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Aligned metal oxide nanotube arrays: key-aspects of anodic TiO₂ nanotube formation and properties

Francesca Riboni,^a Nhat Truong Nguyen,^a Seulgi So^a and Patrik Schmuki^{*ab}

Over the past ten years, self-aligned TiO₂ nanotubes have attracted tremendous scientific and technological interest due to their anticipated impact on energy conversion, environment remediation and biocompatibility. In the present manuscript, we review fundamental principles that govern the self-organized initiation of anodic TiO₂ nanotubes. We start with the fundamental question: why is self-organization taking place? We illustrate the inherent key mechanistic aspects that lead to tube growth in various different morphologies, such as ripple-walled tubes, smooth tubes, stacks and bamboo-type tubes, and importantly the formation of double-walled TiO₂ nanotubes *versus* single-walled tubes, and the drastic difference in their physical and chemical properties. We show how both double- and single-walled tube layers can be detached from the metallic substrate and exploited for the preparation of robust self-standing membranes. Finally, we show how by selecting specific growth approaches to TiO₂ nanotubes desired functional features can be significantly improved, e.g., enhanced electron mobility, intrinsic doping, or crystallization into pure anatase at high temperatures can be achieved. Finally, we briefly outline the impact of property, modifications and morphology on functional uses of self-organized nanotubes for most important applications.

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1. Introduction

One-dimensional (1D) nano-architectures exhibit a unique set of properties that attracts a great deal of scientific and technological interest. In particular, 1D-nanotube (NT) arrays have gained

increasingly more attention as they provide an exceptional combination of optical, electrical and chemical properties with extreme geometry that has inspired remarkable advances in recent nanotechnology and microelectronics. Compared to bulk materials, NTs can feature characteristics such as high electron mobility and quantum size related effects, along with very high specific surface area and mechanical strength that are highly relevant for numerous applications in physics, chemistry, materials science, and medicine.^{1–4}

Upon the discovery of carbon nanotubes,⁵ and following their large impact on nanotechnology,^{6–12} research efforts have also

^a Department of Materials Science WW4-LKO, University of Erlangen-Nuremberg, Martensstrasse 7, 91058 Erlangen, Germany.
E-mail: schmuki@www.uni-erlangen.de

^b Department of Chemistry, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21569, Saudi Arabia

Francesca Riboni

Francesca Riboni studied Chemical Sciences at the University of Milan, Italy, and obtained her PhD in Chemistry from the University of Milan, Italy, in 2014. She joined the group of Prof. Schmuki at the University of Erlangen-Nuremberg, Germany, in 2015 as a post-doctoral fellow. Her research interests include the synthesis of functional nanomaterials by electrochemical processes and their application as energy conversion and storage devices.

Nhat Truong Nguyen

Nhat Truong Nguyen studied Chemical Engineering at Ho Chi Minh University of Technology, Vietnam and obtained his MSc degree in Material Engineering from University of Science and Technology, Korea, in 2012. He is currently a PhD student in the group of Prof. Schmuki at the University of Erlangen-Nuremberg in Germany. His research interests include the synthesis and functionalization of semiconductor nanomaterials for energy conversion applications.

been extended to a large number of inorganic materials, mainly oxides and sulfides of metals and transition metals.^{13–19} For oxide/sulfide nanotubes, a variety of synthesis routes has been reported such as hydrothermal,^{20–22} sol-gel or template-assisted methods.^{23–26} In recent years, another most frequently adopted and straightforward approach for growing highly ordered 1D-nanostructures is self-organizing electrochemical anodization (SOA).^{27,28} It allows the fabrication of vertically oriented, size-controlled and back-contacted (*i.e.*, anchored to a metallic substrate) nanostructured arrays (*e.g.*, aligned pores, nanochannels, and nanotubes) on various metals and alloys (Fig. 2).^{29–37} As illustrated in Fig. 1a and b and described in more details in the following sections, anodizing can be carried out in a simple anode/cathode arrangement, where the metal of interest (M) serves as anode. The oxide growth process is based on the oxidation of M ($M \rightarrow M^{z+} + ze^-$) and its conversion to metal oxide ($MO_{z/2}$) under a suitable voltage, the source of oxygen ions being typically H_2O in the electrolyte.

Historically, landmarks on the growth and use of such electrochemical nanostructures were certainly represented by the initial reports of Rummel³⁸ and Baumann³⁹ on the fabrication of porous-type aluminum oxide layers, and by the work of Thompson and Wood⁴⁰ who first highlighted the great potential of porous alumina for organic dyes or inorganic pigment loading as well as corrosion protection. Another cornerstone towards functional uses of porous alumina was the report of Masuda *et al.* in 1995 that demonstrated a virtually perfect hexagonal arrangement of closely-packed cells if porous alumina is grown under optimized conditions in acidic electrolytes.⁴¹ Over the last 20 years, porous alumina has been extensively applied as a template for the synthesis of functional nanomaterials, particularly for the fabrication of nanorods, nanowires and nanotubes by deposition of metals, semiconductors or polymer materials.^{41–45} In addition, also the direct use of nanoporous Al_2O_3 for decorative, wear- and corrosion-resistant applications, as a filter or as a

photonic crystal, has been strongly developed.⁴⁶ Over decades, aluminum was considered the only metal that can form anodic self-ordered oxide structures and early works by Assefpour-Dezfily⁴⁷ and Zwilling⁴⁸ on TiO_2 nanotube formation on Ti went almost unnoticed. A few years later, this type of first generation of TiO_2 nanotubes grown in acidic aqueous electrolytes was further investigated and essentially confirmed the earlier findings.^{49,50} However, all these layers were not highly organized, limited in length to ~ 500 nm, and with considerable wall inhomogeneity, but anyway proved that the key-factor for growing self-organized TiO_2 nanotubular arrays is the addition of fluoride species to the electrolyte. Reasoning for this specific role of fluorides is that they provide the feasibility to establish an equilibrium between anodic oxide formation and chemical dissolution (Ti^{4+} is relatively easily solvated by F^- in the form of $[TiF_6]^{2-}$). Further significant improvements were the introduction of electrolyte pH mediation,⁵¹ the use of non-aqueous fluoride electrolytes (glycerol, ethylene glycol, DMSO),^{52–55} and fine tuning of voltage control and alteration procedures,^{56–58} that allowed a higher degree of self-ordering and a strongly enhanced morphology control. Progressively, the use of fluoride-based electrolytes was shown to enable the growth of similar nanotubular anodic oxides also on a wide palette of metals, such as Fe,^{59–61} W,^{62,63} Nb,^{64,65} V,⁶⁶ Co,⁶⁷ Ta,^{68–71} Zr,^{72–74} Hf^{75,76} as illustrated in Fig. 2 and even metal-alloys, such as Ti-Nb,^{29,77–82} Ti-Zr,⁸³ Ti-Ta,^{34,84–86} Ti-W,³⁷ Ti-Cr,⁸⁷ Ti-Mo,⁸⁸ Ti-V,⁷⁸ Ti-Ru.⁸⁹ In particular, anodizing metal-alloys turned out to be a unique and elegant way of direct doping the tube oxide layer by introducing well-defined amounts of a secondary species in the oxide, or to intrinsically decorate tubes with noble metal nanoparticles.^{90,91}

Owing to the extended control over nanoscale geometry, direct back-contacting, and due to the large versatility of this approach to grow nanotubular structures of various metal oxides and mixed oxide compounds, electrochemical anodization is in many cases a most straightforward nanotube synthesis path.

Seulgi So

Seulgi So obtained her MSc degree in Materials Chemistry from Korea University, Korea in 2011 and her PhD degree in Materials Science and Engineering from University of Erlangen-Nuremberg, Germany, in 2015. She worked as post-doctoral fellow in the groups of Prof. Schmuki at the University of Erlangen-Nuremberg, Germany, and of Prof. Sadoway at the Massachusetts Institute of Technology, US. She is currently a postdoctoral fellow in the group

of Prof. Corn at the University of California Irvine, US. Her research interests include the synthesis of functional nanomaterials by electrochemical processes and their application in various energy conversion fields.

Patrik Schmuki

Patrik Schmuki obtained his PhD from ETH Zurich, Switzerland, in 1992. From 1994–1997 he worked at Brookhaven National Laboratory, US, and at the Institute for Microstructural Sciences of the National Research Council of Canada. From 1997–2000, he has been an Associate Professor for Microstructuring Materials at EPFL, Switzerland, and since 2000 he has been Full Professor and Head of the Institute for Surface Science and Corrosion at the

Department of Materials Science and Engineering of the University of Erlangen-Nuremberg. His research interests target electrochemistry and materials science at the nanoscale, with a particular focus on functional materials and self-organization processes.

Fig. 1 (a) Typical 2-electrode electrochemical anodization set-up and possible anodic morphologies: (EP) metal electropolishing, (CO) formation of a compact anodic oxide, (PO) self-ordered nanostructured oxide (nanopores or nanotubes). (b) Schematic representation of the TiO_2 nanotube formation process: first a compact layer is grown; afterwards, breakdown of the barrier film occurs and an ordered porous structure, covered with the thin initial layer, forms; finally, under an optimized set of experimental parameters, regular self-organized TiO_2 nanotubes are obtained. (c) High field oxide formation in the presence of fluoride ions: a steady-state is established between the oxide formation at the inner interface and its dissolution at the outer interface (due to dissolution/complexation of Ti^{4+} as TiF_6^{2-}). Rapid fluoride migration leads to the formation of a fluoride-rich layer at the Ti/TiO_2 interface. (d) Typical current–time (j – t) characteristics and different stages in nanotube formation: (i) initial formation of a compact oxide layer; (ii) initiation of irregular nanoscale pores under optimized anodizing conditions; (iii) formation of a regular nanoporous/nanotubular layer. (e) Time evolution of stress $\times$ thickness ($\sigma_{\text{ox}}h_{\text{ox}}$, left axis) and cell voltage (right axis) during self-organizing anodization of a Ti thin film under galvanostatic condition. The inset shows the instantaneous roll-up of a thin NT layer (~ 200 nm) detached from the metallic substrate that is indicative of a residual compressive stress (scale bar of the SEM image 5 nm).

Therefore, self-organized nanotubular structures find application in a variety of fields: TiO_2 nanotubes are extensively investigated in solar cells (DSSCs), photocatalysis and biomedical applications, $\alpha\text{-Fe}_2\text{O}_3$ and Ta_3N_5 NTs as anode for (photo)electrochemical water splitting reactions,^{60,61,92–95} ordered nanoporous V_2O_5 and Co_3O_4 structures for batteries and ion intercalation devices or as oxygen evolution catalysts,^{66,67} WO_3 nanochannels for gas sensing and electrochromic applications,^{96–98} etc.

However, TiO_2 represents by far the most investigated metal oxide.^{28,50,60,65,66,98,99} This can be ascribed to the outstanding breadth of properties of this compound: classically used for its non-toxic, environmentally friendly, corrosion-resistant and biocompatible characteristics, many functional applications rely on the specific ionic and electronic properties of TiO_2 . Among these, a wide range of photo-electrochemical applications (photocatalytic splitting of water into oxygen and hydrogen, self-cleaning surfaces, organic pollutant degradation) or the use of TiO_2 in

Fig. 2 SEM images illustrating the structure of ordered oxide nanotube and nanopore layers electrochemically grown on different valve metals. Al: Reproduced with permission from ref. 33. Ti: Reproduced with permission from ref. 146 with permission from the Royal Society of Chemistry; inset: Reproduced with permission from ref. 150. W: Reproduced with permission from ref. 98. Nb: Reproduced from ref. 65 with permission from the Royal Society of Chemistry. V: Reproduced with permission from ref. 66. Co: Reproduced with permission from ref. 67. Ta: Reproduced with permission from ref. 35.

solar cells (most frequently in Grätzel-type DSSCs) are most common.^{100,101} Aligned one-dimensional arrangements are particularly beneficial for the performance in (photo)electrochemical applications, as orthogonal carrier separation in these structures is facilitated, *i.e.*, electrons and holes are driven apart (that is, e^- are collected at the back contact and h^+ accumulated at the semiconductor/electrolyte interface). This particularly helps overcoming the limitations of a short diffusion length of holes in TiO_2 (~ 10 nm) while exploiting the comparably long electron diffusion length (~ 20 μm in TiO_2 nanotubes).¹⁰² As TiO_2 nanotubular structures simultaneously combine the highly functional features of TiO_2 with a regular and controllable nanoscale geometry (that is, tube-length, -diameter, and self-ordering that can be tailored over large length scales), intense research activities have been devoted to anodic TiO_2 nanotubes over the last ten years (see, for instance, research trends reported in ref. 28 and 103).

While a number of recent reviews focus on properties and applications of TiO_2 nanotubes and other aligned channels,^{27,28,104}

the present review mainly focuses on mechanistic aspects of nanotube growth and self-organization: why do tubes (not pores) form, what are the critical factors to achieve self-organization and how to improve it, why is the tube wall morphology sometimes rippled sometimes smooth, how to grow multi-layered tubes, why are single-walled TiO_2 nanotubes so superior compared to double-walled tubes? Along with the factors determining nanotube formation and leading to various tube morphologies, we will also briefly discuss the significance of various types of tubes and tube features for electric, electronic and optical properties that in turn dramatically affect the performance of tube arrays in virtually any (photo)electrochemical application.

2. Stages and key aspects of nanotube formation

As mentioned, anodization is frequently carried out in a 2-electrode electrochemical arrangement as illustrated in Fig. 1a, with the metal of interest (M) as working electrode (anode) and a counter electrode (typically platinum or carbon) as cathode. Overall, the process can be described in terms of following equations:

On various metals (valve metals), oxidation (1) and conversion to a thick metal oxide (2) can be achieved in an aqueous electrolyte at sufficiently high anodic voltages. For non-valve metals, only thin oxides can grow, as O_2 evolution (3) is the preferred anodic reaction.^{27,104,105} In either case, a counter reaction, typically the reduction of H^+ (from the electrolyte) to gaseous H_2 (4), takes place at the cathode.^{27,28} Depending on the electrolyte and on several anodization conditions, three different scenarios are possible: (i) if the oxide is completely soluble (M^{z+} ions are entirely solvated) in the electrolyte, the layer is continuously etched and metal corrosion (or electropolishing, EP) is observed (Fig. 1a, EP); (ii) if the formed oxide is entirely insoluble in the electrolyte, a compact oxide (CO) layer is formed on the surface of the metal (Fig. 1a, CO); (iii) if the oxide is partially soluble (M^{z+} cations can be solvated) and under a specific set of experimental conditions, a steady-state between oxide formation and dissolution can be established and a porous or tubular metal oxide can grow (Fig. 1a, PO).

Mechanistically, anodic oxide formation is controlled by a high-field ion formation/transport process, where the kinetics of oxide growth (at the metal/oxide or at the oxide/solution interface) depends to a large extent on the rate of ion migration where M^{z+} migrates with the field outward and O^{2-} (abstracted from water) inward (see Fig. 1c). Ion movement is influenced by the relative mobility of the cation and the anion in the oxide. Accordingly, the film can grow at the inner and outer interface.¹⁰⁶ Generally, the overall oxide growth (as long as high field

conditions hold) is related to the electric field ($E = \Delta U/d$) applied across the oxide layer:

$$I = A \exp(BE) = A \exp(B\Delta U/d) \quad (5)$$

where I is the current, ΔU is the voltage across the oxide layer of thickness d , and A and B are material-dependent constants.¹⁰⁷ If an insoluble compact oxide is formed, the anodization process is self-limiting: *i.e.*, for a given voltage (ΔU) and with an increasing thickening of the oxide layer (d), the field E drops over time to such an extent that significant ion migration cannot be promoted any longer and a compact oxide (CO) layer with finite thickness $d = f \times U$, where f is the film formation factor ($f(\text{TiO}_2) \sim 2.5 \text{ nm V}^{-1}$),¹⁰⁸ forms (Fig. 1a, CO).^{109–111} By contrast, if all M^{z+} ions are solvated, for instance, in the form of water soluble metal-fluoro complexes $[\text{MF}_x]^{(z-x)-}$ in fluoride-based electrolytes (6)

and dissolved, no oxide film is grown and active corrosion or electropolishing of the metal is observed (Fig. 1a, EP). Only if an equilibrium between oxide formation (2) and dissolution (6) is established, oxide growth can continue and form 3D structures, *i.e.*, under a specific set of conditions, such as temperature, applied potential, aqueous or organic electrolyte, pH and specific ions, self-organized anodic nanostructures can be achieved (Fig. 1a – PO, Table 1).

A versatile tool to describe thermodynamics and kinetics of electrochemical reactions are current–voltage curves (where the potential can be regarded as thermodynamic axis and the current as kinetic axis).¹¹² To monitor the evolution of nanotubes over time, it is interesting to follow j – t curves. A typical current–time curve (Fig. 1d) that describes the conditions to nanotube formation can be divided into three sections: (i) in the early stage of anodizing, a compact oxide layer is formed; as the barrier layer thickens, j accordingly decreases (this, in line with (5)); (ii) under optimized growth conditions (Table 1), irregular nanoscale pores penetrate into the initial compact oxide; here, the current rises as the reactive area (exposed to the electrolyte) increases; (iii) a regular nanoporous/nanotubular layer forms and the current drops again until a steady-state situation is established between oxide formation at the metal/oxide interface and the dissolution at the oxide/solution interface (M^{z+} ions from dissolved oxide and ions directly ejected from the oxide by the high field are solvated by F^- , (6)). Due to this dissolution, a current significantly higher than that corresponding to compact oxide formation (assuming the same applied voltage) is observed. According to (5), this means that under steady-state condition for tube growth a higher field is present at the tube bottom (that drives ion migration).

However, except for this steady-state formation–dissolution equilibrium, a second key factor to tube formation is the buildup of compressive stress during the early stages of anodic oxide formation. As predicted by the Pilling–Bedworth (PB) ratio (Φ , the ratio of oxide volume created by oxidation *vs.* the metal volume consumed),¹¹³ stress is generated by volume

expansion (for many metal/oxide systems) when converting the metal to oxide and is due to the constraint of volume conservation at the metal/oxide interface. This stress is present in any anodic film but, if a compact layer is formed, the stress remains “frozen in” or leads to some cracks in the oxide layer. *In situ* measurements of internal stress evolution (Fig. 1e) reveal that two different characteristic stages are observed when anodizing a metal substrate: in the first stage, a relatively large compressive ($d(\sigma_{\text{ox}}h_{\text{ox}})/dt < 0$) internal stress, in the range of 2–4 GPa for anodic TiO_2 , is observed that has been, except for the PB effect, also attributed to oxygen evolution (OER) from the electrolyte that occurs inside the oxide film. Here the anodization efficiency (ε , that corresponds to the fraction of oxidized metal ions retained in the final anodic film relative to the film dissolution)¹¹³ is comparably low (*i.e.*, low dV/dt and $\varepsilon \sim 10$ –20%) as the majority of charge is consumed in the anodic side reaction (OER). The presence of an overall residual compressive stress in the tube layers is most evident from the instantaneous roll-up of thin NT layers when removed from the substrate (inset of Fig. 1e). When the anodic film thickness reaches a certain value (critical thickness, T_{cr}), OER ceases due to kinetic limitations. At this stage, also the compressive stress disappears and in some cases, an instantaneous tensile stress component is observed. (*i.e.*, to maintain a compressive stress situation, the oxide should not grow thicker than T_{cr}).¹¹⁴ Or, in other words, only if a steady-state “formation–dissolution equilibrium” is established, compressive stress can permanently act on the continuously formed oxide and finally, in a flow mechanism, shift the oxide up to form tube walls as described in more detail below. Also, it should be noted that during oxide growth a second component of stress, *i.e.* electrostrictive stress, is acting on the anodic system. The extent of this is not only strongly voltage- but also material-dependent.^{115,116}

2.1 Pore initiation and nanopattern selection

As pointed out above, during self-ordering electrochemical anodization essentially four concomitant reactions occur: (i) formation of metal ions upon metal substrate oxidation (1), (ii) generation of O^{2-} from the reaction of H_2O at the film surface (3), (iii) dissolution and loss of metal ions to the electrolyte, driven by field-assisted cation ejection (5), and (iv) chemical dissolution of the film (6). Arguments (i) and (ii) are responsible for forming the film, while (iii) and (iv) lead to oxide loss.

Experimentally, in the very early stage of anodization, first the formation of a few nanometer-thick conformal, compact oxide layer (often referred to as “barrier layer”) takes place. Then, morphological instabilities occur, such as a corrugated surface (Fig. 3a). This process leads to a stochastic distribution of sites with “thinned” oxide locations – this surface pattern is in a lateral length scale of some nm to some 10 nm.^{108,111} This causes electrochemical processes to occur accelerated at the thinner parts of the layer, that is, in the “valleys” (Fig. 3a) where the intensity of the applied electrochemical field is enhanced (5). Noteworthy, at these most active sites also the generation of H^+ is enhanced ($\text{Ti}^{4+} \xrightarrow{\text{H}_2\text{O}} \text{TiO}_x + \text{H}^+$; $\text{Ti}^{4+} \xrightarrow{\text{HF}} \text{TiF}_x + \text{H}^+$),

Table 1 Effect of the different anodization parameters on the morphology of TiO₂ NTs. A more extensive description can be found in recent comprehensive Reviews, e.g., 27, 28

TiO ₂ nanotubes				
Experimental parameters	Length	Diameter	Additional features	Ref.
Electrolyte	Max ~ 2.5 μm (limited thickness due to high chemical etching rate)	10–150 nm (voltage-dependent)	– Rippled-walls	220
	20 nm^{-1} μm (1–25 V, 0.3 wt% HF)	15–120 nm (1–25 V, 0.3 wt% HF)	– Longer tubes grown at neutral pH	144
	200 nm (15 V, 3 M HF)	80 nm (15 V, 3 M HF)	– Highly ordered and short aspect ratio NTs	158
	Up to several 100 μm	Up to 800 nm	– “nanoglass” formation on NT tops, due to long anodization time	157
	Dependent on anodization time and applied voltage	V-shaped morphology (<i>i.e.</i> , thinner wall at NT top)	– Double-walled NTs	221, 222
	~ 15 μm	200 nm	– Carbon-rich layer (inner shell)	54, 55, 157
Temperature	Thicker layers are grown at higher F [−] conc. (<i>e.g.</i> , 25–30 μm , 0.2 M HF – 120 V)	Depends to a certain extent on the F [−] conc. due to chemical etching	– Single-walled NTs	128
	Highly ordered nanotube arrays for limited H ₂ O amount	Larger diameter with higher H ₂ O content	– For too high F [−] amount, electropolishing takes place	
	• Low (10 °C) • High (> 20 °C)		– Smooth wall NTs (no ripples)	52, 222
Additive complexing agent	Slower growth rate (~ 7 μm) Faster growth rate (~ 11 μm)	200–230 nm ~ 150 nm	– Nanocolumn structure at $T < 10$ °C	223
	• EDTA • Lactic acid	Fast growth rate (41 $\mu\text{m h}^{-1}$) Fast growth rate (20 $\mu\text{m min}^{-1}$)	– No dielectric breakdown events (comparably high voltage, <i>e.g.</i> 120 V, can be applied)	224 225
Anodization voltage	Linear dependence on applied voltage		– Morphology depends on the electrolyte	222
Anodization time	• Constant • Alternating		– Bamboo-type, branching-type	57, 226
	• Short time • Long time	Anodization time influences the NT length, until a steady-state between their growth (at the bottom) and the chemical etching (at the top) is established	– Formation of initiation layer	222
Patterned substrates	• Two-step anodization • FIB • Nanoimprinting		– Formation of nanoglass, due to etching of tube wall	112
			Maximizing ordering and ideal arrangements	160, 167, 171

Fig. 3 (a) TEM micrograph of an anodic alumina film after anodization, where "ridges" and "valleys" are highlighted. Reprinted with permission from *J. Electrochem. Soc.*, 2010, **157**(11), C399. Copyright 2010, The Electrochemical Society. (b) TEM image of Al_2O_3 nanopores with a tungsten tracer layer. Reprinted with permission from *Electrochem. Solid-State Lett.*, 2006, **9**(11), B47. Copyright 2006, The Electrochemical Society. (c) Schematic of TiO_2 nanotube formation: displacement of the fluoride-rich layer towards the cell boundaries by a plastic flow mechanism (left-side) and dissolution of the fluoride-rich cell boundaries and consequent formation of nanotubes (right-side). (d) Schematic of the field concentration effects at the bottom of anodic nanotubes and model for length expansion: stress pushes some of the oxide up in the direction of tube walls. Reprinted with permission from *J. Electrochem. Soc.*, 2007, **154**(9), C472. Copyright 2007, The Electrochemical Society.

which may additionally affect the local chemical dissolution (thinning) of the oxide (6).^{32,108,117}

Linear stability analysis, based on perturbation analysis^{118,119} or numerical treatments,¹¹³ indicate that compressive stress in a thick anodic oxide (compact oxide) is rather small and not sustained by a certain flux of ions (electromigration) across the film/electrolyte interface (*i.e.*, formation–dissolution equilibrium). Therefore, only for thin films, conditions are provided for stress evolution sufficient for anodic pattern formation. As outlined above, this is also dictated by oxide dissolution at the oxide/electrolyte interface. Time-evolution of this interface is a function of electric potential, ϕ (*i.e.*, the driving force for metal-ion transport), and

of oxygen chemical potential, μ_{OX} (or driving force for oxygen-ion transport). Both ϕ and μ_{OX} are uniform at the oxide/solution interface, that is, ϕ is set to zero as all the small potential drops through the interfacial electrical double layer do not affect the interface dynamics, and μ_{OX} is also zero as the oxide surface is assumed stress-free; therefore, ϕ and μ_{OX} gradients within the film are distorted. In particular, their gradient is maximized at valleys and attenuated at ridges (Fig. 3a). Correspondingly, both metal and oxygen ions migrate more rapidly at valleys than at ridges. However, given a distinct volume change when a specific metal is converted to oxide (corresponding to a certain Pilling–Bedworth ratio Φ), only a limited set of parameters, and thus of efficiency ε , applies for pattern selection and formation of nanoporous film. For instance, in the case of TiO_2 , $\varepsilon = 0.50$ – 0.65 was determined under various experimental conditions for nanotube growth,¹²⁰ which is in good agreement with theoretical predictions.¹¹³ According to this model, if the efficiency lies outside the predicted range, no ordered nanotubes would be obtained. In particular, at lower efficiencies the fraction of oxidized metal atoms retained in the oxide is small and, therefore, the dynamics of the oxide/solution interface is dominated by oxygen migration that leads to valleys recession and deepening, destabilizing the interface (*i.e.*, extensive etching of the oxide and, ultimately, corrosion and/or electropolishing are observed). By contrast, at higher efficiencies the interface evolution is regulated by the deposition rate of new oxide and the upper limit is represented by ε approaching 100%, where a compact (thickness-limited) anodic film is formed as any depressions on the oxide/solution interface instantly fill with new material. Thus, nanoporous pattern selection (*i.e.*, an optimal ε range) is governed by a combination of oxygen flow (μ_{OX}), responsible for destabilizing the interface, and of metal ion flow (ϕ) that promotes stability.^{113,120,121}

2.2 Growth of nanostructured oxide

Further steady growth of nanotubes is explained in literature by two common models: (i) either assuming an enhanced field-assisted dissolution of titania along with a field-assisted ejection of Ti^{4+} ions at the base of the pores,^{122–124} or (ii) a field-assisted viscous flow of film material from the barrier layer towards the cell wall regions.^{106,125–127} In either case, field enhancement at the curved bottom oxide (Fig. 3d) or flow, self-organization can be achieved only for an optimized set of parameters (*e.g.*, applied potential, current density, temperature and fluoride concentration)¹²⁸ which in turn reflect that a set of conditions needs to be established to adjust an optimal oxide formation–dissolution equilibrium. This is consistent with the frequent observation of a tube-bottom-oxide layer that is thinner than an equivalent compact oxide under the same applied voltage conditions. The final thickness of compact anodic oxide on Ti is usually $d = f \times U$.¹⁰⁸ In other words, the thinner oxide at the tube bottom reflects that a high field is present that cannot be lowered by oxide growth as the corresponding dissolution rate prevents this. In pure field driven models, such as established by Gösele *et al.*,¹²⁹ the enhanced field (see distribution in Fig. 3d) promotes ejection of Ti^{4+} species to the electrolyte and this

would be a sufficient condition for continuous growth. However, recently established models estimate that the forces in the growing oxide are sufficiently high to cause viscous flow of the oxide. While a number of arguments such as the introduction and distribution of incorporated electrolyte ions can be explained by both approaches, there are a number of findings supporting the presence of a field-assisted flow:

(i) An experiment carried out using a thin W-tracer layer in an Al substrate and then growing Al_2O_3 nanopores through this^{127,130} (similarly for TiO_2 nanotubes)¹⁰⁶ showed a flow-type distribution of the tungsten metal oxide tracer from the barrier layer towards and up the cell walls (Fig. 3b).

(ii) Some reports present data that, at this stage of the tube growth, cation ejection to the electrolyte is negligible¹³¹ and inward migration of anion species mainly contributes to the ionic current in the high-field barrier oxide. Therefore, the formed oxide must be pushed out of the way, *i.e.* up the wall.

(iii) The nanotube or nanopore film thickness (the tube length) exceeds the expected thickness of a corresponding compact oxide. For anodic TiO_2 , the thickness of a compact film is 2.43 times that of the consumed titanium (corresponding to the Pilling–Bedworth ratio (PBR)). The PBR can be measured or calculated assuming a certain oxide density.¹⁰⁶ If the oxide growth would be ruled by a high field oxidation process only, then the tube or pore length would be 2.43 times the amount of metal consumed. Nevertheless, for Al and Ti the corresponding tubes or pores are longer. (According to models that are restricted to the high field oxidation, an explanation of this finding requires an assumption of an oxide density that is lower than usually reported for amorphous anatase or rutile material.)¹⁰⁶ In flow models, this length extension is ascribed to a stress-induced viscous flow of oxide vertically to the metallic film. In other words, TiO_2 nanotube growth occurs, at least partially, by a flow of TiO_2 up the wall (any lateral expansion of the oxide is negligible).¹³² This is illustrated in Fig. 3d where broken and solid lines represent the position of the atoms before and after oxidation, respectively. As the reaction proceeds (stages 1–4), increasingly larger stress is generated in the oxide (*i.e.*, solid lines bend to the vertical axis) and the bent location shifts to the center between two adjacent tubes.^{108,126,132,133} Measured expansion factors, F_m (estimated as the thickness of the film relative to that of the oxidized metal) can be expressed as a function of the total volume of the film (P), influenced by incorporated contaminants (k):

$$F_m = \frac{k\varepsilon\Phi}{(1 - P)} \quad (7)$$

where ε is the oxide growth efficiency and Φ the Pilling–Bedworth ratio. Experimental investigations show that F_m for TiO_2 nanotubes grown under self-organizing conditions may vary over a relatively wide range (~ 1.4 – 3.0) and strongly depends on experimental conditions. While the fluoride content is not of significant influence, the anodization potential and the water content in the electrolyte were found to clearly alter F_m .^{106,126,132} This indicates that the onset (or occurrence) of flow is dependent on the latter parameters.

2.3 Nanopores vs. nanotubes

A main difference in porous alumina and TiO_2 nanotubes is that, for TiO_2 , the tube morphology is created by the presence of a fluoride species and the formation and dissolution of a fluoride rich layer at the bottom and around the tubes. In terms of tube growth, the formation of a fluoride-rich layer at the tube bottoms and walls can be explained by the fact that F^- ions compete with O_2^- inward migration (Fig. 1c) and that the rate of inward migration of F^- ions is clearly higher than that of O_2^- .¹³⁴ As a result, a TiF_4 (or oxyfluoride) layer forms at the metal/oxide interface. As anodization proceeds, this layer also decorates the tube walls (Fig. 3c).^{106,127} Experimental evidence for the formation of a distinct fluoride-rich layer at the bottom and in-between the TiO_2 nanotubes has been provided by means of high resolution scanning Auger Electron Spectroscopy (AES) and TEM analysis with elemental mapping.¹³⁵ AES allows a detailed mapping of compositional variations (both horizontal and vertical mappings, Fig. 4a and b) across self-organized TiO_2 nanotube layers grown in fluoride containing organic-based electrolytes.^{135,136} Concentration scans of fluoride signal are superimposed on the original SEM images for both horizontal (Fig. 4a) and vertical (Fig. 4b) modes. Clearly, the fluoride concentration peaks in-between individual tubes (Fig. 4a) and at the bottom of tubes (Fig. 4b). Moreover, Ti and O signals recorded in horizontal mapping mode follow the same trend as F, while

Fig. 4 High resolution Auger Electron Spectroscopy (AES) scans of different elements (Ti, O, C and F) recorded for a TiO_2 nanotube layer in (a) horizontal and (b) vertical modes. (c) High angle annular dark field scanning TEM (HAADF-STEM) image and (d) F elemental mapping of a double-walled TiO_2 nanotube. (a) Reproduced with permission from ref. 136. (b–d) Reproduced with permission from ref. 135.

C-rich regions correspond to remnants in the inner tube shell (Fig. 4a).¹³⁶ High-angle annular dark field scanning TEM (Fig. 4c) and elemental mapping (Fig. 4d) also point out that the distribution of F element is higher approaching the tube walls, which confirms the comparably higher concentration of F[−] in-between tubes.¹³⁵ As most Ti fluorides or oxy-fluorides are water soluble, this fluoride-rich layer is prone to chemical dissolution in aqueous electrolytes. As a result, this layer is permanently etched out – the faster, the higher the water content in the electrolyte, and this leads to a transition of nanopores-into-nanotubes. This pore-wall-splitting is apparent in Fig. 3c and in line with various experimental findings. In general (for various porous/tubular oxides), the solubility of the cell walls in an anodizing electrolyte is the critical factor that decides whether self-ordered oxide tubes or pores are formed.^{32,117} Firstly, with a decreasing water content in an ethylene glycol electrolyte at a distinct concentration of 0.7 vol% H₂O, the dissolution stops and a nanoporous TiO₂ layer is obtained rather than a tube layer.¹¹⁷ Thus, water not only plays a crucial role during anodization being the source of oxygen to grow the oxide, but it is also an essential factor for the formation of tubes rather than pores. Accordingly, for Al anodized in acidic electrolytes a self-organized porous nanostructure is obtained.^{31,32} But even if alumina is anodized in fluoride solutions, pores (not tubes) are observed as Al forms water-insoluble fluoride compounds.³² Also the effect of an increased F[−] concentration in the electrolyte (0.025 M–0.20 M) was found in line with the incorporation into the cell boundaries of TiF₄ species, as it leads to clearly larger splitting of adjacent pores.¹¹⁷ These observations show that transitions from porous to tubular morphologies are gradual, with a decisive factor being the solubility of cell boundaries in the anodization electrolyte. However, if anodization is carried out in water-based electrolytes, the dissolution of the fluoride is so high that splitting down the tubes can be faster than growth of tubes. This leads to a rippled morphology of the walls of those tubes (as we discuss below).

Noteworthy, by thermal annealing in air (typically performed at 450–500 °C) not only amorphous-into-crystalline conversion of TiO₂ nanotubes is achieved, but also a loss of the fluoride-rich layer at tube bottoms occurs. This may be ascribed to the relatively low sublimation temperature of TiF₄ (*i.e.*, 285 °C).¹³⁷

3. Various tube morphologies

Above we discussed mainly the formation of straight, smooth-walled tubes. Variations in experimental conditions can yield specific morphologies, such as the occurrence of side wall ripples,⁵² bamboo-type tubes,⁵⁶ double/single-walled tubes,^{54,55} top-open/partially top-closed tubes,^{138–140} branched-tubes,⁵⁷ inter-tubes^{58,141} and tubes-in-tubes.¹³⁵ The formation of ripples along tube walls is a result of the competition between tube growth and splitting speed.^{52,142,143} When the fluoride rich layer between the tubes is dissolved faster than the tubes grow, this leads to a situation where the electrolyte between the tubes reaches the underneath metal. This in turn causes a local rapid

Fig. 5 SEM images of: (a) TiO₂ nanotubes with a rippled-wall morphology, (b) bamboo-type tubes, (c) branched-tubes, (d) inter-tubes, (e) TiO₂ and Ta₂O₅ superlattice tubular oxide. (f and g) Top and cross sectional views, respectively, of tubes-in-tubes. (a) Reproduced with permission from ref. 142. (b and c) Reproduced with permission from ref. 57. (d) Reproduced with permission from ref. 58. (f and g) Reproduced with permission from ref. 135.

oxide formation (a repassivation spike) and a sealing of this point by oxide – a rib is formed. For some time, this point seals the intertube space while the tubes continue to grow, until the oxide “seal” (the rib) gets penetrated by the etching action of the electrolyte and a rapid dissolution of the fluoride-rich layer between the tubes occurs again. The repetitive auto-sealing/dissolution cycle leads to periodic ribs (Fig. 5a) that can be accompanied by minor regular current oscillations recorded during anodization experiments. If the water content in the electrolyte is sufficiently reduced, such as for nanotubes grown in typical organic-based electrolytes (glycerol, ethylene glycol, DMSO), no detectable current fluctuations are observed and smooth tubes are obtained.⁵² Other variations in morphology can be caused by alternation of the applied voltage during anodization. This is based on the fact that the tube diameter of ordered nanotubular layers is closely related with the anodic growth factor (*f*) of the metal. Assuming that anodization starts from a frontier spot on the metal surface (*e.g.*, an oxide breakdown site), the oxide grows in all directions starting from this source point and a hemispherical shaped dome with radius *r*, given by $r = f \times \Delta U$, will form. This, to a large extent, determines the diameter of growing tubes. Diameter control is of great significance for various applications of TiO₂ tubes, *e.g.* when nanotube layers are used as morphology-directed template, hierarchical structure, size-selective flow-through membrane, or for their interaction with living matter in biological applications.^{32,108,112,144–146}

Bamboo-type tubes,^{142,143} branched and inter-tubes,^{57,58,147} as well as tube stacks^{81,83,141,148} can be grown by a stop and continuation of the anodization, or pulsing the voltage during anodizing. By using appropriate alternating voltage cycling, a morphology that resembles bamboo is formed (Fig. 5b).

With this approach, oxide that connects tubes at their bottom is grown at each voltage step and by using different anodization durations the distance between the stratification layers can be adjusted.⁵⁶ By reducing the voltage to distinct lower voltage,^{57,58} also branched tubes can be grown with distinct lower tube diameters. Depending on the anodization conditions, the second tube layer is either grown through the bottom of the first layer (Fig. 5c)⁵⁷ or in the gaps between the existing tubes of the upper layer, that is, inter-tubes are formed (Fig. 5d).^{58,147} Heteromaterial superlattices can be produced using sputter-deposited multilayer metal stacks as substrate for anodization – this has been shown for alternating metal layers (e.g., Ti-Ta, Ti-Nb, Ti-Zr).^{81,83,148} Key is that experimental conditions can be established that lead for both elements to a self-organized tubular nanostructure (Fig. 5e). Given the large number of materials for which self-organized oxide nanostructures can be grown, this technique can produce a wide palette of multi-layered nanostructures. A peculiar morphology are tube-in-tube structures as shown in Fig. 5f and g that can be regarded as a special case of double-walled nanotubes as discussed below. More detailed descriptions of different tube morphologies can also be found in ref. 27, 28, 52, 57, 103, 149.

4. Double- vs. single-walled

An important aspect of tube growth that is widely neglected or overlooked in literature is the self-induced double-layered, or double-walled, morphology of anodic oxide nanotubes grown in many organic electrolytes, which for several applications is detrimental. We will discuss, in the following, the origin of these double-walled tubes (Fig. 6a–d) and ways to produce single-walled tubes (Fig. 6e and f) of a much higher oxide quality.^{53–55,146,150}

The most widely used electrolytes to grow ordered and seemingly well-defined TiO₂ nanotubes are based on ethylene glycol, water and fluorides. While these tubes in top or side view SEM appear uniform, a close look at ion milled cross sections in SEM (Fig. 6a and b) or tubes in TEM (particularly at the lower tube end), reveals that the walls of these TiO₂ nanotubes consist of two different types of oxide, namely an outer shell (OS) and an inner shell (IS), as also illustrated in Fig. 3c. The two-shell nature becomes even more apparent when the tubes are annealed to crystallize their tube walls. If the annealing temperature is sufficiently high and/or for a more rapid annealing than $\sim 10^\circ\text{C min}^{-1}$, a clear separation between inner and outer shells can no longer be observed as IS and OS sinter together (maintaining the lower quality oxide characteristics).^{53–55,151} As discussed in more detail in Section 7, this can be a critical factor in affecting not only the geometry but also the properties of TiO₂ nanotube layers. Detailed investigations showed that the as-grown outer shell consists of comparably pure TiO₂, while the inner layer is composed of carbon-rich titanium oxide or oxy-hydroxide.^{53,55,146,152} To a large extent, this TiO_xH_yC_z layer stems from precipitated Ti-ions, ejected from the oxide but not solvated as TiF₆^{2–}, combined with carbon species embedded from the electrolyte during the anodization process.

Fig. 6 Cross-sectional SEM images of ion-milled (a) “as formed” and (b) annealed tubes (showing the typical double-walled morphology). (c) Full cross-sectional SEM image of a double-walled TiO₂ nanotube layer (formed in EG-based electrolyte) with top-view SEM images taken at the top, from the fractures in the middle, and close to the bottom of a tube layer. (d) Schematic drawing of inner layer removal through chemical etching with a 1 : 3 solution mixture of H₂O₂/H₂SO₄ for 6 min at 70 °C. (e and f) Single-walled tubes after core removal process leaving behind only the outer tube shell. (a, b and d–f) Reproduced from ref. 146 with permission from the Royal Society of Chemistry. (c) Reproduced from ref. 55 with permission from the Royal Society of Chemistry.

This inner layer typically dictates the inner tube morphology as it narrows the inner diameter of the tubes and limits the possibilities of a uniform and functional coating of the inner tube wall.^{53–55} This inner layer is more sensitive to etching in the fluoride-containing electrolyte, compared with the outer shell TiO₂. This results in a V-shaped inner tube morphology (Fig. 3c), while OS preserves a nearly constant thickness along the whole tube length. For tubes grown for some time, a proper evaluation of double wall formation can therefore only be done close to the bottom of the tubes, where the thickness of IS is still maintained (Fig. 6c). The type of electrolyte used has a strong impact on whether or not, or to what extent, an inner contamination shell is formed. As mentioned, the most frequently adopted ethylene glycol (EG)/H₂O mixtures that contain NH₄F or HF lead to double-walled nanotubes, whereas dimethyl sulfoxide (DMSO) or EG/DMSO mixtures can be applied to grow single-walled tubes. This effect can be ascribed to different reactions of the electrode (anode) with the adjacent electrolyte (DMSO vs. EG) during anodization. High anodic voltages cause Schottky barrier breakdown in the oxide, which generates valence band holes that, similarly to photocatalysis, can react with the environment, either directly with electrolyte species or with H₂O, and form OH• radicals.^{55,153} A range of carbonaceous

oxidation products can be produced that adsorb on TiO_2 and are incorporated in the OS. In contrast to EG, DMSO is capable of capturing radicals nearly 10-times faster¹⁵⁴ and the reaction products are solvated in the electrolyte while, in the case of EG, they are incorporated in the IS.^{54,55} More recent reports introduced an even more widely useful technique for fabricating single-walled TiO_2 nanotubes. It was found that for essentially all double-layered TiO_2 nanotubes, the IS can be selectively etched leaving behind the OS, as an intact single wall, by exposing the samples to a piranha solution under optimized etching conditions, as shown in Fig. 6d–f.¹⁴⁶ This has been demonstrated recently in detail for tubes grown from EG electrolytes containing NH_4F , and lactic acid, LA (here, LA acts as an additive that allows for an unprecedented ultrafast growth of ordered TiO_2 nanotubes due to a field supporting effect).¹⁵⁰ Noteworthy, the IS-removal process can be carried out successfully over the entire nanotubular layer, for a wide range of tube lengths *i.e.*, from 2.5 μm up to 16 μm as reported in ref. 146 and 152.

A more detailed comparison of the composition of double-walled and single-walled tubes produced by selective etching of IS has been obtained by means of Thermo-Gravimetric

Analysis, coupled with Mass Spectrometry (TGA-MS) – characteristic decomposition patterns are shown in Fig. 7a and b. It is apparent that $\sim 2\text{--}3\text{ wt}\%$ loss occurs in both layers, owing to water desorption (notably, the desorption of physically adsorbed water occurs at $\sim 180\text{--}200\text{ }^\circ\text{C}$, due to the presence of hydroxyl groups that interact with uncoordinated surface atoms).¹⁵⁵ In contrast, a clear difference in CO_2 release signals can be observed: CO_2 evolution in single-walled tubes produces a relatively low weight loss ($\sim 5\text{ wt}\%$) that can be reasonably explained with the pyrolysis of environmental contaminants that are adsorbed on TiO_2 surface,⁵⁴ while remarkably higher amount of carbon is released as $\text{CO}_{2(g)}$ if double-walled tubes are heated up to $\sim 350\text{--}400\text{ }^\circ\text{C}$. This is ascribed to a thermal oxidation of the carbon species in the inner shell of the tubes.¹³⁵

Finally, the recently reported tube-in-tube morphology (Fig. 5f and g) is an unusual arrangement obtained under conditions similar to that for ultra-fast growth of double-walled TiO_2 nanotubes.¹⁵⁰ Though more detailed investigations are required, the formation of this unconventional morphology is ascribed to the low temperature adopted during the anodization process that both limits the tube growth speed and enables a particularly slow fluoride-etching of C-rich layers.¹³⁵

Fig. 7 Thermal desorption profile for $m/z^- = 18$ (H_2O) and for $m/z^- = 44$ (CO_2) measured by Thermo-Gravimetric Analysis coupled with Mass Spectrometry (TGA-MS) for (a) double-walled and (b) single-walled tubes. (a and b) Reproduced with permission from ref. 135.

5. Towards maximized ordering and ideal arrangements

Systematic experimental investigations of growth parameters led over the years to a remarkably improved control over the morphology of the tubes, as well as of the degree of self-organization. While the historically first used water-based electrolytes yield nanotube layers with a relatively poor degree of self-ordering,^{47–50,52} today a variety of electrolytes and conditions^{112,156,157} can provide virtually ideal hexagonal-order over long surface ranges – but typically ideal order is limited to the size of an individual Ti crystal grain.¹⁵⁸ For TiO_2 nanotubes, strategies that can provide an extended degree of self-organization have been adopted from approaches developed for ordered porous alumina, *e.g.*, the use of pure and large-grain substrates that reduce the detrimental effect of substrate contaminants, inclusions and grain boundaries on the degree of ordering.¹⁵⁹ A most facile fabrication technique for improved order is double-anodization. This multiple-anodization technique was introduced by Masuda *et al.* for anodic Al_2O_3 .⁴¹ The concept is based on the fact that the degree of self-organization in anodic layers is improved as the tubes grow, and gradually increases towards their bottom (misfitting tubes are eliminated). Therefore, if a first grown sacrificial nanotube layer is removed from the metallic substrate, hexagonally ordered footprints (dimples) are left behind that serve as pretextured initiation sites for the following anodization (Fig. 8a). The so-fabricated tubes feature a more regular hexagonal shape (thus, the standard deviation in the tube diameter is narrowed), and the number of defects is strongly decreased (Fig. 8b and c).^{156,160–162}

However, long-range ordering, with a narrowly dispersed pore diameter distribution and a domain size larger than substrate grains, is fundamental for some emerging applications

Fig. 8 (a) Schematic of the fabrication of TiO_2 nanotubes by a double-anodization approach. SEM bottom views of ordered domains of TiO_2 NTs after the 1st (b) and 2nd (c) anodization. (d) SEM image of TiO_2 nanotubes grown by FIB-guided anodization on a concave pattern. (e) Schematic diagram of the fabrication of an ideally ordered anodic TiO_2 layer on a Ti foil pretextured through nanoindentation. (f and g) Typical SEM micrographs of long-range ordered anodic titania nanotubes grown on a nanoindented Ti metal substrate. (b and c) Reproduced with permission from ref. 160. (d) Reproduced with permission from ref. 166. (e–g) Reproduced with permission from ref. 171.

such as photonic crystals and high density magnetic storage media.^{44,163,164} Strategies that can induce long-range surface pretexturing are mold imprinting or focused-ion-beam (FIB) surface nanopatterning. FIB-induced surface pretexturing¹⁶⁵ offers the possibility of producing ordered concave arrays as initiation sites for anodization, with uniform and controllable depth, that enables the fabrication of TiO_2 nanotubes with different patterns with square, triangular and flower-like cell shapes, also with accurate control on inter-tube distance (Fig. 8d).^{166–168} Nevertheless, FIB patterning (pixel after pixel) is a time-consuming sequential writing process and thus inadequate for patterning of large areas of a Ti metal substrate. It may be noteworthy that mask-based, and thus parallel ion

beam patterning processes have been proposed, but these still are widely unexplored.¹⁶⁹

A straightforward parallel process to create initiation sites that keep the registry across Ti metal grains is nanoimprinting the Ti surface with an ordered array of convexes using a metal mold (Fig. 8e–g). In this case, the mold is produced using e-beam lithography. The advantage of this technique is that the mold can be used repeatedly, and spacing and patterns are adjustable by the lithography process that produces the mold. Most inhomogeneity typically observed under non-guided self-organizing anodization (such as initiation layers and the grain-dependent orientation dictated by the polycrystallinity of metallic substrates) is also largely eliminated. However, given

the high Young's modulus of Ti (116 GPa), only molds of very hard materials can be adopted.^{170,171}

6. Advantages of lifted-off TiO₂ nanotube layers

The defined geometry of nanotubes and the possibility of controlling their length and diameter make anodic tubes particularly suitable for membrane-type applications that additionally exploit TiO₂ functional features, such as flow-through microreactors for photocatalysis and dye-sensitized solar cells.^{145,146,151,172–175} For solar cells, not only the ease of electrolyte access in a two side open membrane (Fig. 9a) is of advantage, but even more beneficial are the superior electronic properties (lower electrical resistance) provided by bottomless tubes.

Nanotube membranes are produced by separating the anodic tube layer from the metallic substrate, followed by tube bottom opening. Albu *et al.* reported the first self-organized, free-standing TiO₂ nanotube membrane prepared by selectively dissolving the Ti substrate with a metal etching treatment in a CH₃OH/Br₂ solution. After substrate dissolution, the tubes were

still closed; thus exposing the layer to HF vapors was necessary in order to open the bottom.¹⁴⁵ Afterwards, a range of different approaches were reported for both lift-off and opening procedures, such as chemical etching, sonication, and voltage alteration.^{176–178} The main challenge encountered when separating nanotubes from the substrate is due to the relative brittleness of the anodic layer, particularly if the membrane is thinner than 50 μm or when large membrane areas are desired. Also, bottom removal mainly by HF, oxalic acid, H₂O₂ or other etchants has to be carefully controlled.

More reliable approaches have recently been developed that allow the detachment of TiO₂ nanotube layers from the Ti metal substrate to form self-standing membranes as thin as $\sim 2 \mu\text{m}$.^{151,172,174,179–181} Here an anodization–annealing–2nd anodization sequence is employed: following the first anodization step, the nanotube layers are annealed in air at a comparably low temperature, *i.e.*, 150–300 $^{\circ}\text{C}$ (to make the tubes water-free and partially crystalline); then the second anodization is carried out to produce a thin underlayer of amorphous TiO₂ NTs. This second amorphous layer can then be selectively dissolved by a treatment in HF or H₂O₂ solutions. Due to the much lower etching rate of the annealed layer, the amorphous tubes are selectively dissolved

Fig. 9 (a) Sketch of anodic TiO₂ nanotube-based front-side illuminated DSSC. TiO₂ tube arrays are detached from Ti substrates, bottom-opened, and transferred onto FTO slides in a tube-top-down configuration. (b) Dye loading, short-circuit current, and power-conversion efficiency of DSSCs fabricated from tube membranes transferred onto FTO glass in a tube-top-down configuration. The SEM images show a close view of the different degrees of tube bottom opening. Reproduced with permission from ref. 172. (c and d) XRD patterns of membranes annealed at different temperatures and under different atmospheres: (c) 450–1050 $^{\circ}\text{C}$ in air; (d) 450–750 $^{\circ}\text{C}$ in O₂ (the patterns were collected after transferring the annealed membranes on quartz glass slides). Reproduced with permission from ref. 175.

and free-standing membranes can be produced that are defect-free over the entire surface area.¹⁷⁵ Noteworthy, only when the lift-off process is performed in H₂O₂, tube bottom opening is simultaneously achieved.¹⁷² Alternatively, the first layer can be produced from a double anodized layer^{156,160–162} that then is annealed and chemically undermined. This treatment has been applied to self-standing and stable TiO₂ NTs membranes of ~1.8–50 μm thickness.¹⁸¹

A unique possibility offered by bottomless TiO₂ NT membranes is the fabrication of size-selective flow-through microreactors that can be used for virtually any photocatalytic reaction (*e.g.*, pollutant degradation and membrane de-clogging in protein separation).^{145,175,182} For example, if a tube membrane is used to separate two (differently filled) compartments of a flow-through reactor, a concentration gradient is created that governs the solution diffusion until an equilibrium is reached. Interestingly, if the surface of the membrane is illuminated, photocatalysis (and membrane de-clogging that is particularly useful for re-opening of the membrane channels)¹⁸² can be activated that, by permanently degrading the arriving reactant molecules, contributes to accelerate the solution diffusion.^{145,175}

Recently, also considerable benefits of using lift-off membranes as anodes for dye-sensitized solar cells (DSSCs) have been reported. To construct photo-anodes such membrane layers are, either with^{151,174} or without^{172,173} bottom, glued to a conducting glass surface typically using TiO₂ nanoparticle suspensions. These arrangements have several advantages: not only the photo-anodes provide the classic advantage of 1D-nanostructures, namely the one-dimensional transport, but additionally if the anodic TiO₂ NT layer is detached from the Ti substrate and transferred onto FTO, the photo-anode can be irradiated through the FTO glass in a “front-side” illumination configuration (Fig. 9a). With this geometry, the DSSC reaches higher efficiency as the light losses typically observed in a back-side application due to light absorption in the electrolyte and by the Pt counter electrode are minimized.^{151,172,174,183} Moreover, the solar cell efficiency is significantly enhanced for bottom-opened tube membranes (Fig. 9b).¹⁷² This has been ascribed to a higher electron mobility within the tube layer, owing to the absence of the high-resistivity tube bottom, and to an optimal electrolyte percolation through the dye-sensitized fully-open tube scaffold. This in turn minimizes charge recombination as, upon electron injection into TiO₂, the dye can readily react with the electrolyte in its vicinity; even more, when a bottomless tube configuration is adopted, the ability of the dye solution to penetrate the entire TiO₂ structure is significantly enhanced; this also implies that an open-bottom morphology allows for optimal dye-loading.

It should also be mentioned that the detachment of tubes from the metal prevents the formation of rutile at the metal/oxide interface during annealing (rutile is formed by thermal oxidation of Ti metal). Rutile is detrimental for TiO₂ in photo-electrochemical applications due to the poor electronic properties compared with anatase.^{184–186} It is well established that direct annealing of metallic Ti in air at temperatures above 450 °C leads to a relatively thick rutile layer – this also occurs

with the metal underneath the tubes. If the metal layer is absent, as in detached membranes, no rutile is detected up to annealing temperature of 950 °C (Fig. 9c and d).^{174,175} Although no remarkable difference in the phase composition of TiO₂ membranes annealed up to such a high temperature can be observed, it is evident that a gradual increase in the crystallinity degree, that is, a more intense main anatase reflection (at $2\theta \sim 25.3^\circ$), is obtained when increasing the annealing temperature up to 650 °C.¹⁷⁵ This in turn enhances the charge transport properties of the layer as electron transport in the tubes becomes considerably faster (this is advantageous for maximizing charge collection at the oxide/electrode interface in DSSC).¹⁷⁴ Finally, also annealing in O₂ produces fully anatase TiO₂ membranes up to 750 °C (that is, no rutile is detected), if the nanotube layers are detached from the Ti metallic substrate. As discussed below, O₂-annealing, for instance, is particularly useful to fill native oxygen vacancies in TiO₂ and, hence, produces a “higher quality” oxide, with optimized conductivity.¹⁸⁷

7. Tube morphology and optical and electronic properties

Most relevant applications of TiO₂ nanotube layers ensue from the beneficial combination of the material's intrinsic properties with the one-dimensional nanoscale geometry. A key point is that this geometry can in principle provide a directional (*i.e.*, faster) charge transport through the oxide. In any form of TiO₂, another factor that strongly affects the electronic properties is the crystal structure of the material. In its amorphous form (such as in as-grown tubes), TiO₂ has a mobility gap of 3.2–3.5 eV and a very low electron mobility. Upon crystallization to anatase or rutile (typically achieved under air annealing conditions) an indirect optical band gap of 3.2 eV and 3.0 eV is obtained, respectively.¹⁸⁸ Both polymorphs show a higher mobility than amorphous TiO₂ but, in particular, a crystallization into anatase is often reported to be crucial to obtain a high electron mobility.^{189,190} Optical and electronic properties of TiO₂ are largely influenced by oxygen vacancies and Ti³⁺ states in the lattice, that is, electrons may be trapped in the Ti³⁺ states or holes in the oxygen vacancies and injected in the nearby conduction and valence bands by thermal excitation. The conductivity of TiO₂ is dominated by Ti³⁺ trap states and, in the polycrystalline material, also by grain size. Therefore, a variation in the annealing conditions of TiO₂ nanotubes (such as temperature, time, and atmosphere) can alter the layer resistance (and the electron mobility) over several orders of magnitude.^{191,192}

As previously pointed out, annealing of TiO₂ on the metal substrate (Ti) strongly differs from annealing free-standing membranes. In both cases, upon increasing the annealing temperature (*i.e.*, 250–500 °C) a significant decrease in the tube resistivity can be obtained, owing to amorphous layers being converted to crystalline anatase. However, for TiO₂ nanotubes on the Ti substrate, annealing as described above may cause rutile formation due to the thermal oxidation of the metal substrate. As a negative consequence (in view of photo-electrochemical applications),

Fig. 10 (a) Comparison of specific resistivity values of TiO_2 nanotubes vs. annealing temperature obtained by 4-point (left axis) and 2-point (right axis) measurements. Reproduced with permission from ref. 193. (b–d) Procedure of four-point conductivity measurement with a single nanotube: (b) single TiO_2 nanotube before fixing it on the substrate, (c) the nanotube fixed with WC_x , and (d) after producing the electrical contacts. Reproduced with permission from ref. 194. (e) Comparison of electrical resistance of the single-walled and double-walled nanotube layers measured at different temperatures. Reproduced from ref. 54 with permission from the Royal Society of Chemistry. (f) Electron transfer time (τ_e) constants obtained from IMPS measurements performed under UV light irradiation (325 nm) for double-walled (double) and single-walled (single) TiO_2 nanotubes, also modified with a layer of TiCl_4 nanoparticles (double + T1 and single + T1, respectively). Reproduced from ref. 146 with permission from the Royal Society of Chemistry. (g) TEM micrographs of bare TiO_2 NTs before annealing (left-side) and of carbon-cladded TiO_2 NTs modified with the deposition of RuO_2 nanoparticles (right-side). Reproduced from ref. 199 with permission from the Royal Society of Chemistry. (h) Incident Photon-to-Current Efficiency (IPCE) spectra of different C-contaminated TiO_2 nanotube layers that show sub-band gap response: (■) amorphous NTs, (●) NTs annealed in air, (○) NTs annealed in CH_3OH -containing atmosphere. Reprinted with permission from *J. Electrochem. Soc.*, 2010, **157**(3), G76. Copyright 2010, The Electrochemical Society.

the overall resistivity of these tube layers rises again (Fig. 10a).¹⁹³ In contrast, free-standing membranes can be annealed up to $\sim 1000^\circ\text{C}$ while maintaining a pure anatase phase – rutile is not formed owing to the absence of the Ti metal substrate (Fig. 9c and d), and such layers show clearly improved electronic properties.^{151,174,175,187}

Typical resistivity values in the range of 10^4 – $10^5 \Omega \text{ cm}$ ¹⁹³ are obtained (from both four- and two-point measurements) for anatase tube layers anchored on the metal substrate – four-point measurements may however better reflect the resistivity

dependence on the annealing temperature. However, two- and even four-point measurements carried out with metal contacts on the tubes, but the metal substrate underneath, are somewhat ambiguous. Most informative are four-point techniques applied to a single TiO_2 nanotube (Fig. 10b–d).¹⁹⁴ A crucial finding is that the conductivity measurements in this case show orders of magnitude higher values than measurements on the substrate. This large difference cannot be ascribed to the presence of the rutile underlayer but rather reflects an high resistivity of the tube bottoms (this explains why bottom-opened tubes lead

to significantly higher solar conversion efficiencies when used in DSSCs, Fig. 9b). Moreover, the T-dependence of resistance for a single tube was found compatible with a Mott variable range hopping mechanism, that is, conductivity is provided by electron hopping within localized states in a mobility gap.^{194,195} In other words, these measurements indicate that not grain boundaries (crystal size) in the tube wall are limiting the conductivity, but the intrinsic defect states within TiO₂ crystals forming the nanotubes. While these measurements on single tubes are most informative, many data were obtained using a Ti/TiO₂/metal top contact two-point measurement – simply due to the facility of this approach. In spite of all the shortcomings of two-point measurements, phenomena such as water loss, anatase/rutile formation and defect-elimination by pure oxygen annealing can be detected and are in line with expectations.^{193,196,197}

Using this two-point approach, the effect of the inner C-rich layer on conductivity was also investigated, by comparing double-walled and single-walled NTs.⁵⁴ A clear difference in the conductivity can be already observed with as-formed tubes, with the double-layered exhibiting a somewhat lower resistance. However, after annealing, a drastic increase (about 10–100 times) in the conductivity properties is obtained for the single-walled tubes while a resistivity increase is observed for the double-walled tubes (Fig. 10e). Most likely the trend observed for double-walled tubes is due to the high amount of residual water that remains entrapped in the tubes up to ~180–200 °C, as evident from TGA-MS results and, even more, can be ascribed to the high C-contamination content that originates from the IS layer (Fig. 7a);¹³⁵ the enhanced electrical conductivity of single-walled tubes therefore indicate that removal of the inner contamination layer leads to beneficial electrical properties in the tubes after crystallization (single-walled tubes show a pure (no contamination) and large crystalline TiO₂ structure, whereas in double-walled tubes contamination is still present and a typically smaller TiO₂ grain size within the tube wall is observed).¹³⁵ Nevertheless, even better electron transport properties can be achieved exposing single-walled tubes to a TiCl₄ treatment. Not only the tube walls become then decorated with a nanoparticle layer, but the treatment seems also able to passivate defect states, leading to clearly faster electron transport (Fig. 10f).^{146,198}

However, the C-contaminated IS of double-walled tubes has also been used to create beneficial effects when annealing EG-based tubes under inert gas conditions. A thin carbon layer can be formed that uniformly coats the inner walls of TiO₂ NTs.^{54,55,150,199} Such a cladding with a graphitic-like layer leads to enhanced conductivity, and provides a path to attach additional functionalities to the tubes, as the entire chemistry for modifying carbon-based layers becomes accessible^{200,201} and applicable to TiO₂ NTs. This strategy can serve for example to fabricate scaffolds for anchoring a thin layer of RuO₂ nanoparticles (*i.e.*, a standard material for supercapacitors, Fig. 10g), and considerable performances of TiO₂ NTs as supercapacitor device can be obtained.¹⁹⁹

Photo-electrochemistry and, in particular, Incident Photon-to-Current Efficiency (IPCE) measurements (*i.e.*, the photocurrent collected per incident photon flux as a function of illumination wavelength) are generally employed to investigate the optical

properties of a semiconductor material, provide quantitative information on its band-gap and evidence true charge conduction at the corresponding wavelength (this in contrast to light absorption measurements).²⁰² Typically, the main mechanism of light absorption in semiconductors is due to inter-band electron transitions. While a number of physical properties may be altered in small nanocrystals,^{203,204} in TiO₂, optical quantum confinement and band-gap widening (that is, a measured E_g of ~3.8 eV) can be practically observed only in tube walls or nanosheets that are prepared through hydrothermal procedures (that is, in “real nanotubes”) as they feature a wall thickness in the range of atomic sheets,²⁰ while in general nanotubes grown by electrochemical anodization, having a wall thickness typically larger than ~5 nm, show a band-gap corresponding to that of the bulk material (*i.e.*, E_g ~3.0–3.2 eV). As TiO₂ is an indirect band-gap semiconductor, electronic transitions are phonon-coupled and, for size ranges <20 nm, phonon confinement effects can be observed and identified from TiO₂ Raman peak widening and shift. For instance, in TiO₂/Ta₂O₅ superlattice nanotube structure, TiO₂ size units are confined to ~10 nm in two dimensions and typical blue-shift and significant broadening of anatase peak in Raman spectra, as compared to the reference TiO₂ material, have been reported.¹⁴⁸

Typically, for anodic titania nanotubes, two factors play major role in the light absorption and in affecting photo-induced electrochemistry: (i) a contribution to the photoresponse from tube walls is observed only if NTs are crystalline, (ii) upon annealing, the donor concentration in nanotubes is usually very high (10^{18} – 10^{19} cm⁻³), *i.e.*, two orders of magnitude higher than for conventional TiO₂ nanoparticles.²⁰⁵ Although, compared to nanoparticles, tubes feature more inter-band trap states (*e.g.*, oxygen vacancies) charge carrier transport in NTs is faster than in a nanoparticulate film.¹⁹² Electron diffusion lengths reported for nanotubes are 30 times longer than in nanoparticles, particularly under low-intensity irradiation.¹⁰²

In view of these considerations, another promising way to improve electron transport in TiO₂, and hence its performance in photo-electrochemical applications (*e.g.*, DSSCs and photocatalysis), and to extend its light absorption spectrum in view of enabling visible-light photoactivity, is to introduce a dopant (that is, suitable inter-band states) into the TiO₂ lattice. The dopant can either be a non-metal or a transition metal cation. In the latter case, metal cations, *e.g.* Ta and Nb, usually replace Ti in the TiO₂ lattice and promote electron conductivity in the NT layer.^{77,85} For non-metal doping, most frequently investigated are N,²⁰⁶ C,²⁰⁷ S,²⁰⁸ and P²⁰⁹ that either replace O-atoms in the TiO₂ structure (substitutional doping) or are stacked in interstitial spaces (interstitial doping), and generate suitable states in the band-gap and increase the conductivity of TiO₂ nanotubes (low dopant concentration) or lead to band-gap narrowing (high dopant concentration).

Different approaches are reported to prepare doped TiO₂ nanostructures, among which thermal treatment in a suitable gas atmosphere, *e.g.* NH₃, is mostly adopted. Although findings of C-doping in TiO₂^{26–28,210,211} are to a certain extent ambiguous,²⁰²

C-containing tubes (that is, tubes with a double-walled morphology where carbon-uptake is due to the decomposition of the anodizing organic electrolyte under applied voltage) exhibit a change in the TiO₂ optical properties. Light absorption and photocurrent spectra taken for tubes and membranes show that carbon contaminants (~3 at%) lead to a sub-band gap response (Fig. 10h). Also, the conversion of TiO₂ nanotubes to semimetallic TiO_xC_y, by thermal treatment in an acetylene atmosphere, or to TiN nanotubes, by a high temperature treatment in NH₃, drastically changes the electronic properties of the starting material to a semimetallic nature and also improves its mechanical stability.^{212,213} Most recently, high pressure hydrogenation²¹⁴ as well as high-energy proton²¹⁵ and low-dose nitrogen²¹⁶ implantation into TiO₂ tube layers have been reported to alter not only the electronic structures of TiO₂, but also to create catalytically active surface sites for improving the photocatalytic H₂ evolution of TiO₂ NTs.

Finally, a most unique possibility offered by anodic TiO₂ nanotubes is the doping of tubes with a certain metal X, using suitable Ti–X alloys as metallic substrate for electrochemical anodization, where the alloyed species gets incorporated into the oxide. A number of reports show doping of tubes with Cr,⁸⁷ V,⁷⁸ W,³⁷ Ta^{84–86} and Nb.^{77,79,80,82,217} In particular, in optimally doped and annealed TiO₂ tubes, both Nb and Ta act as electron donors and hence increase the electron conductivity of the NT layers. This was *e.g.* demonstrated for nanotube arrays doped with small amounts (up to 0.1 at%) of Nb^{79,80,217} or Ta,^{85,86} for which a significantly enhanced performance in photo-electrochemical water splitting and dye-sensitized solar cells was observed. Other outstanding features, remarkable for nanotube application in electrochromic devices and ion intercalation based batteries, that can be obtained by anodizing Ti–X alloys are a higher optical contrast and a higher structural cycling stability for reversible Li-intercalation processes compared to pure TiO₂ nanotubes. Particularly interesting is the case of superlattice NTs grown from sputter-deposited multi-layer metal stacks of *e.g.* Ti–Nb that, due to the small size of the alternating TiO₂/Nb₂O₅ segments (less than 10 nm), showed clearly less mechanical rupture by stress-induced burst.⁸¹ A superior mechanical stability has also been reported for TiO₂ nanotubes grown in the presence of lactic acid in the electrolyte. TiO₂ NTs grown under these specific conditions could be exposed to a more than three-time larger external force in tensile tests, compared to conventional tubes, before mechanical failure (cracking) of the tubes occurred.²¹⁸ This characteristic makes LA tubes particularly interesting for robust membranes, with the single tubes maintaining their integrity during the membrane fabrication process.

In contrast to previous Ti–X alloy examples (where X is typically a non-noble metal), anodization of noble metal alloys of Ti lead to noble metal nanoparticle-decorated tubes,^{90,91,219} *i.e.*, noble metals, such as Au and Pt, are not oxidized during the anodization process. With this approach, the decoration density of Au or Pt nanoparticles can be easily controlled by the amount of the noble metal in the alloy and by the anodization time. This tuning of nanoparticle interspacing is in turn particularly useful

for obtaining an optimal (photo)catalytic activity, such as in the splitting of water or as chemo-selective catalytic sites.^{90,91}

All these examples illustrate that for anodic TiO₂ NTs outstanding knowledge and control over a large set of inherent physico-chemical properties has been acquired within the last decade of research. These findings provide key strategies to tailor the characteristics of TiO₂ NTs, *e.g.*, their morphology, light absorption, conductivity, electron–hole mobility, *etc.* in a synergistic manner, in order to provide versatile platforms for various remarkable functional applications, such as photocatalytic and photo-electrochemical water splitting (H₂ generation), DSSCs, and size-selective microreactors for photocatalytic and biochemical reactions.^{27,28,90,145,146,182,215,216}

8. Conclusion

Titanium dioxide is by far among the most investigated functional metal oxide. This is due to the set of specific properties (*e.g.*, non-toxicity, corrosion resistance, relatively long electron diffusion length, and biocompatibility) that makes TiO₂ attractive for various applications including photocatalysis, photo-electrochemistry, and biochemistry. The possibility of growing porous anodic nanostructures and, in particular, self-organized and highly-aligned TiO₂ nanotubes through electrochemical anodization has further increased the research interest on titania due to inherent advantages of tubular structures, such as large surface area, directional charge and ion transport properties, size exclusion effects, and defined diffusion behavior.

The present review emphasizes critical aspects in the formation mechanism of self-ordered TiO₂ nanotubes, and a wide range of morphology and property variations. We discuss the current understanding of the key factors that drive self-organization and attempt to show features common to ordered anodic nanoporous structures, such as porous Al₂O₃ and ordered TiO₂ nanotubes. In spite of common principles underlying their growth, there are crucial differences not only in terms of alumina and titania anodic nanostructure morphologies, but also the influence of various electrochemical growth parameters, that have been shown to strongly affect the morphology, composition and structure of the resulting nanotube layers. With this review we try to highlight the importance of such variations and, at the same time, to provide guidelines for the selection of growth conditions specific for the intended use of the tube layers. We introduce most recent nanotube arrangements, such as stacks, bamboo-type tubes, branched and inter-tubes, tube-in-tube morphologies and, in particular, we point out key differences between single- and double-walled tubes along with their intrinsic properties. We give an overview of the optimized preparation and use of TiO₂ tube membranes that in the recent few years have attracted strong interest in view of applications such as efficient DSSCs and size-selective flow-through photo-microreactors. Among most remarkable advantages of free-standing TiO₂ membranes is certainly the possibility of establishing the desired pure anatase phase without conversion to rutile upon annealing TiO₂ at high temperature. We discuss the most relevant electronic and optical properties

of differently grown TiO₂ nanotubes, giving a general overview on the approaches most frequently adopted to achieve desired modifications. Overall, we try to emphasize that anodic tubes are not simply tube-shaped TiO₂ but there are a number of crucial (controllable) factors that can substantially affect their performance in application. Therefore, building on the expertise established up to now on TiO₂ and on one-dimensional nanostructuring, one may identify some important future efforts. Improvements of synthetic strategies may not only ameliorate some intrinsic “weaknesses” of TiO₂ (*i.e.*, in optical and electronic properties, compatibility with bio-materials, ion-intercalation) but also address some of the current features of anodic nanotubes (*i.e.*, crystallinity, degree of self-organization, control over tube morphology, length and diameter). Clearly, still a large potential exists for maximizing the performance of 1D TiO₂ NT-based devices (*e.g.*, adequate treatments to reduce the defects in NTs, or to intentionally create intrinsic defects that could affect light absorption and electron conductivity for higher efficiencies in photocatalysis and DSSCs-based applications; anodizing under specific conditions to adjust a desired material robustness for membrane and flow-through applications; improvement of the ordering and control of tube wall thickness to achieve electronic size effects) and for designing specific surface structures and chemistry. The last decade has shown that TiO₂ nanotubes prepared through self-organizing anodization are nanostructured materials providing continuous surprises that trigger advances of nanotechnology and the development of energy-, environment- and bio-applications, owing to their intrinsic properties and to the versatility and scalability of the fabrication technique, and we hope this review provides some tools and strategies to facilitate further future achievement.

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