

Anodic growth of large-diameter multipodal TiO₂ nanotubes

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Abstract

We report on the formation of a new class of nanostructures, namely multipodal hollow titania nanotubes possessing two or more legs, achieved during the electrochemical anodization of titanium in diethylene glycol-based electrolytes. Multipodal nanotubes form by a process we term ‘nanotube combination’, which only occurs in viscous electrolytes at high anodization potentials in the presence of a low concentration of fluoride-bearing species.

Introduction

N-type semiconducting, vertically oriented, self-organized TiO₂ nanotube arrays formed by electrochemical anodization constitute a mechanically robust, high surface area, easily functionalized architecture with vectorial electron percolation pathways^{1, 2}. Consequently, they have demonstrated superior performance as gas sensors^{3, 4}, photocatalysts^{5, 6} and also as scaffolds for excitonic solar cells⁷⁻⁹. Other promising applications where the tubular structure and tunable pore-size of TiO₂ NT arrays are the properties of interest, include drug eluting coatings for medical implants¹⁰, solid-phase microextraction (SPME) fibers¹¹ and stem cell differentiation^{12, 13}. Despite the impressive progress in tuning the length, wall-thickness, diameter

and pattern order of anodically formed TiO₂ NT arrays, there is still an unmet need for more complex hierarchical nanostructures which not only improve their functionality in present applications but also make novel applications possible. Applications and techniques which rely on volumetric filling or surface functionalization of nanotubes ¹⁴⁻¹⁸ will particularly benefit from the production of multipodal nanotubes with a more complex topology. The differential chemical functionalization of the individual legs allows for multiplexed sensing and the loading of multiple drugs. Moreover, since the multipodal structure provides more than one leg for each of the nanotubes, a more robust attachment of nanotubes onto desired substrates is possible which also renders them good load bearing elements for mounting heavier structures. The branched topology of multipodal titania nanotubes consisting of a large diameter nanotube dividing at the end into several smaller size nanotubes, could be applied for phase separation in a fluid comprising several ingredients and for microfluidic and optofluidic applications. The multipodal topology also lends itself to use in three-terminal devices, electrical interconnect networks and nanoelectromechanical systems ¹⁹. The syntheses and applications of multipodal quantum dots—mainly tetrapodal nanocrystals of II-VI semiconductors such as ZnO, CdS and CdTe ²⁰ are a focus of intense research activity. The multipodal structure is highly advantageous in applications such as photocatalysis ²¹ and photovoltaics ²² due to the larger surface-to-volume ratio and more facile charge separation at the core-leg interfaces.

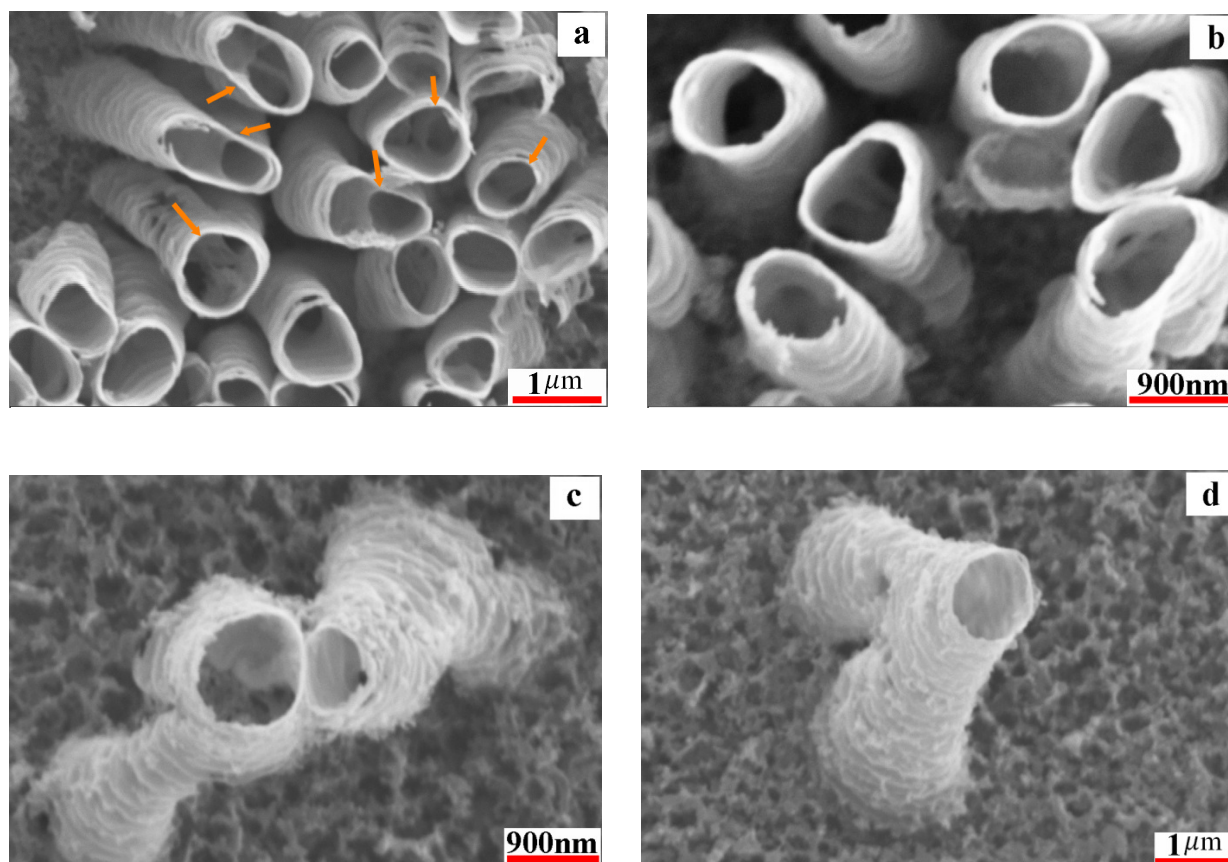


Figure 1. SEM images of multipodal titania nanotubes anodized in a DEG electrolyte with 0.25% HF and 2% water (a) at 120V for 44 h, (b) at 120V 47 h, (c) and (d) at 150V after 47 h. Arrows in Fig. 1a point to easily identifiable multipodal nanotubes not obscured by the topology or tilt angle.

To the best of our knowledge multipodal titania nanotubes have not been reported so far. Herein we report on the production of multipodal titania nanotubes (see **figure 1**) which result from a newly introduced process that we call *nanotube combination*. Almost every nanotube in the images of **figure 1a** and **1b** is at least bipodal. **Figure 1c** shows two bipodal nanotubes in the process of forming a tetrapodal nanotube whilst **figure 1d** is a tetrapodal nanotube, which appears bipodal at first glance, because the process of nanotube combination for the constituent bipodal nanotubes is complete. We propose a mechanism which explains the formation of multipodal nanotubes and also explains some of the unique features associated with the growth

of TiO₂ nanotube arrays in diethylene glycol (DEG)-based electrolytes. Anodization in DEG-based electrolytes exhibit some unusual features such as the formation of nanotubes with very large pore-sizes (up to 900 nm)²³ and discretization of nanotubes by large inter-tubular spacings²³⁻²⁵, a deviation from the close-packed architecture found in other electrolytes. Our studies indicate that the process of nanotube combination has a decisive role in the simultaneous increment of the both pore size and inter-tubular spacing of nanotube arrays anodically formed in a HF containing DEG electrolyte.

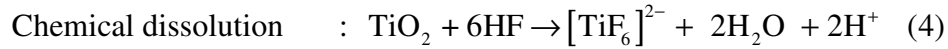
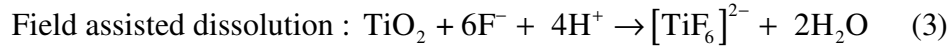
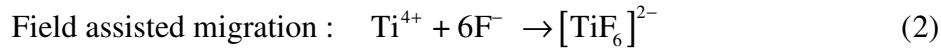
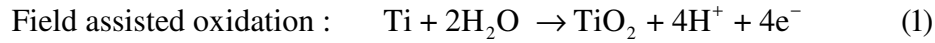
Experimental

Titania nanotube arrays were obtained by anodization of a 0.25 mm thick titanium foil (99.7%, Sigma Aldrich) in a two electrode anodization setup in which titanium foils were used as both the anode and cathode and only half of their length was immersed into the solution. Titanium foils were cleaned ultrasonically prior to anodization with soap, de-ionized water and isopropyl alcohol and were dried with nitrogen gas. Anodization was carried out at room temperature in an electrolyte consisting of a mixture of DEG (Fisher Chemical), HF (48% solution, Sigma Aldrich) and de-ionized water under the applied voltages of 120V and 150V. After anodization, the titanium foils containing the nanotubes were rinsed with isopropyl alcohol and dried in air. Subsequently, the cleaning process was completed by immersing the foils into 0.1 M HCl acid for an hour and drying it in the oven for one hour at 100° C. Morphology of the nanotubes including their length, diameter, wall thickness and separation was investigated using a scanning electron microscope (SEM, ZEISS) as well as a field-emission scanning electron microscope (FESEM, JEOL 6301F). Contact angles with the sessile drop technique and the

surface tension with pendant drop technique were measured using Krüss DSA 100 (Krüss GmbH, Hamburg, Germany). For the surface tension measurement, electrolytes of different degree of aging were selected whereas the contact angle of a fresh electrolyte on various TiO₂ substrate was measured. In case of surface tension measurement, an image of drop in hydromechanical equilibrium condition is captured. DSA drop shape analysis, in-built software in the Krüss DSA 100 system, was used for the image processing to determine the surface tension and contact angle of the electrolytes. The software relies on the derivation of surface tension based on the Laplace pressure equation. As the hydromechanical equilibrium condition of the pendant drop is a more important parameter than the drop volume, the change in the drop volume was ignored during the surface tension measurement. Five measurements on each sample with a specific degree of aging were taken and the average surface tension of the corresponding electrolytes was determined. For the contact angle measurement, the drop was disposed from needle to obtain a sessile drop on the substrate. It was observed that, the substrate shows perfect wetting conditions. Further details of such measurement procedure can be found elsewhere.²⁶

Results and discussion

Field assisted oxide dissolution and cation migration, field assisted oxidation of Ti and chemical etching are the competing reactions responsible for the growth of TiO₂ nanotube arrays (a key difference from the formation of nanoporous alumina, in which only the field assisted processes are important). The field assisted reactions occur on either side of the barrier layer at the bottom of the nanotubes and are responsible for driving the Ti/TiO₂ interface deeper into the Ti foil, a process that increases the length of the nanotubes. Chemical etching shortens the length of the nanotubes^{27,28}.



Nanotubes formed in HF bearing DEG-based electrolytes at large anodization potentials exhibit a definite taper with a wider base and a narrower mouth as shown in **figure 2a**. The taper occurs as a consequence of the significant variation in the conductivity of the electrolyte, which occurs over the course of the anodization process. The low conductivity of the DEG-based electrolyte has been remarked upon by others and occurs due to a combination of three factors : a) The high viscosity of DEG and the concomitant low ionic mobilities ²⁹ b) Low concentration of ionic charge carriers due to low dissociation of the weak acid (HF) and c) large hydrodynamic radius of dissociated ions due to solvation ³⁰ by water and DEG molecules. As the anodization of Ti proceeds, the concentration of $(\text{TiF}_6)^{2-}$ ions increases with time due to the chemical reactions represented by equations (2), (3) and (4). Due to a more delocalized distribution of charge in the complex ³¹, $(\text{TiF}_6)^{2-}$ ions are also less solvated and therefore more mobile. Consequently, the conductivity of the electrolyte increases with anodization duration, which manifests itself in a higher anodization current density at the same potential, an effect clearly seen in the anodization current transient plot of **figure 2b**, during the first 20 hours of anodization. The increase in the conductivity of the electrolyte makes a large proportion of the applied anodization potential available for the anodization process since the potential drop across the electrolyte (anodization current i x electrolyte resistance R) reduces with time. Therefore,

the base of the nanotubes which form later in the process, experience higher effective anodization voltages than the top (mouth) of the nanotubes, which are formed relatively early in the process. Due to the well-known dependence of the diameter of the nanotubes on the anodization voltage, a tapered nanotube morphology wider at the base than at the top is produced.

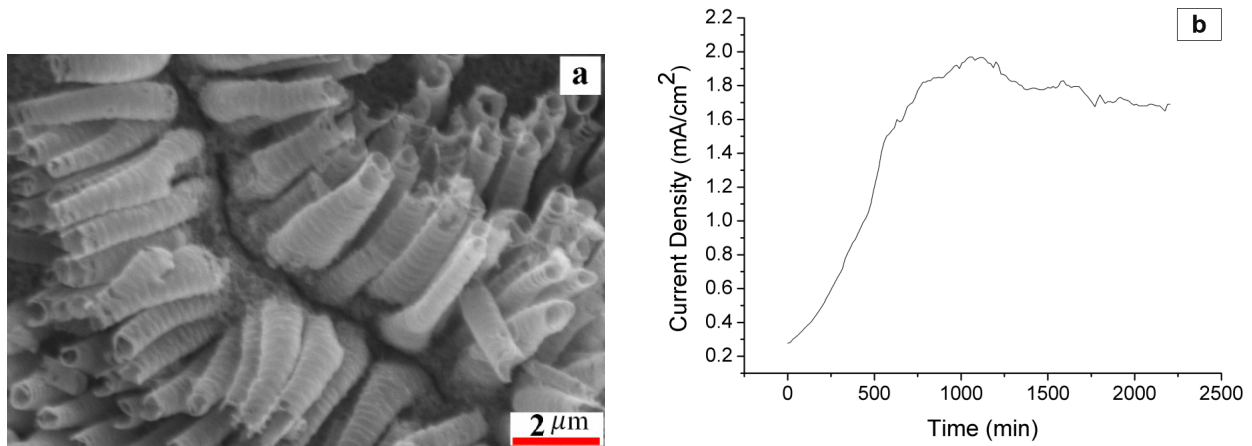


Figure 2. (a) SEM image of the cross-section of titania nanotubes formed by anodization at 120V in a DEG electrolyte with 0.25% HF and 1% water showing a clear taper from mouth to base. (b) Anodic current density as a function of anodization time for 120 V anodization identical DEG electrolyte (0.25% HF and 1% water).

The field assisted oxidation process generates H^+ ions according to equation (1) and results in local acidification at the pore bottom³². On the other hand, F^- ions are consumed by dissolution reactions. Therefore, while F^- concentration is maximum at the mouth of the tubes (nearly equal to concentration in the bulk electrolyte) and drops to a minimum at the pore bottom, H^+ ion concentration is maximum at the pore bottom and decreases towards the mouth of the tubes. Such a fluoride ion concentration gradient along the length of the nanotubes has been confirmed by compositional analysis using X-ray photoelectron spectroscopy (XPS)³³. It is also

fairly well-known that less fluoride results in a thick oxide layer which suppresses the transport of titanium, oxygen and fluorine ions, and excess fluoride results in a thin oxide layer which enhances the transport of titanium, oxygen and fluorine ions, thus inducing inward growth faster³⁴. Nanotube length increases so long as the rate of movement of the Ti/TiO₂ interface is faster than the rate of loss of TiO₂ NTs by chemical etching. The anodization current is roughly proportional to the strength of the field assisted reactions and is thus indicative of the rate at which the Ti/TiO₂ interface is moving into the Ti foil³⁵. As shown in **Figure 2b**, the anodization current increases for the first ~20 hours of anodization and then decreases nearly monotonically. As discussed previously, the increase in anodization current occurs due to an increase in electrolyte conductivity. Thus the rate of movement of the interface peaks ~20 hours into the anodization process and declines thereafter due to a paucity of fluoride ions at the pore bottom. At this point in the anodization process, field assisted dissolution weakens relative to field assisted oxidation, resulting in an increase in the thickness of the barrier layer. The thicker barrier layer retards the solid state ionic transport of reactants through the barrier layer and causes a decrease in the anodization current density. If purely high field ionic conduction was involved, then the current would be expected to continuously decrease with time. If purely mass transport control was involved, the anodization current would be expected to level off instead of decreasing. In our scheme, the anodization reaction is under mixed control of the high field solid state ionic transport and mass transport. Chemical etching, in contrast, is relatively constant and becomes more dominant as the anodization current decreases.

We propose a mechanism that explains our observations and accounts for the unique formation of multipodal TiO₂ nanotubes in HF-DEG-water electrolytes. As mentioned

previously, a gradient in fluoride bearing species exists along the length of the growing nanotube with the highest concentration corresponding to that of the bulk existing at the mouth of the tube and decreasing towards the barrier layer. Consequently, in the first 20 hours of the anodization process, when nanotubes are increasing in length, chemical etching, even though isotropic, only shortens the height of the nanotubes by etching from the top. The solid state transport of reactant ions through the barrier layer occurs through a high-field process exponentially dependent on the electric field across the barrier layer and therefore sensitive to barrier layer thickness. When the anodization current begins to decrease after 20 hours, there is increased competition for the lower current from all the nanotubes and minor variations in barrier layer thickness play a significant role in allocating current among nanotubes. As chemical etching becomes more dominant, nanotubes in regions where the barrier layer is slightly thicker grow into the Ti foil more slowly but experience the same rate of chemical etching, thus gradually becoming shorter than nanotubes in regions where the barrier layer is slightly thinner. Due to the tapered structure of the nanotubes, a decrease in the height of such nanotubes also increases inter-tubular spaces where the viscous bulk electrolyte (richer in fluoride) can now penetrate-thus the same nanotubes experience more accelerated rates of dissolution due to chemical attack from the sides in addition to etching from the top. Soon, these nanotubes are completely consumed. Also, since the Ti/TiO₂ interface in the regions of thicker barrier layer moves into the metal more slowly, these regions are gradually more elevated with respect to adjacent regions with a thinner barrier layer. This effect is clearly seen in **figure 3**, which shows two such regions adjacent to each other. The region enclosed by the yellow border in figure 3 has relatively close-packed nanotubes as well as dark regions indicative of depth and greater topographic contrast. The barrier layer is visible in region outside the yellow border, which is lighter on account of being at a higher elevation. In

this elevated region, several nanotubes have been consumed by chemical etching resulting in a wider separation. Several of the still-remaining nanotubes in this region have experienced severe sidewall etching (some of these are pointed out by the orange arrows in **figure 3**).

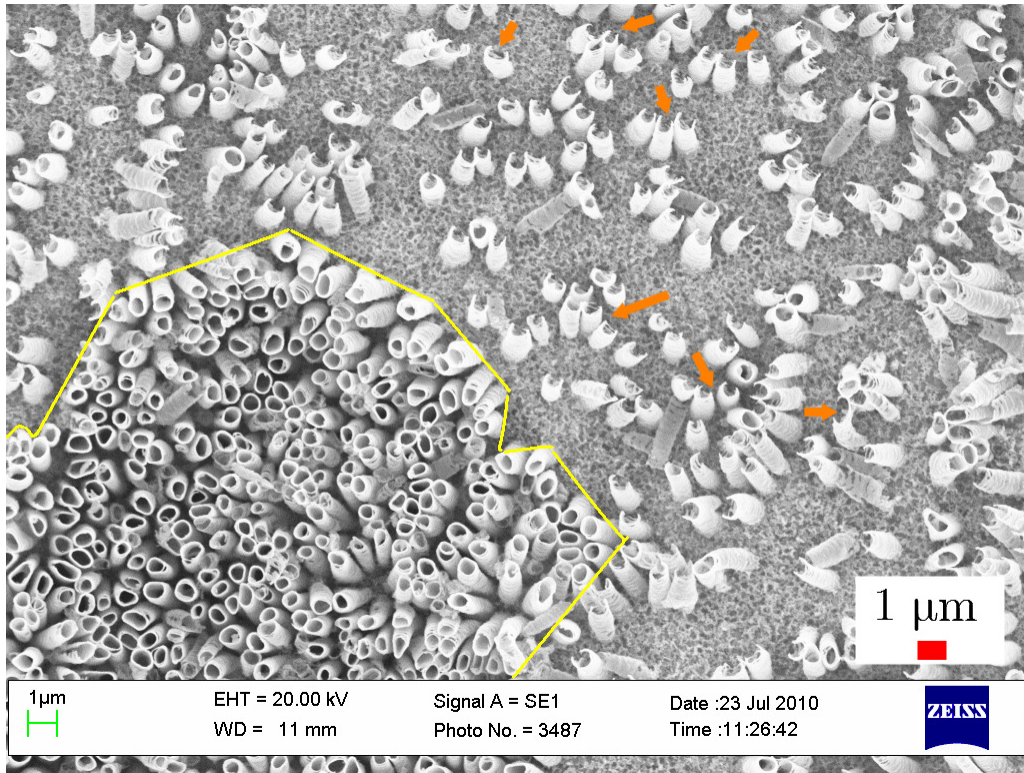
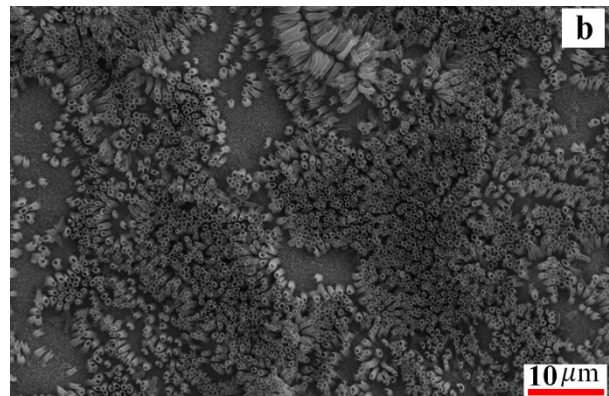
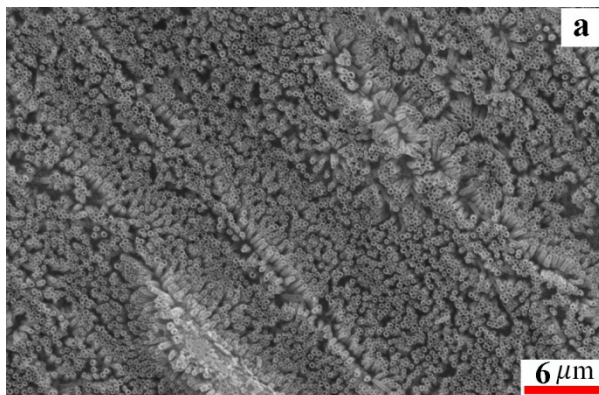


Figure 3. SEM images of the surface of a Ti foil anodized in a DEG-based electrolyte containing 0.25% HF and 1% H₂O for 43 hours at 120 V. Two distinct regions consisting of close-packed and widely separated nanotubes are demarcated by the yellow border.



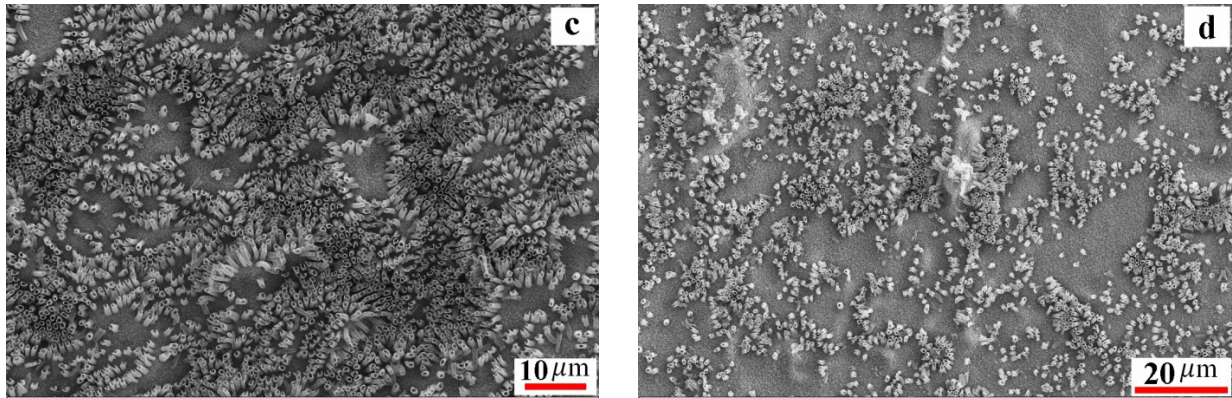
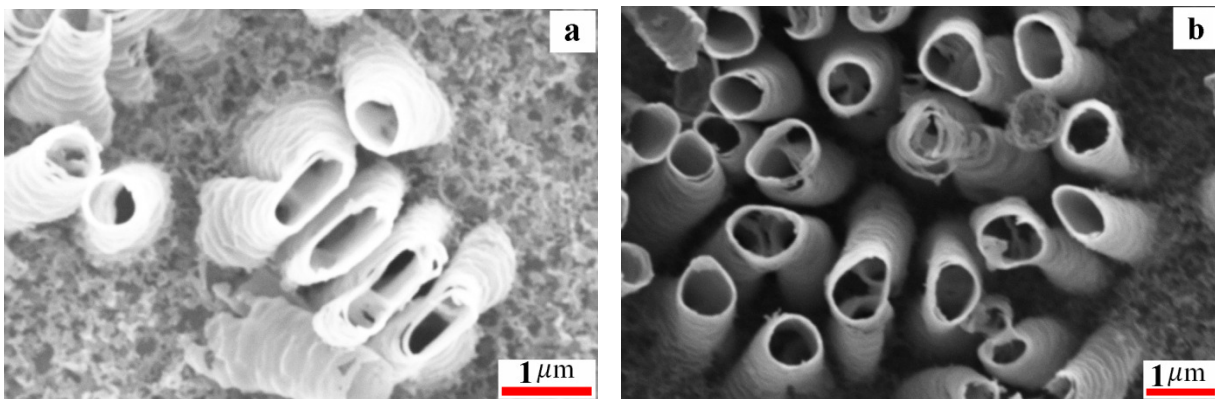


Figure 4. SEM images of titania nanotubes anodized at 120V in a DEG electrolyte with 0.25% HF and 1% water after a) 40 h, b) 43 h, c) 45 h and d) 47 h.

Figure 4 shows SEM images of the obtained titania nanotube arrays at different anodization times. After 40 hours of anodization (**Figure 4a**), the nanotubes are still fairly close-packed but from this point onward, chemical etching becomes dominant. From **figures 4b, 4c** and **4d**, it can be clearly seen that the nanotube structures become successively less close-packed in the course of the next few hours resulting in a dramatic decrease in the areal density of nanotubes on the substrate. The absence of sidewall chemical etching in the regions of closely compact nanotubes preserves those nanotubes.



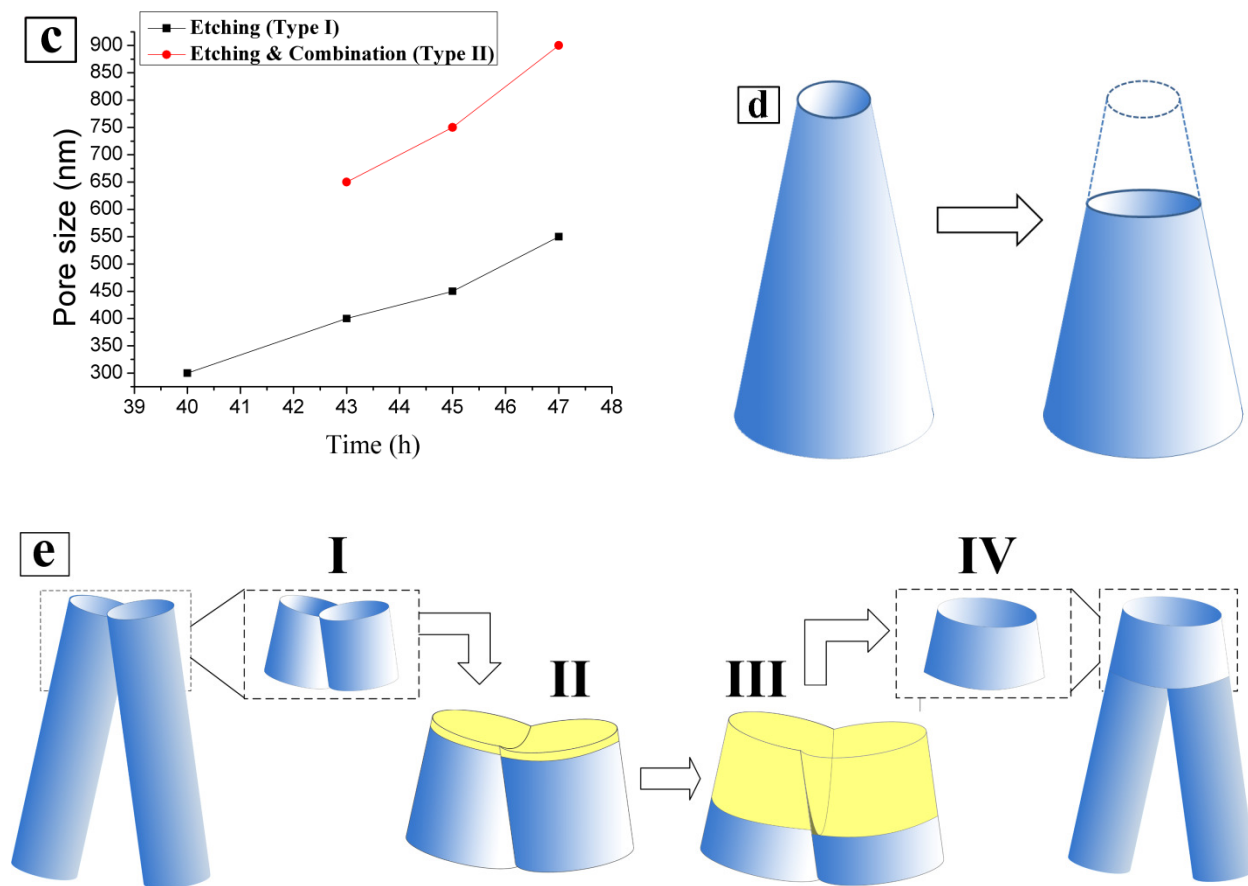


Figure 5. SEM images of titania nanotubes anodized at 120V in a DEG electrolyte with 0.25% HF and 1% water a) after 45h of anodization and 1 hour in the same bath without electric field ; Four consecutive bipodal nanotubes can be seen and b) top view after 45 h of anodization c) Pore size increment diagram of the individual and combined nanotubes vs. anodization time and schematic image of the pore size increment in d) individual and e) combined nanotubes.

Nanotubes of very large diameter (extending to optical and near-infrared wavelengths) may be obtained in DEG-electrolytes²³ as seen in **figures 5a** and **5b**. Two concurrent processes are responsible. Although closely packed nanotubes do not undergo significant chemical etching of their sidewalls, they do experience etching from the top, which shortens them because of the presence of the electrolyte at their mouth. Type-I nanotubes of large pore-size are formed by the top-etching process, which increases their diameter due to their tapered conical shape. Type-II

nanotubes of large pore-size form by the combination of small pore size ones. As shown in the diagram of the **figure 5c**, the pore size of the both type I (individual nanotubes) and type II (multipodal nanotubes) was increased for longer anodization times subsequent to the formation of the self-organized nanotubar structures on the surface growing from just more than 300 nm after 40 h of anodization to about 900 nm after 47 h for combined nanotubes. The reason for the pore size increment of the type-I nanotubes is shown schematically in **figure 5d**. The nanotube combination process is schematically shown in **figure 5e** in which **figure 5e.I** represents the common surface area of the two leaning nanotubes. Like ethylene glycol (EG) and water, DEG is a highly structured solvent with a three-dimensional spatial network of hydrogen bonds. It is known that H^+ ions, OH^- ions and glycoxide ions have anomalously high conductance and mobility in these electrolytes due to the proton jump mechanism. Halide ions, on the other hand have much lower conductance and mobility in EG and DEG ^{36, 37}. A consequence of this asymmetry is that hydroxyl ions and glycoxide ions consumed at the Ti/TiO₂ interface during oxidation are replenished from the bulk electrolyte more quickly than fluoride ions consumed in the electrochemical dissolution of the barrier layer and this asymmetry becomes more pronounced as nanotube length increases. Also, the bulkier $[TiF_6]^{2-}$ ions produced at the pore bottom do not disperse quickly into the bulk electrolyte due to their low mobility in the viscous electrolyte and their coulombic attraction to the anode. It should be mentioned that the chemical etching at nanotube mouth occurs continuously and high viscosity of the electrolyte limits the long distance movement of the dissolved material which increases its concentration in the electrolyte/nanotube interface region. As depicted in **figure 5e.II**, this highly saturated electrolyte etches both the side wall and interface between the leaning nanotubes and the small amount of saturated electrolyte at the mouth becomes super-saturated and additional dissolved

nanotube material becomes deposited onto the inner surface of the nanotube (the electrolyte/nanotube interface). Hence, the side wall becomes thicker which results in the reduction of in chemical etching rate *relative* to that of the nanotube inter-wall. The SEM images in **figure 5a** and **5b** clearly show this stage after 45 h anodization with the same electrolyte mentioned before. According to **figure 5e.III**, the difference in the chemical etch rate dissolves the inter-wall deeper into the nanotube which results in the combination of nanotubes leaning toward each other as seen in the SEM image in **figure 1d** for 47 h of anodization.

As can be seen in **figure 5a** and **5b**, if the leaning nanotubes possess a larger interface from top to bottom, the resulting combined nanotube looks like a single large pore size nanotube otherwise it would be a multipodal large diameter nanotube having several legs depending on the number of combined nanotubes. Less than 40 hours of anodization resulted in a closely-packed compact nanotube architecture. To investigate the effect of the presence of electric field in preserving the nanotubes against the chemical etching the electric field was removed after 40 hours of anodization and the results for different etching times are provided in Supplementary Information. It can be clearly seen from **figure 5a** that during the first hour after voltage removal, the combination process was at its initial stage and the inter-wall between the nanotubes was not proceeded deeply into the nanotubes. Nevertheless, at longer times, the nanotubes are completely etched and an irregular film is redeposited from the supersaturated electrolyte (Figure S1-S4).

It is clear from SEM images such as those in **Figures 1c, 1d, 4a** and **4b** that the nanotubes bend before combining. Bending and bunching of high-aspect ratio ($AR > 150$) TiO_2 nanotubes grown in fluoride ion bearing glycerol-water electrolytes has been previously observed due to surface tension effects during the drying process. By supercritical drying in

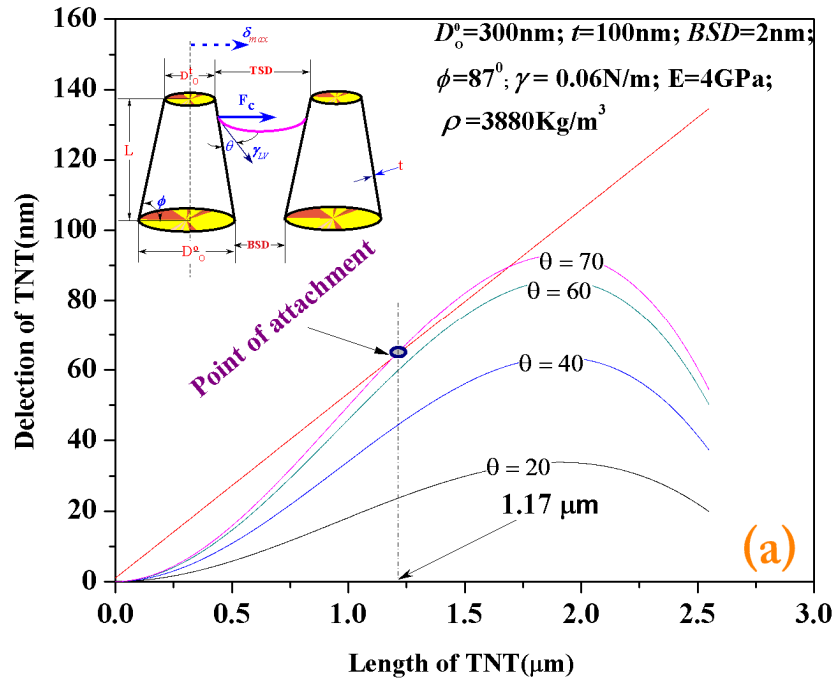
CO₂, such bending has been minimized or even eliminated³⁸. The nanotubes formed in the present study have much lower aspect ratios of ~5-25, therefore implying that the force causing the bending is much larger. We present a theoretical analysis to support the bending of nanotubes to form bipodal nanotubes based on the calculation of deflection of the nanotube due to the capillary force on its surface. The capillary force is exerted on the nanotubes by the wetting of the electrolyte during the growth of the nanotubes. With high-viscosity ionic liquids, Roy et al³⁹ found that preferential wetting occurred in the inter-tubular spaces of TiO₂ nanotube arrays. Furthermore, hardly any penetration of the ionic liquid into the nanotubes occurred even after 5 hours whereas the inter-bular spaces were wetted. The wetting in such a scenario takes place preferentially between the nanotubes only and the electrolyte penetration into the nanotubes is minimal.³⁹ In the present study using highly viscous DEG electrolytes, it is assumed that such wetting takes place along the circumference of the tubes only, which creates a circumferential interface formed between the nanotubes. The separation distance between the nanotubes is termed as the base separation distance (BSD). Based on the electrolyte and surface of the nanotubes wetting properties like surface tension of the electrolytes and contact angle of the same electrolyte with nanotube surface, one can determine the capillary force as

$$F_c = \pi\gamma_{LV} \sin\theta \sin\phi D_o^t$$

where, γ_{LV} is the surface tension of electrolyte, θ is the static equilibrium contact angle of the electrolyte with the nanotube surface, ϕ is the taper angle of the nanotube at the base and D_o^t is the outer diameter of the nanotube at distance L from base i.e., at the tip of the nanotube. It is assumed that, this is the only force responsible for the deflection of the nanotube at the tip. One can determine the deflection of nanotube of Young's modulus E with capillary force as the prescribed load at the tip as follows,

$$\delta_t = \frac{F_c L^3}{3EI}$$

where the moment of inertia I can be determined with the geometrical dimensions of the nanotubes. As-anodized TiO_2 nanotubes are amorphous. The density of amorphous TiO_2 is known to vary from 3.0 to 4.0 depending on the conditions of growth. We calculated the deflection of titania nanotubes in DEG due to capillary forces for limiting cases of the density of amorphous TiO_2 , 3.88 g cm^{-3} representative highly dense TiO_2 tube-walls and 3.0 g cm^{-3} for the condition of amorphous TiO_2 of much lower density.



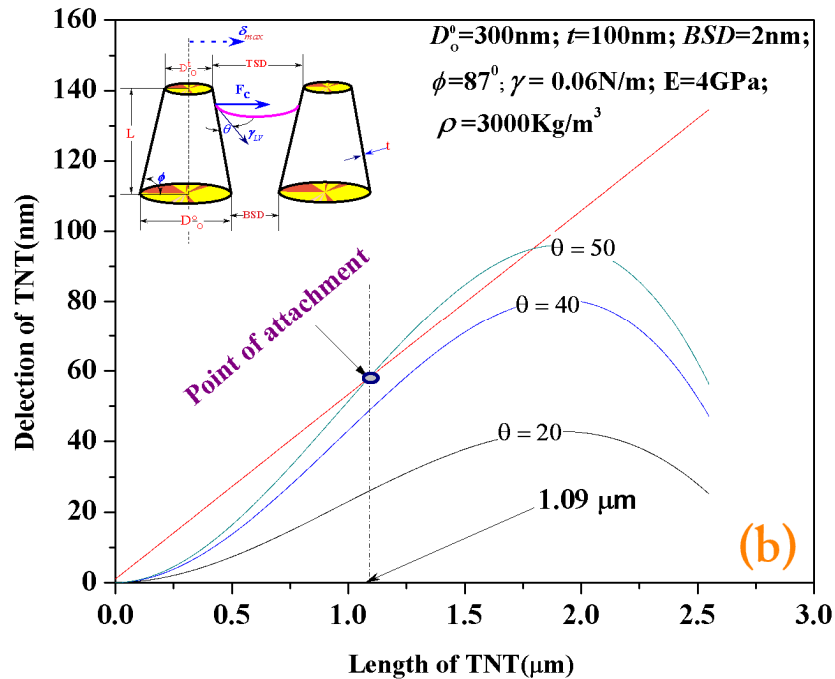


Figure 6: Variation in the deflection of the nanotube with the increment in the length of the nanotubes under different contact angle conditions assuming the density of amorphous anodized TiO_2 to be (a) 3.88 g cm^{-3} and (b) 3 g cm^{-3} . BSD and TSD are the Base Separation Distance and Tip Separation Distance respectively.

Figure 6 shows the variation in the deflection of the nanotube with different contact angles of the electrolytes. The point of attachment is the length at which the deflection of the nanotube crosses half the distance between the nanotubes i.e., 0.5 times the Tip Separation Distance (TSD). The tapered configuration of the nanotubes has a direct bearing on the calculation of I and capillary force. It is observed that for lower contact angle i.e., 20° with surface tension of 0.06N/m , the magnitude of the deflection is too small to achieve the point of attachment. Further increment in the contact angle increases the deflection for the same length of the nanotube. Under the assumption that the amorphous TiO_2 constituting the nanotube-walls is highly dense ($\rho=3.88 \text{ g cm}^{-3}$), the point of attachment is obtained for a contact angle of 70° and a tube-length of $1.17 \mu\text{m}$.

When the amorphous TiO_2 is assumed to be less densified ($\rho=3.88 \text{ g cm}^{-3}$), the nanotubes are easier to deflect. Therefore, for this case, the point of attachment occurs at a much lower contact angle of 50° but the tube-length remains very similar at $1.09 \mu\text{m}$. The nanotube length for the point of attachment observed from experiments is in the range of $\sim 1 \mu\text{m}$, which supports the present analysis. It is to be noted that the measured value of the surface tension of electrolyte (98.75 DEG+0.25HF+1H₂O) increases from 0.386 to 0.403 N/m for 56 hours whereas, with the same electrolytes, the TiO_2 nanotube array substrate shows perfect hydrophilic conditions. It is known that the chemical process and the operating conditions during the growth of the nanotubes has the ability to alter the surface tension and the contact angle in comparison to those measured values under *ex situ* sessile and pendant drop methods. Hence, it is conceivable that the actual value of surface tension and contact angle are within the prescribed limits of those presented in Fig. 6. Such a process dependent change in contact angle for completely hydrophilic surfaces has been reported in the literature.^{40, 41}

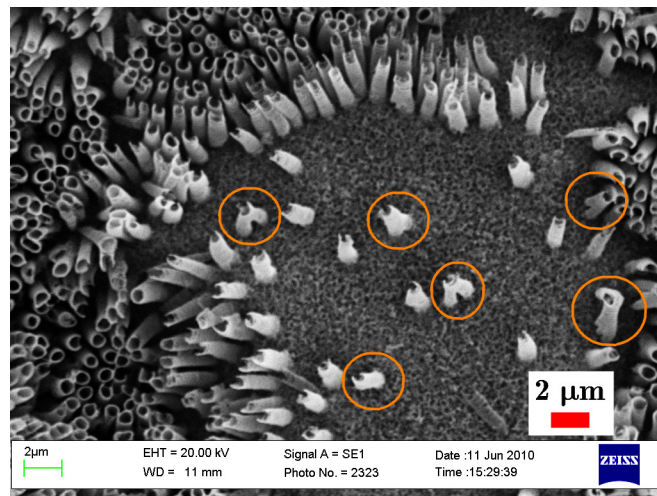


Figure 7. SEM image of the surface of a Ti foil anodized in a DEG-based electrolyte containing 0.25% HF and 1% H₂O for 45 hours at 120 V. Similar to Fig. 3, two distinct regions consisting of close-packed and widely separated nanotubes are seen; however the chemical dissolution of the widely separated NT region is more advanced. Note

how a majority of the surviving nanotubes in the chemically etched region are multipodal (orange circles point to obvious multipodal nanotubes; other surviving NTs are likely multipodal too, but with one or more legs obscured).

Nanotube combination efficiently allocates scarce fluoride bearing species since two or more nanotubes can obtain fluoride bearing species from the same puddle of bulk electrolyte after nanotube combination. Consequently, multipodal nanotubes that obtain access to fluoride bearing species in the bulk electrolyte by the process of pore combination, continue to grow (the Ti/TiO₂ interface below them keeps moving deeper into the Ti metal). This is clearly evident in **Figure 6**, where multipodal NTs are able to survive much longer than others subsequent to the first 40 hours of anodization, when field assisted processes weaken leaving chemical etching dominant. This is why we propose that the weaker dissociation of HF, which results in fluoride ion scarcity, and the nature of the solvent (DEG in this case) used to form the electrolyte are the critical factors for nanotube combination. When ammonium fluoride (which has higher dissociation) and tetrabutyl ammonium fluoride (which dissociates completely) are used instead of HF as the fluoride bearing species in the anodization electrolyte, F⁻ ions are not scarce and the formed nanotubes remain close-packed for very long anodization durations and the diameters are capped at ~300 nm. We observe the formation of multipodal nanotubes in a narrow window of process parameters in DEG electrolytes : anodization voltages of 120 V or greater, anodization durations > 40 hours and HF concentrations lower than 0.5%.

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