation in DMSO electrolyte containing less than 2 wt% HF, resulting in the formation of short nanotubes. The addition of H$_2$O facilitates the extraction of O$^{2-}$ and OH$^-$.
from electrolyte to form oxide, contributing to the formation of long nanotube with thick walls. However, high H$_2$O amount (> 2 wt%) dominates chemical dissolution and thus reduces the nanotube length (Figure 3c). Figure 3d shows that nanotube length increased up to 70 h and then decreased continuously. The shorter nanotube length after 70 h is caused by slow diffusion of F$^-$, due to the accumulation of reaction products at the tube bottom, as well as significant loss at atop of nanotube by high chemical dissolution [5, 13].

2.2.2. Amide – Formamide (FA) and N-methylformamide (NMF)

Formamide (FA) and N-methylformamide (NMF) have been used as electrolyte for fabricating long nanotubes with high growth rate [15]. FA and NMF are both protophilic like DMSO, meaning that their acidity nature is weaker than water [21]. The dielectric constant of FA and NMF are 111 and 182.4, respectively, which are much higher than water; ~78.39. Higher dielectric constant of electrolyte induces more charges on the oxide layer and thus improves
the extraction of Ti$^{4+}$ ions, and facilitates the dissolution of HF for it to be chemically available at the oxide/electrolyte interface [13]. Paulose et al. [15] fabricated TNA of ~69 μm long in FA electrolyte containing 0.27 M NH$_4$F at 35 V for 48 h. It is noticeable that the growth rate increased to ~24.3 nm min$^{-1}$, which is relatively higher than that formed in DMSO [19] or aqueous electrolyte [36]. Shankar et al. [13] further investigated the influence of applied potential at 20–30 V, and NH$_4$F concentration in the range of 0.11–0.37 M. The nanotube length and pore size increase with increasing applied potential and concentration of NH$_4$F, achieving a maximum length of ~78 μm in FA containing 0.37 M NH$_4$F. Besides, the incorporation of high polarity electrolyte, NMF into FA also accelerates the chemical dissolution and thus results in nanotubes with larger pore size.

2.2.3. Glycerol

The diffusion of ionic species in electrolyte greatly affects the growth of TNA by local acidification at the pore bottom [12]. Macak and colleagues [34] investigated the influence of electrolyte viscosity on the formation of TNA by anodization in various types of electrolyte; 1 M ammonium sulfate [(NH$_4$)$_2$SO$_4$] containing 0.5 wt% NH$_4$F, 1:1 glycerol and H$_2$O mixture containing 0.5 wt% NH$_4$F, and glycerol containing 0.5 wt% NH$_4$F. The viscosities of these electrolytes were ~0.001, ~0.004 and ~1.5 Pa.s, respectively. The anodization in (NH$_4$)$_2$SO$_4$ electrolyte allowed the formation of TNA with length of ~2 μm while the anodization in glycerol electrolyte resulted in nanotube arrays with ~1.3 μm in length. However, the incorporation of large amount of water leads to the presence of ripples at the nanotube walls, resulting from high chemical dissolution in electrolyte. The nanotube length formed in glycerol-based electrolyte increases almost linearly with increasing anodization time, and achieved ~6.1 μm after anodization at 20 V for 18 h.

The viscosity of electrolyte can be also affected by anodization temperature [34, 37]. The viscosity of glycerol containing 0.5 wt% NH$_4$F decreases from 12 Pa.s to 1.5 and 0.3 Pa.s by increasing temperature from 0°C to 20 and 40°C, respectively. Low viscosity facilitates the diffusion of reactants at the pore tip, resulting in long nanotube with large pore. As mentioned earlier, the incorporation of organic species from organic electrolyte into the oxide film during anodization allows the growth of nanotube arrays under a wide range of applied potential. Alivov et al. [31] investigated the formation behavior of TNA in a broad range of applied potential of 5–350 V and F$^-$/C$_0$ concentration of 0.1–0.7 wt%. TNA were formed in glycerol under applied potential of 10–240 V, and the applied potential is disproportional to F$^-$ concentration.

2.2.4. Ethylene glycol (EG)

The anodization in high viscosity (μv) electrolyte of about 945 cP at 25°C resulted in relatively shorter nanotube length as compared to that formed in aqueous electrolyte. Hence, the potential of low viscosity polyol solvent, such as ethylene glycol (EG, μv = 16 cP at 25°C) for the formation of TNA was investigated by [34]. TNA with ~1.6 μm in length were obtained by anodization in EG containing 0.5 wt% NH$_4$F at 12 V for 3 h. The significant increase in the nanotube length in EG-based electrolyte could be attributed to lower diffusion resistance in electrolyte with lower viscosity [21]. The potential of EG as efficient electrolyte was later
confirmed by [32]. The anodization in EG containing 0.25 wt% NH$_4$F at 60 V allowed the rapid formation of nanotube arrays with the growth rate up to 131.4 nm min$^{-1}$. The resulting nanotube arrays exhibited length of 134 μm and pore size of 25 nm after 17 h of anodization. The nanotube length was further increased to 220 μm by anodization in EG containing 0.3 wt% NH$_4$F and 2 wt% H$_2$O [13], implying the significant role of H$_2$O addition on the growth of long nanotube arrays.

The influences of anodization parameters, including H$_2$O content, NH$_4$F concentration, applied potential and anodization time on the growth of TNA in EG-based electrolytes were systematically investigated by Prakasam et al. [35]. The increase in the H$_2$O content and NH$_4$F concentration stimulate electrochemical oxidation at the metal/oxide interface and chemical dissolution at the oxide/electrolyte interface, resulting in longer nanotube length up to 220 μm by anodization in EG containing 2 wt% H$_2$O and 0.3 wt% NH$_4$F. Further increase of water content and NH$_4$F concentration leads to disequilibrium reaction between electrochemical oxidation and chemical dissolution and thus resulted in shorter nanotube in the range of 54–136 μm (Table 1).

In the presence of optimum H$_2$O content, O$_2^-$ and/or OH$^-$ are injected into the body of the oxide layer, and affect the structure efficiently to impede the ionic transport at barrier layer [38]. This greatly accelerates the inward movement of the metal/oxide interface into the metal surface and thus resulting in long nanotubes with thick walls. Higher content of H$_2$O largely increases the number of extracted oxygen and/or hydroxyl ions per unit area of the oxide layer, leading to higher chemical dissolution. The increase in the F$^-$ concentration provides higher chemical dissolution at the oxide/electrolyte interface, thereby allowing higher number of ion migrate across thin barrier layer. This resulted in the formation of long nanotube with thin walls. However, high chemical dissolution in electrolyte containing high F$^-$ concentration induces a significant loss from the pore mouth and thus formed short nanotubes.

The anodic growth of TNA in used electrolyte significantly increased the nanotube length. Lower electrical conductivity of used electrolyte hinders ionic migration across barrier layer, thereby reducing loss at the pore tip by high chemical dissolution. Inner and outer diameters and nanotube length were found to increase with increasing applied potential from 20 V to 60 V (Table 2). Further increase of applied potential to 65 V resulted in further increase in inner and outer diameters but decreased the nanotube length. This implies a significant loss at the pore tip by high chemical dissolution under applied potential higher than 60 V. The anodization time is

|        | 0.1 wt% HN$_4$F | 0.3 wt% HN$_4$F | 0.5 wt% HN$_4$F |
|--------|----------------|----------------|----------------|
| 1 % Vol H$_2$O |              |                |                |
| Fresh  | 54            | 67             | 47             |
| Used   | 70            | 156            | 115            |
| 2 % Vol H$_2$O |              |                |                |
| Fresh  | 85            | 165            | 106            |
| Used   | 105           | 220            | 45             |
| 3 % Vol H$_2$O |              |                |                |
| Fresh  | -             | 136            | 85             |
| Used   | -             | 100            | 66             |

Table 1. Summary of nanotube length (in μm) obtained by varying the concentration of H$_2$O of 1–3 wt%, and NH$_4$F of 0.1–0.5 wt% in EG with respect to fresh and once-used solution [35].
also an important available. The nanotube length increased with increasing anodization time, and achieved a maximum of 360 μm at 96 h. The growth rate was found as 241.7 nm min⁻¹ at 4 h. It decreased exponentially and reached a minimum of 62.5 nm min⁻¹ at 96 h. Paulose and co-workers [15] later achieved the formation of ultra-long TNA with 1000 μm in length by anodization in EG containing 3.5 wt% H₂O and 0.6 wt% NH₄F at 60 V for 216 h.

2.2.5. Polyol – Diethylene glycol (DEG), triethylene glycol (TEG), polyethylene glycol (PEG)

The investigation of organic electrolyte was extended to several types of polyol solvents, for example diethylene glycol (DEG), triethylene glycol (TEG) and polyethylene glycol (PEG) in comparison to EG [39]. Large amount of oxy and hydroxyl groups in TEG and PEG allows higher self-association via intra- and intermolecular hydrogen bonds, and consequently forms anatase crystallite by bridging the oxygen atom and hydroxyl groups in TiO₂. However, their high viscosity and molecular weight retard the growth of nanotubes, and thus does not satisfy the requirement of practical applications. In 2010, Sreekantan et al. [3] demonstrated extremely fast-formation of TNA with approximately ~15 μm in length by anodization in EG containing excessive-fluoride 0.5 wt% NH₄F and 1 wt% H₂O. The nanotubes were formed with high growth rate up to 308.3 nm min⁻¹. However, high chemical dissolution in EG containing excessive-fluoride limits the anodization time at 1 h. Recently, the addition of alkali species appears as alternative approach to improve the balance between electrochemical oxidation and chemical dissolution. The incorporation of sodium carbonate (Na₂CO₃) into EG allowed the rapid growth of TNA with the growth rate up to 1 μm min⁻¹ [40]. It is noteworthy that the anodic growth of TNA in EG is only method that induces the carbon species into the nanotube through the pyrogenation of ethylene (C₂H₂) in EG [41], thereby enabling visible-light absorption [42] without further processing [43, 44].

3. Conclusion

TNA is by far among the most investigated functional metal oxide. The possibility of growing porous anodic nanostructure, particularly self-organized and highly-ordered TNA through anodization has further enlarged the research interest on this TNA due to specific advantages, such as large surface area, relatively long electron diffusion length and biocompatibility. In this

| Voltage (V) | Inner diameter (nm) | Outer diameter (nm) | Length (mm) |
|------------|---------------------|---------------------|-------------|
| 20         | 45                  | 65                  | 5           |
| 40         | 70                  | 115                 | 30          |
| 50         | 90                  | 140                 | 45          |
| 60         | 105                 | 155                 | 165         |
| 65         | 135                 | 185                 | 105         |

Table 2. Summary of nanotube inner diameter, outer diameter and length obtained by anodization in fresh-EG containing 2 and 0.3 wt% NH₄F at different applied potential for 17 h [35].
chapter, the formation of TNA and various parameters, which affects the tube formation and properties of TNA were discussed. The tube length, thickness, and diameter were varied according to the pH, electrolytes, anodization potential, and time. Today, TNA are used as solar cell, self-cleaning coating, orthopedic and dental implants, and also an effective drug delivery carrier for the cancer therapy.

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Conflict of interest

There is no conflict of interest in this chapter.

Author details

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