Critical Factors in the Anodic Formation of Extremely Ordered Titania Nanocavities

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In the present work, we discuss the formation of a highly ordered form of TiO₂ nanotubes (U-tubes) which are grown by anodizing Ti metal in a concentrated HF/H₃PO₄ electrolyte. The crucial parameters determining geometry and order of the tubes (such as, temperature, applied voltage, concentration of HF, and anodizing time) are investigated and discussed. Under optimized conditions, not only very high degree of order, but also a perfectly open tube top morphology is obtained. The amorphous titania tubes (cavities) consist of a phosphate rich inner layer and a fluoride rich outer layer. Thermal crystallization of these short amorphous cavities to anatase/rutile at temperatures (>400°C) in air leads to partial oxidation of the underneath metal - this and the short length of the tubes, usually around 200 nm, pose challenges for potential photoelectrochemical applications. However, the limited tube length can be overcome by a double anodizing technique. The extremely high order and unique nature of these types of self-ordered tubes allows for unprecedented control and enables various uses of the tubes.

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Over the past decades, nanostructured TiO₂ and particularly self-ordered anodic TiO₂ nanotubes have attracted wide scientific and technological interest.^{1–11} The main reason for this interest is that these nanotubes not only provide a large active surface area but also a highly defined electrode geometry that is beneficial for a wide range of applications, e.g. in photocatalytic self-cleaning or H₂ generation, electrochromic devices, biomedical coatings, sensors, and photovoltaics.^{12,13}

In 1984, Assefpour-Dezfuly et al. grew the first self-ordered TiO₂ nanostructures by anodizing Ti in an acidic fluoride-containing electrolyte; however, only a few hundred nanometers of layer thickness with a high degree of disorder could be obtained.¹⁴ These structures turned out to have a tubular shape and were optimized in the following years through the second generation formed in aqueous neutral electrolytes.¹⁵ The third generation of TiO₂ NTs was formed in organic electrolytes and showed a smooth and controllable geometry.¹⁶ Today, the most commonly used electrolytes for electrochemical growth of TiO₂ nanotubes are based on NH₄F or HF in water/ethylene glycol (EG) or water/glycerol electrolytes.¹⁷ In these electrolytes, generally the voltage used for anodizing Ti determines the tube diameters, and the anodization time does not only affect the tube length but also the top morphology of the tubes.

Generally, for the TiO₂ NTs grown in organic electrolytes, inhomogeneous layers on the top (i.e. initiation layers or so-called nanograss) are observed. Moreover, these tubes show a core-shell structure with an inner carbon rich (contamination) layer. One promising method for obtaining open top tube structures for TiO₂ NTs is based on the classical approach growing ordered porous alumina.^{18,19}

The tubes grow usually as amorphous TiO₂ with an outer fluoride layer that originates from growth under high field conditions.^{20,21} In order to use the tubes in many photoelectrochemical applications, they are usually air annealed to anatase or anatase/rutile mixtures (in this process usually also the fluoride layer is lost).²² While an adequate annealing not only leads to crystallization of the tubes – including highly effective twinned anatase structures – also the concomitant oxidation of the Ti substrate needs to be considered²³ (we will address this also in this work).

In the present work we discuss critical parameters in the formation of extremely ordered TiO₂ nanotube structures that form as nanocavi-

ties in electrolytes consisting of highly concentrated HF and o-H₃PO₄. This form of tubes, also referred to as “U-tubes”, show the highest degree of self-ordering of all nanotubes, if not an imprinting approach is used, as recently described in literature.²⁴ Moreover, these tubes do not have the drawbacks of tubes that were formed from organic electrolytes (closed tube mouth, “grass”, C-contamination layer).

Experimental

In order to fabricate anodic TiO₂ layers, Ti foils (0.125 mm thickness, 99.6% purity Advent, 15 × 30 mm) were used as anode material. The Ti foils were degreased by sonication in acetone, ethanol, and deionized (DI) water for 20 min, respectively, and dried in a stream of nitrogen. The electrolyte was prepared with melted o-H₃PO₄ which was mixed with 3 M of HF (40% purity, Sigma-Aldrich). The electrolyte was held at 100°C for 30 min to reduce the water content, and the temperature was kept at 100°C during anodization.

For the growth of optimized ordered TiO₂ nanotube arrays, anodization was carried out under various conditions, such as applied potential: 2–40 V by a power supply (VLP-2403 pro, Voltcraft), temperature: 80–120°C on hot plate (C-MAG HS 7 digital, IKA), and time: 10 min–24 h. After the anodization, the nanotube layers were rinsed with ethanol and dried in an N₂ stream. During anodization, current density was recorded by a Keithley multimeter connected to a computer through a General Purpose Interface Bus (GPIB) card.

Double anodization was performed to enlarge the thickness of the U-tube layers. The 1st step was carried out in 3 M HF in o-H₃PO₄ at 2–15 V for 2–12 h, and then the anodic NTs were rinsed with ethanol. The 2nd step was performed at 20–60 V for 2–10 min in an organic electrolyte consisting of 0.15 M NH₄F and 3 vol% of H₂O. The potential and anodizing time of the 2nd step were optimized for the diameter and length of nanotubes from the 1st step; i.e. 2 V 12 h // 20 V 10 min, 5 V 5 h // 30 V 5 min, and 15 V 2 h // 60 V 2 min.

To fabricate replica structures, TiO₂ nanotubes were filled with molten polystyrene (PS, Sigma Aldrich, Mw 35,000) by heating at 110°C. The Ti/TiO₂ substrates were removed from the samples by immersing the samples in 1 M HF aqueous solution for 5 h.

A field-emission scanning electron microscope (Hitachi FE-SEM S4800) was used for morphological characterization at the same acceleration voltage. Most of the cross-sectional images were obtained on mechanically scratched samples. In addition, cross-sections of tubes were obtained by ion-milling (IM IM4000, Hitachi).

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Figure 1. a~c) SEM images of highly ordered TiO_2 nanotube arrays (U-tubes) prepared in 3 M $\text{HF}/\text{H}_3\text{PO}_4$ solution at 15 V and 100°C for 2 h. Ti foil sheet and Pt sheet were used as working and counter electrode respectively. d) Fast Fourier Transform (FFT) conversion of Figure 1c. e~g) Optical pictures of as-formed U-tubes on Ti substrate which were anodized in 3 M $\text{HF}/\text{H}_3\text{PO}_4$ solution at 15 V and 100°C for 2 h, f) 10 min, and g) 5 h. f) SEM image of as-formed U-tubes (anodized in 3 M $\text{HF}/\text{H}_3\text{PO}_4$ solution at 15 V and 100°C for 2 h) after exposure to water.

XRD analysis (X'pert Philips MPD with a Panalytical X'celerator detector) using graphite monochromatized $\text{Cu K}\alpha$ radiation (wavelength 1.54056 Å) was used for determining the crystallographic structure of the samples.

The photoelectrochemical water splitting experiments were carried out under simulated AM 1.5 (100 mW cm^{-2}) illumination provided by a solar simulator (300 W Xe with optical filter, Solarlight; RT) in 1 M KOH solution. Photocurrent versus voltage (I–V) characteristics were recorded by scanning the potential from -0.7 to $+0.5$ V (vs. Ag/AgCl (3 M KCl)) with a scan rate of 1 mV s^{-1} using a Jaissle IMP 88 PC potentiostat.

Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range of 100 kHz to 10 mHz with an AC amplitude of 10 mV, at open circuit potential in 0.1 M Na_2SO_4 solution, using a Zahner IM6 setup (Zahner Elektrik, Kronach, Germany).

Results and Discussion

Figure 1 gives an overview of the morphology and typical features of highly ordered TiO_2 nanocavities (U-tubes) grown at 15 V for 2 h in a mixture of 3 M HF and $\text{o-H}_3\text{PO}_4$ at 100°C . From the SEM top views (in Figures 1a, 1c) it is clear that these tube layers show an extremely well ordered arrangement. Figure 1d represents a fast Fourier trans-

form (FFT) of Figure 1c; the occurrence of regular “reflection peaks” illustrates the high degree of order present in this structure (classic nanotube layer top views do not show any well-defined FFT pattern, as they do not provide a sufficient degree of order). The nanotube layer presented in Figure 1 is the result of optimized anodization conditions. The tubes show an extremely uniform ordering, with a precise homogeneous diameter, size and layer thickness over a wide range of the anode surface (Figures 1a~1c). The cross sectional image in Figure 1b shows the tubes to be ~ 200 nm long with a U-shaped profile. Importantly, the layers are free from any initiation layer and/or nanograin structures often observed for other type of nanotubes, and show a uniform and open tube top mouth. In view of various applications of these tube layers, this morphological feature is very important, as it allows for the deposition of secondary materials, or the use of the layer as a template.^{25–27}

The image of the electrode after anodization (Figure 1e) shows interference colors with a color-homogeneity and shine; that is typical for these highly organized TiO_2 NTs. Thin anodic layers exhibit various interference colors that vary with layer thickness; blue for 110 nm (Figure 1f), green for 180 and light pink for 230 nm (Figure 1g). The tube layer in Figure 1 is approximately 200 nm thick, corresponding well to the green-yellow color. It should be noted that a post treatment after anodizing is of utmost importance. In order to obtain the intact layer

Figure 2. a) Optical microscope image of as-formed U-tubes (anodized in 3 M HF/H₃PO₄ at 100°C and 15 V for 2 h). b) SEM image of Ti substrate. The grains were revealed after etching Ti foil in H₂O₂ solution (insert: zoomed out SEM image of U-tubes). c~d) I-t curves during anodizing Ti in HF/H₃PO₄ electrolyte at 100°C for 2 h; c) with different concentrations of HF; d) at different applied potentials.

morphology shown in Figure 1, after formation the layer needs to be immersed directly in ethanol for overnight and then dried in N₂ steam. If instead the formed nanotube layers are immersed in water, the layers can be further etched and the nanotubes can be easily separated (SEM images in Figure 1b). Controlled water treatment can thin down the wall of nanotubes; they become transparent in SEM images taken at the same acceleration voltage giving them a ghost-tube appearance, but the well-aligned ordering of nanotubes can still be retained.

Figure 2 shows a mildly crystallographically etched electrode surface after nanotubes are grown, (Figure 2a) in an optical microscope image, and (Figure 2b) in a SEM image. From both images substrate grains become visible, the size of the Ti grains is approximately 10–20 μm. While within a grain highly ordered tubes are formed, from high-resolution SEM images at the grain boundaries it is apparent that the nanotubes grow with a change in their alignment, i.e. they show a different registry on different grains. Recently, this correlation of grain orientation between TiO₂ NTs and Ti substrate has been examined by polycrystalline Ti foils anodized in various aqueous and organic solutions.²⁸ I.e. also in our electrolyte, the formation of U-tubes is dependent on the orientation of the underlying Ti substrate. During the formation of the tubes, two key parameters are the HF concentration and the anodizing voltage. This is also apparent from the current density vs. time (I-t curves) in Figures 2c~2d for different HF concentrations and different anodizing voltages. All I-t curves show typical characteristics for passivation and self-organization: First, the current increases and then drops exponentially with increasing layer thickness, as an initial oxide layer forms that hampers ion transfer. Then tube growth starts and is in competition with oxide dissolution – the situation levels off to a steady current flow, where tube formation and dissolution are in dynamic equilibrium.^{9,15,29} Clearly, the overall current densities increase with increasing HF concentration or higher anodizing potential. The effects become more apparent when the conditions are harsher. At the same time, order increases (as shown in Figure 3 and Figure 4).

Figures 3a~3e illustrates the effect of HF concentrations on the diameter and morphology of U-tubes; the anodization was carried out at 100°C for 2 h. From the SEM images it is evident that in every case the thickness of tube layer is around 200 nm and all of the tubes have an open top (no initiation layer, no nanoglass). The top and cross sectional views of TiO₂ NTs grown in the low concentrated HF electrolyte (e.g. 0.2 and 0.5 M) obviously show an inhomogeneous arrangement of nanotubes. For TiO₂ NTs formed in high concentrated HF solutions (1 and 3 M), the nanotube morphologies show a high homogeneity and extreme ordering over a large surface area; this not only in the top view but also in cross-sectional images. From these observations it is evident that a high electric field is essential to achieve extremely high ordering of TiO₂ nanotube arrays. However, if even more concentrated HF solutions are used (>5 M), an electropolished surface instead of nanotubular structures is obtained (Figure 3e). This is in line with work of Ono et al. who reported that mainly the effective “electric field” influences self-ordering.³⁰ Ono et al. showed this for porous alumina structures where it was demonstrated that at high electric fields (i.e., with high applied voltage), alumina nanoporous structures experienced strong “growth pressure” from all directions.³⁰ Finally, this effect can generate the perfect hexagonal arrangement of nanotubular structures (or honey comb structures). This maximum ordering is typically observed for current conditions close to breakdown (burning). I.e., in this case a maximum HF concentration leads to a maximum field, resulting in maximum ordering (up to a point where film breakdown or dissolution dominates).

In addition, the concentration of HF affects the tube diameter which is shown in Figure 3f. As the HF concentration increases, the diameters of nanotubes decrease from 140 nm (0.2 M) to 52 nm (5 M), and the homogeneity of diameter is improved when the nanotubes are prepared in a highly concentrated HF solution; i.e. the size difference is reduced from ±10 nm (low concentration of HF: 0.2 M) to ±2 nm (high concentration of HF: 5 M). Consequently, a concentration of 3 M HF was chosen for obtaining ideally ordered U-tubes.

Figure 3. a~e) SEM images of anodic TiO₂ NTs grown in different concentrations of HF in o-H₃PO₄ solution at 15 V and 100°C for 2 h. f) Tube diameter as a function of the HF concentration. g) Effect of the applied voltage on thickness and diameter of tubes anodized for 2 h (☆ marks a T of 80°C). h) Effect of the anodizing time on thickness and diameter of tubes.

The diameter and length of the nanotubes were also studied as a function of the applied voltage. Figure 3g and Figures 4a~4d show a linearly increasing diameter and tube length with increasing voltage. A minimal diameter and length of the TiO₂ nanotubes were obtained at 2 V (D ~22 nm, L ~20 nm), and the maximum values were observed at 40 V (D ~220 nm, L ~700 nm). As shown in Figure 3g and Figures 4a~4d, the voltages could only be varied successfully in a range from 2 to 40 V (at 100°C for 2–30 V or at 80 or 90°C up to 40 V). For higher voltages (e.g. 50 V), strong bubble formation occurred and the current density rapidly increased as typical for breakdown conditions (burning). Furthermore, Figure S1 shows that if the electrolytes were

kept below 80°C, non-homogenous structures were formed and not the ideal round shaped bottoms of the nanotubular structures were obtained. In contrast, by maintaining the temperature at 90°C and above, the homogeneity of the tube arrays and the shapes of the tube tops were evidently improved (Figure 4d). Clearly, in this electrolyte the anodizing temperature is one of the crucial factors in forming highly ordered TiO₂ nanotube arrays. As evident from the SEM images in Figure S2, well organized TiO₂ nanotubes could be formed only at high temperatures (over 80°C). Furthermore, among the various high temperatures (80, 100 and 120°C), the TiO₂ nanotubes prepared at 100°C show the highest homogeneity over the entire arrays (Figure 1c). Anodizing

Figure 4. SEM images of anodic TiO₂ NTs anodized in 3 M HF/H₃PO₄ at 100°C for 2 h at different potentials: a) 2 V, b) 5 V, c) 10 V and d) 40 V. At the applied potential of 40 V a temperature of 100°C could not be applied, due to decomposition of the electrolyte accompanied by gas evolution. e~h) SEM images and FFT images of anodic TiO₂ NTs in 3 M HF/H₃PO₄ at 15 V and 100°C for different anodizing times: e) 10 min, f) 30 min, g) 7 h, h) 24 h.

at other temperatures leads to etched morphologies (120°C) or to an inhomogeneous morphology of the nanotube layers (80°C). At room temperature, the TiO₂ structures consist of small dimples with a depth of only ~40 nm. The arrays are not homogenous and some tube tops are closed. The key effect of temperature in this electrolyte is to adjust the H₂O content in H₃PO₄.

Figure 3h shows the effect of anodization time on the length of the nanotubes. The growth rate of anodic TiO₂ NTs is relatively fast up to 3 hours, but after a length of 230 nm is reached, the growth rate slightly decreases reaching a steady state, i.e. growth and dissolution are in equilibrium. This is related to high-field controlled growth and

dissolution of the TiO₂ nanotubes.^{29,31} The critical parameters of the growth rate are the O-ion mobility and Ti⁴⁺ migration in the tube bottom TiO₂ layer at fixed applied potential. A thicker or better quality tube bottom limits the O-ion and Ti⁴⁺ movement through the bottom layer, hence the tube growth is slower than at the beginning of anodization, in the present case this may be described to chemical changes at the tube bottom.⁶ Please note that as dissolution of the TiO₂ surface into the electrolyte continues, the thickness is kept at around 250 nm, but the TiO₂ NTs show very thin and sharp edges.

Figures 4e~4h shows the impact of the anodizing time on the diameter and the ordering of the U-tube arrays. The SEM top views

Figure 5. a) TEM HAADF image, b) elemental mapping (TEM-EDS) of U-tubes before annealing. XPS and HR-XPS for highly ordered TiO_2 NTs c) as-formed (U-tubes in 3 M $\text{HF}/\text{H}_3\text{PO}_4$ at 100°C and 15 V for 2 h), and d) after annealing at 450°C for 1 h in air. e) XRD patterns of the U-tubes after heat-treatment in air for 1 h at different temperatures (A - anatase, R - Rutile, T - Titanium).

show a clear transition to more connected morphologies and better aligned nanotubes with time, while the thickness stagnates after ca. 7 h of anodization (Figure 3h). The insets in Figures 4e~4h clearly illustrate that the degree of ordering is increased with increasing anodization time (leading to drastic changes in the FFT data). In case of anodization for 2 h, the alignment is achieved in essentially perfect shape and the degree of ordering is not significantly changed any further for longer times.

Figures 5a~5b shows TEM HAADF image and an elemental mapped (TEM-EDS) of the as-formed U-tubes through the entire 200 nm thick layer that was peeled off from the surface. The elemental map clearly shows a phosphorous-rich layer on the inside of the cavities and a fluoride-rich layer on the outside of the tube walls. This is in line with XPS results (Figures 5c,5d) that confirm the presence of these elements in the as formed tubes. The high resolution P2p peak is at a position of 133.2 eV that can be assigned to a P-O

Figure 6. SEM images of the U-tubes in 3 M HF/H₃PO₄ at 100°C and 15 V for 2 h after heat-treatment in air for 1 h a) at 350°C and b) at 450°C. The layer above the dotted line (·····) shows TiO₂ and the layer under the line represents Ti substrate. c) Effects of the annealing temperature on the thickness of the thermal oxide layer. d) Bode plot for U-tubes after heat-treatment at different temperatures in air for 1 h.

bond as in phosphates.^{32,33} Figure 5d illustrates that this phosphate layer is stable after annealing at 450°C. The formation of fluoride-rich layers at the bottom of the tubes (between the Ti-metal and the oxide) has been previously observed and discussed for other titania tubes grown in fluoride electrolytes (literature describes this as a result of a high field transport of F⁻ in competition to O²⁻ through the growing oxide).^{34,35} However, the formation of a uniform inner wall coating of the nanotubes with phosphate-species is unique to the here introduced electrolyte.

XRD patterns in Figure 5e show the as grown tubes to be amorphous. Figure 5e moreover shows the XRD patterns for tubes annealed at different temperatures, and Figures 6a~6b, Figure S3 show corresponding SEM images. After annealing at different temperatures, it is apparent that anatase phase (peak position at 25.3°) appears at an annealing temperature of 350°C and rutile phase (27.5°) at a temperature of 450°C. From XPS (Figure 5d), after annealing at 450°C clearly the fluoride peak is largely lost (in line with literature),^{9,20} however, the phosphate-peak is still present, similar to as-formed tubes (Figure 5c).

From XRD, the peak intensity of rutile increases steadily with temperature, at temperatures of 450°C, the anatase and rutile peaks show similar intensities. For higher temperatures, the XRD oxide response becomes dominated by rutile. However, the origin of rutile is not primarily due to a phase conversion of the tubes. Namely, SEM images in Figures 6a~6b show top and cross-sectional images (ion milled cross-sections) of heat-treated TiO₂ NTs. The white dotted lines (·····) in the images represent the boundaries of Ti metal and TiO₂. Evidently thermal oxide is formed from the Ti metal substrate, and the thickness of these oxide layers can increase up to 1.5 μm with increasing annealing temperature (Figure 6c).^{20,21}

Comparing XRD (Figure 5e) and SEM (Figures 6a~6b, Figure S3), it can be deduced that the thick thermal oxide layers consist of rutile. This is in line with literature²⁰ that shows Ti to be preferentially oxidized to rutile (rather than anatase) when annealed under O₂ containing conditions. The growth of the rutile layers spoils the nanotube arrays by invading rutile into the anatase nanotube structures (inserts

in Figure S3). This growing behavior of rutile layers from the Ti metal for highly ordered TiO₂ NTs is in line with earlier literature which reports that the rutile phase is firstly grown at the metal/TiO₂ interface and then proceeds up the tube walls and toward the tube tops (with higher annealing temperatures or longer thermal treatments).^{20,21,36}

In view of the use of the nanotubes as electrodes (or photoelectrodes), the differently annealed TiO₂ NT layers were tested with electrochemical impedance spectroscopy (EIS). According to Figure 6d, the TiO₂ NT layers heat-treated at 450°C (a mixture of anatase and rutile) show the lowest overall impedance and the lowest charge transfer resistance among the differently annealed nanotubes, while a significantly higher impedance is observed for NTs annealed at 550°C, due to the large amount of rutile (anatase is reported to have significantly higher conductivity than rutile).^{36,37} Noteworthy, TiO₂ NTs annealed at 350°C (no rutile peaks in Figure 5e) show also a very high resistance, as still a high amount of amorphous phase (low conductivity) is present in the TiO₂ NTs.

To enable the use of these highly organized TiO₂ NTs for various applications, a higher aspect ratio of the tubes is desired. However, as the electrolyte used here (concentrated H₃PO₄/HF at ~100°C) is strongly etching the formed tubes, in a one-step process only a limited tube length of (~300 nm) is achievable (see Figure 3). Therefore we explored a two step-anodization treatment.

Two-step anodization techniques have been used for growing well-aligned nanotube arrays with open top surfaces.³⁸ In the conventional approach, during the first anodization step, a TiO₂ nanotube layer with a relatively large thickness is needed (to be able to remove it by sonication) - then the underlying texture of substrate (a highly arranged dimple structure) is used as a template for the second step of TiO₂ nanotube growth. However, in the case of the here presented U-tubes, the elimination of the first layer is not necessary, since the arrangement of TiO₂ NTs is already nearly perfect and the thickness of the layer and properties of the layer allow to directly form the second layer. In the second anodization step, the bottoms of the nanotubes act as new nanotube growth initiation points. As the anodization proceeds, the

Figure 7. SEM images of; a~b) double anodized TiO₂ NTs under optimized conditions (at 15 V in HF/H₃PO₄ at 100°C for 2 h // at 60 V in NH₄F/EG at RT for 2 min); c~d) A polystyrene replica structure of the tubes of Figure 7a~b. SEM images of double anodized TiO₂ NTs e) at 5 V in HF/H₃PO₄ for 5 h, // 30 V in NH₄F/EG for 5 min; and f) at 2 V in HF/H₃PO₄ for 12 h // 20 V in NH₄F/EG for 10 min. Photocurrent measurements of double anodized TiO₂ NTs: g) comparison of double anodized nanotubes with single anodized nanotubes, h) comparison of different optimized double anodized nanotubes.

bottom becomes thinner and then eventually the tubes develop open bottom-structures with a connection between the first layer and the second layer (as shown in Figures 7a~7f).

Figures 7a~7b show a top-view and a cross-sectional image of the nanotubes after double anodization. The first anodization was carried out as described above at 15 V and 100°C for 2 h in the HF/H₃PO₄ electrolyte; the second anodization was performed at 60 V and room temperature for 2 min in ethylene glycol (EG) based NH₄F solution.

This results in a match of the two structures in diameters and registry. The structures are extremely well organized, and in addition lengths controllable between 200 nm to 1.5 μm can be achieved. In order to demonstrate the all open structure between upper and lower tube part we fabricated polystyrene (PS) replica from the nanotubular structures (see Figures 7a~7b). These PS replica (Figures 7c~7d) structures were prepared by dropping molten polystyrene into the nanotubes and then dissolving the TiO₂ NT layers by HF solution (the PS

structures bundle together due to electrostatic force while they are dried by N₂ gas.). These structures evidently show that the second nanotube layers do perfectly match with the first nanotube layer. It should be noted that in classic 2-step processes (in the same electrolyte), the applied potential for both layers is similar, as the diameters of the first layer match that of the underneath tube layer. However, in our case the second electrolyte (NH₄F/EG) is different from the first electrolyte (HF/H₃PO₄). Therefore, to reach a match between the upper and the lower layer, the anodization voltage needs to be adjusted. This is illustrated in a second example: Figure 7e shows well-organized double anodized TiO₂ nanotubes where the first layer was prepared at 5 V for 5 h in the HF/H₃PO₄ electrolyte. To match this, the second layer grown in NH₄F/EG had to be grown at 30 V for 5 min. Figure 7f shows relatively small diameter (~25 nm) tubes which were grown at 2 V in the first anodization, and 20 V was employed in the second step, resulting in highly ordered TiO₂ NTs with small diameters which were grown to a length of up to 1.2 μm. Above examples show that by this approach highly ordered nanocavities can be extended to highly ordered nanotube layers. Using this approach allows, as shown in Figure 7, to grow these ordered nanotubes of the same length but with a variable diameter.

In order to demonstrate the benefit of tube extension and control over diameter and length, we carried out photoelectrochemical potential sweep measurements (under solar light - AM 1.5) for i) double anodized samples versus single anodized samples (Figure 7g), and ii) double anodized samples with a length of 1.2 μm and different diameters (Figure 7h). The photocurrent obviously increases with the tube length, since the light absorption and the active surface area are much higher than for shorter tubes (Figure 7g). By comparing the photocurrent results of “60 V 2 min” (classic nanotubes) and “15 V 2 h // 60 V 2 min” (highly ordered nanotubes), it is noticed that although the tubes have an identical geometry, the arrangement of TiO₂ NTs is indeed affecting the photoresponse: well aligned nanotube structures enhanced the photocurrent from 0.125 to 0.15 mA cm⁻² at 0.5 V.

Figure 7h shows the photocurrent measurements with double anodized TiO₂ NT layers grown under optimized conditions. The thicknesses of all nanotube layers are around 1.2 μm, but the diameters of the nanotubes are different, i.e. “2 V // 20 V”: ~25 nm, “5 V // 30 V”: ~40 nm and “15 V // 60 V”: ~80 nm. From the considerable amount of literature regarding high aspect ratio TiO₂ NTs,^{9,17,31} it was assumed that the highest aspect ratio (“2 V // 20 V”, aspect ratio ≥ 48) – that is the smallest diameter – would lead to the highest efficiency of the light response under solar light, yet the sample of “5 V // 30 V” (aspect ratio ≥ 30) shows the highest current density (0.175 mA cm⁻²) at 0.5 V, which is a higher value than the photocurrent density from the sample of “15 V // 60 V” (aspect ratio ≥ 15). This may indicate that at small tube diameters the advantages of directional carrier transport in nanotubes³¹ are increasingly lost as carrier transport becomes increasingly likely in the lateral direction (such as in nanoparticulate layers).

This example illustrates that a precise control over order, length and diameter of TiO₂ nanotubes is essential to fine-tune the optimum electrochemical response. Moreover, with the highly ordered cavities presented here, as well as their use to trigger highly ordered high-aspect ratio nanotube arrays, a wide number of direct applications in photoelectrochemistry, photocatalysis, and electrochemistry become possible. Additionally, indirect uses such as templating secondary material with an extremely high precision and order becomes feasible.

Conclusions

In the present work we investigated the formation of extremely well-organized TiO₂ nanostructures (nanotubes) by anodizing Ti foils under drastic conditions (HF/H₃PO₄ containing electrolytes). Through the examination of a broad range of electrochemical conditions, such as electrolyte composition, temperature, anodizing time (related to the length of tubes), and applied voltage (related to the diameter of tubes), we established optimized conditions for highly ordered TiO₂ NTs with open top and a U-shape combined with a smooth wall. We describe and discuss tools to control tube geometry and order.

We show that heat-treatments of the short aspect ratio, amorphous U-tubes, lead to anatase and rutile formation (as characterized by XRD), with a ratio that depends strongly on the annealing temperature. In fact, thick thermal rutile layers are formed under the nanotube layers at higher temperatures. These variations lead to strong alterations in electrical and photochemical properties.

To overcome the drawbacks of the short aspect ratio, we introduced a double anodization strategy to extend the length of TiO₂ nanotubes. Both short and extended tubes formed in the concentrated H₃PO₄ electrolytes lead to extremely highly ordered geometries and a high level of control over length and diameter that can be exploited to optimize the electrochemical and photoelectrochemical properties of TiO₂ nanotube layers.

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