

First Approach to the Synthesis and Applications of Titania Nanotube

Primera Aproximación a la Síntesis y Aplicaciones de Nanotubos de Óxido de Titanio

Ernesto Peláez-Abellán, Dennys Fernández-Conde, Maura Valdés-Pedroso, Lorenzo Caputi* y Carlos Núñez-Valdés.

Facultad de Química, Universidad de La Habana, Calzada de Zapata s/n esquina a calle G, El Vedado, Código Postal 10400, La Habana, Cuba. *Dipartimento di Fisica, Università della Calabria, Italia pelaez@fq.uh.cu

Recibido: 9 de junio de 2011.

Aceptado: 12 de mayo de 2012.

Palabras clave: óxido de titanio, TiO_2 , capas de nanotubos, oxidación anódica, aspectos mecanísticos.

Key words: titanium oxide, TiO_2 , nanotube layers, anodic oxidation, mechanistic aspects.

RESUMEN. En los últimos años, se ha explorado una amplia variedad de aplicaciones funcionales de capas de nanotubos auto-organizados de TiO_2 que incluyen entre otras la fotocatálisis, la conversión de energía solar y el efecto electrocrómico y que utilizan este material como una plantilla o soporte del catalizador para aplicaciones en los campos de la salud, la energía o el medio ambiente. El presente trabajo brinda una panorámica a manera de resumen sobre capas de nanotubos de TiO_2 con estructuras tubulares crecidas por oxidación anódica controlada (anodizado) a partir de un sustrato metálico como el titanio. Se describen trabajos, publicados principalmente en los últimos cinco años, que estudian el efecto de las condiciones experimentales en las características estructurales y morfológicas de capas superficiales de nanotubos de TiO_2 en los que se detallan las condiciones experimentales y propiedades importantes de estas capas tubulares. A pesar de que los primeros trabajos sobre nanotubos de TiO_2 fueron reportados al inicio del siglo XXI, este campo ha crecido tan rápidamente, que es difícil hacer un resumen del alcance de todos los trabajos reportados. De esta manera, los autores clasificaron los diferentes trabajos atendiendo a la composición del electrolito utilizado en el anodizado, al material de base y a las propiedades estudiadas que posibilitarán su aplicación en el futuro en los campos de la salud, energía o medio ambiente. Además, se describen aspectos mecanísticos del crecimiento del tubo y las condiciones electroquímicas para sintetizar estas capas.

ABSTRACT. In the past few years, a wide range of functional applications of self-functional TiO_2 nanotube layers have been explored, ranging from photocatalysis, solar energy conversion, electrochromic effects to the use of the material as a template or catalyst support for applications in the field of health, energy or environment. The present paper provides an overview of TiO_2 nanotube layers with tubular structures, grown by controlled anodic oxidation (anodization) on a metallic substrate as titanium. Then, the authors summarize the works reported in the last five years which study the effect of the experimental conditions in the structural and morphological characteristics of TiO_2 nanotube superficial layers, where experimental conditions and key properties of these tubular layers are pointed out. Despite the fact that the first works about the highly ordered TiO_2 nanotube arrays were reported at the beginning of XXI century, this field has grown so rapidly as to make it difficult to summarize the scope of all related work. The authors classified the different works taking into account the composition of the electrolyte used in the anodization, the base material and studied properties that allow their future application in fields as health, energy or environment, mechanistic aspects of the tube growth and the electrochemical conditions to be fulfilled in order to synthesize these layers are also described.

INTRODUCTION

TiO_2 is a material with a number of almost unique properties used for many years in various functional applications as photocatalysis, wetting, solar cell, catalysis, gas sensing, doping, biomedical devices, ceramics, interference coating and optical devices,

as it will be discussed below. For this reasons, in the last years, research activity related to the formation of TiO₂ nanotubes (NTs) has been stimulated because these self-organized NTs combine geometrical advantages given by their array structure with its specific properties. As mentioned above, TiO₂ is used in many functional applications based on the specific semiconducting properties of TiO₂ (particularly anatase) that is, a wide band gap n-type semiconductor with a sufficiently low (anodic) valence band edge to allow a photo-induced generation of highly reactive OH[•] radicals. Strategies to exploit TiO₂ NTs for applications usually try to combine a specific feature of TiO₂ with its tubular geometry. The TiO₂ NT arrays have shown remarkable properties that have successfully given rise to a large number of diverse applications that include, but are certainly not limited to, super capacitors, solar cells, drug eluting surfaces, hydrogen sensors, biofiltration membranes, and photoelectrochemical cells for the solar generation of hydrogen. It appears, for the moment, impossible to completely cover this field as it moves more rapidly than one can report on it. For this reason, the authors have tried to focus at least on key aspects of the field, reviewing the contributions made by various researchers to the fabrication, and application of the NT arrays, as it will be discussed below.

The synthesis of TiO₂ NTs can be carried out by means of electrochemical anodization of a Ti foil in solution containing fluoride ions in neutral or acidic media. The anodization technique is the simplest, cheapest and most straight-forward approach that leads to ordered nanostructures.

This method can lead under the “right” conditions to highly ordered porous systems. It should be mentioned that another fundamentally different approach for the growth of anodic TiO₂ NTs has also been recently reported: the rapid breakdown anodization (RBA) or micro arc oxidation (MAO)¹ method produces faggots of NTs, that grow within tens of seconds typically in perchlorate or chloride containing electrolytes at considerably high voltages (sufficiently high to create a local breakdown of the oxide film that then represents the nucleus for the tube-bundle growth). While being fast, the approach seems not to be easily tunable to become self-organized therefore it will not be considered in this overview.

As the title of this paper implies, the authors examined the conditions of synthesis, properties and some applications of highly ordered vertically oriented TiO₂ NT arrays made by Ti anodization. In this overview, specific topics are dealt with: nanotube array synthesis, some properties such as the structural, optical, mechanical, and electrical properties of the TiO₂ NT arrays; the use as gas sensors for photoelectrochemical water splitting, dye-sensitized solar cells and heterojunction solar cells; in biological applications including their use as a base for osseointegration, biotemplating and enhanced blood clotting.

Anodization in aqueous electrolyte

Electrolyte containing only F⁻ anion

Awitor *et al.*² prepared TiO₂ NT layers by anodization of Ti foils in 0.4 wt. % hydrofluoric acid solution and then annealing them at different temperatures between 300 and 600 °C for 1 h. They reported that after annealing at 500 °C anatase and rutile were about 55 and 45 %, respectively. Such TiO₂ NT layers showed strong photocatalytic activity. Lai *et al.*³ fabricated novel oriented aligned TiO₂ NT arrays by anodizing a titanium foil in 0.5 % HF electrolyte solution. The authors reported that sizes of the TNs greatly depended on the applied voltages in some extent. The electrical properties of the NT arrays were characterized by current-voltage (I-V) measurements.

A nonlinear asymmetric I-V was exhibited which was attributed to the existence of an n-type semiconductor/metal Schottky barrier diode between the NT arrays and the titanium substrate interface. The absorption edges shifted towards shorter wavelengths with the decrease of the anodizing voltages which was attributed to the quantum size effect. At room temperature, a novel wide photoluminescence (PL) band consisting of four overlapped peaks was observed in the PL spectra of NT arrays. Such peaks were attributed to direct transition $X1 \rightarrow X2/X1$, indirect transition $[\text{Gamma}]1 \rightarrow X2/X1$, self-trapped excitons and oxygen vacancies, respectively. Zhao *et al.*⁴ investigated the formation of titanium oxide NT arrays on titanium substrates in HF electrolytes. They reported the topology of anodized titanium to change remarkably with applied voltage, electrolyte concentration and oxidation time. The results indicated that NTs is formed due to competition of titania formation and dissolution under the applied electric field. With these findings the authors proposed a possible growth mechanism, as will be discussed below. Xiao *et al.*⁵ obtained titania NT arrays by anodic oxidation of titanium foils in HF solution, followed by a treatment in a NaOH or $\text{Ca}(\text{OH})_2$ solution to make them bioactive. The results showed that the presence of titania NT arrays on titanium surface was able to shorten the activation time of NaOH-treated from 24 h to 30 min, and induced the growth of nanograins of calcium titanate on the top edge of the NT wall in $\text{Ca}(\text{OH})_2$ solution. During the subsequent *in vitro* immersion in a simulated body fluid, the nanograins of calcium titanate, in turn, induced the formation of an apatite phase. They expected that titanium with such titania NT could be used in clinical orthopedics. Zlamal *et al.*⁶ grew self-organized TiO_2 NT layers with different geometric dimensions by means of anodization of titanium in fluoride containing electrolytes. The influence of an externally applied bias on the photocatalytic performance of TiO_2 NT layers was investigated. Since the layers were grown directly on the Ti substrate, a very good electrical backside contact was directly provided. Therefore, the authors used the NT layers/Ti structures as photo-anodes for the UV light induced photocatalytic decomposition of acid orange 7. To compare, TiO_2 nanopowder (Degussa P25) compacted on a Ti sheet was employed. The results demonstrated that the photocatalytic activity of self-organized TiO_2 NT layers could significantly be increased by electrochemical bias.

Crawford *et al.*⁷ reported the quantitative microstructure characterization and deformation behavior of TiO_2 NTs on Ti substrate. Nanotubes were obtained by anodic oxidation of Ti in NaF electrolyte solution. The increase in anodization time had no significant effect on the tube diameter or the tube wall thickness. Coating thickness, however, increased with anodization time up to 2 h, at which point an equilibrium thickness was established. Nanoindentation was used to probe the mechanical response in terms of Young's modulus and hardness. Progressively higher values of elastic modulus were obtained for thinner films consistent with increasing effects of the Ti substrate. The authors suggested and discussed a possible deformation mechanism of densification of the porous oxide and wear of the dense surface. Crawford *et al.*⁸ showed that TiO_2 NT growth could be tailored by the intrinsic crystallographic orientation of the Ti substrate. This result presented an exciting new approach for tailoring and controlling the rate of NT formation by crystallographic manipulation and modification of the Ti surface. In another work, Crawford *et al.*⁹ described the mechanical properties and deformation behavior of TiO_2 NTs grown on pure titanium substrates by anodic oxidation. The Young's modulus of the TiO_2 NT coating was estimated to be 4 to 8 GPa. TiO_2 NTs were found to inelastically deform by "tube crushing" in the immediate vicinity of indenter tip, increasing the local density. This increase in local density caused an increase in the Young's modulus from roughly 4 to

30 GPa in the first 30 nm of indentation. Densification and the resulting increase in elastic modulus were related to the total work of inelastic deformation, irrespective of the loading history.

Soon *et al.*¹⁰ investigated the formation of anatase TiO₂ NTs by anodic oxidation on a pure Ti substrate in aqueous solution containing 0.5 wt.% NaF. NTs with a length of 3 µm in a nanotubular TiO₂ film were obtained using an electrolyte at pH 4.2. In strong acidic solution (pH 1.5), TiO₂ NTs of short length were formed due to the fast chemical dissolution rate. In this case, there was no variation of average pore diameter and wall thickness of the TiO₂ NTs. From this experiment, it was again confirmed that the pH value of the electrolyte controlled the thickness of the well-aligned TiO₂ NTs. The morphology of anodized TiO₂ films showed a rough surface and irregular wall thickness, since the anodic reaction was performed in an aqueous solution containing F⁻ ions.

Electrolyte containing F⁻ and SO₄²⁻ anions

Prida *et al.*¹¹ reported the experimental conditions and electrolyte influence on the synthesis by anodic oxidation of self-organized Ti nanotube. Arrays of randomly disordered TiO₂ NTs with pore diameter ranging from 60 to 100 nm, wall thickness from 25 to 40 nm and around 300 nm NT length, could be obtained in HF electrolyte and its mixtures with sulphuric acid by anodization at room temperature. Bestetti *et al.*¹² investigated the electrochemical formation of nanotubular TiO₂ films in mixed electrolytes containing 1 mol/L H₂SO₄ + 0.05-0.4 wt.% HF. Depending on the anodization conditions, i.e. cell voltage, anodization time, HF concentration, TiO₂ porous films having thickness from 350 to 500 nm and pore diameter from 40 to 150 nm were obtained. While varying the cell voltage from 10 to 40 V it was possible to gradually change the crystal structure of titanium oxide from anatase to rutile. The effects of annealing temperature and duration time on crystal structure were also considered.

Sreekantan *et al.*¹³ investigated the effect of pH and anodization time on the formation of titania NTs. Well-organized TiO₂ NTs were electrochemically prepared by anodizing titanium foil in 1 mol/L Na₂SO₄ containing 0.3 g/L of NH₄F. TiO₂ NTs with uniform pore diameters could be produced by manipulating electrochemical conditions. This study showed that NTs with length ranging from ~0.7 to 2.5 µm could be formed by varying the electrolyte pH. The rate of formation depends on the specific pH level applied as shown in the following results: pH 3: length 0.7 µm at a rate of 23 nm . min⁻¹; pH 5: length 0.6 µm at a rate of 15 nm . min⁻¹; pH 7: length 0.5 µm at a rate of 8 nm . min⁻¹. In the employed anodizing condition, the NTs had an amorphous structure. Annealing the NT arrays promoted the formation of anatase and rutile phases depending upon the temperature. Furthermore, the sample annealed at 500 °C showed a better photocatalytic activity. This activity is also believed to be closely related to the degree of crystallinity and the crystallography structure of the NT, which consisted of anatase (76 %) and rutile (24 %) phases.

Electrolyte containing F⁻ and PO₄³⁻ anions

Self-organized NT arrays of TiO₂ have been grown from titanium thin films deposited on p-type Si(1 0 0) substrates.¹⁴ The results indicated that the sputtered crystalline Ti thin films used for subsequent anodization to have a hexagonally closed packed structure and showed columnar morphology. Electrochemical anodization of the Ti films was carried out potentiostatically in 1 mol/L H₃PO₄ + 1 mol/L NaOH + 0.5 wt% HF electrolyte at room temperature. The TiO₂ NTs on a semiconductor substrate had an

average tube length of ~560 nm, a diameter in the order of 80 nm and wall thickness of ~20 nm. Ghicov *et al.*¹⁵ prepared self-organized TiO₂ NTs in phosphate solution containing fluoride ion and reported the pore diameter and length of the TiO₂ NT layers to be affected by the used electrochemical conditions (applied potential, electrolyte composition, pH, and anodizing time). Highly self-organized TiO₂ NTs with diameters varying from ~40 to 100 nm and length from ~100 nm to 4 μm were obtained. XPS investigations showed NTs formed in phosphate solutions to contain a significant amount of phosphorous-containing species. Zhao *et al.*¹⁶ obtained TiO₂ NT arrays from mixed solutions containing H₃PO₄ and HF. The diameters of the NTs varied from 10 nm to more than 100 nm with increasing applied voltages. The length of the NTs increased at first with the anodizing time and then reached a maximum value due to the dynamic equilibrium of titania formation and dissolution. Well-ordered NT arrays of TiO₂ with a length up to 1.1 μm were obtained via constant-voltage procedure. Stability of NT structure and crystal phase transition were also studied in different atmospheres. Experiments showed NT structure to be stable up to 600 °C. Other properties of TiO₂ NT arrays including photocatalytic degradation of methyl orange and their hydrophilic ability were also studied by these authors.

Cai *et al.*¹⁷ investigated the formation mechanism of a thin film of self organized TiO₂ NT arrays prepared by anodic oxidization of a pure Ti sheet in electrolyte solutions containing potassium fluoride and sulfate. The titanium surface was first electrochemically oxidized to form a layer of dense oxide under which NTs were originated. With the protection of the oxide layer, long NTs could be formed in electrolyte solutions with relatively high pH. The surface composition analysis indicated NTs not to be totally TiO₂. However, no other elements but Ti and O were found in the oxide film.

Bauer *et al.*¹⁸ investigated the formation of self-organized TiO₂ NT layers at different fluoride concentrations and potentials in H₃PO₄ electrolytes. It was demonstrated in optimized phosphate/HF electrolytes, in contrast to other electrolytes that the tube length and diameter could be controlled over a wide range by the applied potential. It was found for potentials between 1 and 25 V, that tubes could be grown with any desired diameter ranging from 15 to 120 nm combined with tube length from 20 nm to 1 μm. The diameter and the length depended linearly on the voltage. These results represented an unprecedented level of control in the geometry of anodic TiO₂ NT. After coating TiO₂ NT layers with a self-assembled monolayer (octadecylphosphonic acid) Bauer *et al.*¹⁹ showed a diameter-dependent wetting behavior ranging from hydrophobic (108 ± 2)° up to super-hydrophobic (167 ± 2)°. Cell adhesion, spreading and growth of mesenchymal stem cells on the unmodified and modified NT were compared. It was shown that cell adhesion and proliferation one strongly affected in the super-hydrophobic range. Adsorption of extracellular matrix proteins as fibronectin, type I collagen and laminin, as well as bovine serum albumin, on the coated and uncoated surfaces showed a strong influence of wetting behavior and dependence on tube diameter. Balaur *et al.*²⁰ also modified self-organized TiO₂ NT layers by UV induced decomposition of organic molecules as octadecylsilane (C₁₈H₃₇SiH₃) or octadecylphosphonic acid (C₁₈H₃₇PO(OH)₂). These layers showed a super-hydrophobic behaviour while layers prepared by electrochemical anodization only showed a super-hydrophilic wetting behaviour. This process could be used to adjust the surface wetting properties to any desired degree from super-hydrophobic to super-hydrophilic.

Li *et al.*²¹ prepared well-ordered TiO₂ NT arrays by electrochemical anodization of titanium in aqueous solution of H₃PO₄ + NH₄F at a constant voltage of 20 V for 3 h, followed by calcination at various temperatures. The results showed the as-prepared NT

arrays before being calcined to be amorphous and that could transform to anatase phase during heat treatment at temperatures higher than 400 °C. As the calcination temperatures increased, crystallization of anatase phase enhanced and rutile phase appeared at 600 °C. However, further increasing of calcination temperature would cause the collapse of NT arrays. The photoluminescence intensity of NT arrays annealed at 500 °C was the lowest, which could be probably ascribed to a better crystallization together with fewer surface defects of NT arrays.

Anodization in organic-inorganic mixed electrolytes

It is usually used aqueous media but some authors preferred organic-inorganic mixed electrolytes for anodization. Vega *et al.*²² reported structural and morphological features of self-aligned titanium oxide NT arrays grown by electrochemical anodization in different electrolytes comprising aqueous acidic media or organic neutral media, and at several potentiostatic voltages ranging from 12 to 60 V. The results showed an improvement in the self-alignment of the NT arrays and an increase of about 10000 % in the NTs length obtained by anodization performed with NH₄F in ethylene glycol electrolyte, with respect to those obtained employing aqueous electrolytes. Allam *et al.*²³ obtained TiO₂ NT arrays in both aqueous and ethylene glycol (EG) electrolytes and reported this material to present similar or in some cases superior photoelectrochemical properties than those obtained using a Pt cathode. Kaneco *et al.*²⁴ investigated the synthesis of TiO₂ NT arrays in methanol/water solvent. Two conditions affected NT diameter and number density. First, as the anodic current density increased from 10 to 30 mA . cm⁻², the mean inner diameter of TiO₂ NTs increased from 30 to 145 nm. Second, as the ratio of methanol to water increased, the TiO₂ NT number density decreased, which resulted in larger spaces between NTs. Lai *et al.*²⁵ investigated the formation of self-organized TiO₂ NT array films by electrochemical anodizing titanium foils in a organic-inorganic mixed electrolyte. The structure and morphology of the TiO₂ NT layer were found to depend greatly upon the electrolyte composition, anodizing potential and time. Under the optimized electrolyte composition and electrochemical conditions, a controllable, well-ordered TiO₂ NT array layer could be obtained in a short time. The diameters of the obtained TiO₂ NTs could be adjusted from 20 to 150 nm, and the thickness from few hundreds nanometers to several micrometers. The photoresponse and the photocatalytic activity of the highly ordered TiO₂ NT array films were also examined. The NT array film with a thickness of about 2.5 µm had the highest incident photon to photocurrent conversion efficiency (34.3 %) at a wavelength of 350 nm, and had better charge transfer ability under UV light illumination. The photocatalytic experimental results indicated the samples annealed at 450 °C to have the highest photodegradation efficiency for methyl orange pollutant. Tsuchiya *et al.*²⁶ reported TiO₂ NT layers to be formed by electrochemical anodization of titanium in a non-aqueous electrolyte (CH₃COOH/NH₄F). The morphology of resulting layers is strongly affected by the applied potential. At low potentials, the layers consist of ordered NTs that had a diameter of ~20 nm and a length of a few hundreds of nanometers. In this case, the individual tubes were connected with each other via bridging rings on the sidewall of the tubes. At higher potentials, assemblies of NTs resembling coral reefs in morphology were obtained (these arrangements of the tubes could be ascribed to local breakdown events on the layers). The individual tubes in the reef structure had a diameter of ~20 nm and a spacing of ~50 nm and were clearly separated from each other (the connecting rings on the sidewall had disappeared). Sreekantan *et al.*²⁷ prepared TiO₂ NTs by anodizing titanium foils in an electrochemical bath consisting of 1 mol/L glycerol with 0.5 wt.% NH₄F. The pH of the bath was kept

constant at a value of 6 and the anodization voltage was varied (5, 20 and 30 V). It was found that the morphology of the anodized titanium was a function of anodization voltage with pits-like oxide formed by samples made at 5 V while samples made at 20 and 30 V consisted of well-aligned NTs which grew perpendicularly to the titanium foil. However, NTs formed on samples made at 30 V were not uniform in terms of the NTs' diameter and wall thickness. Regardless the anodization voltage, all anodized samples were amorphous. The crystal structure evolution was studied as a function of annealing temperatures. The crystallization of the NTs to anatase phase occurred at 400 °C while the rutile formation occurred at 700 °C. Disintegration of the NT arrays was observed at 600 °C and the structure completely vanished at 700 °C. TiO₂ NT annealed at 400 °C and containing 100 % anatase revealed the highest photocatalytic activity for the degradation of methyl orange. Consequently, these results indicated diameter, wall thickness, crystal structure and degree of crystallinity of the TiO₂ NT arrays to be the main factors which affected the efficiency of photocatalytic activity.

Yang *et al.*²⁸ obtained vertically oriented TiO₂ NT arrays by anodization of pure titanium deposited on silicon substrates. The TiO₂ NTs were grown by anodization in aqueous-base and glycerol-base electrolytes at different potentials between 5 and 30 V. Films with homogeneously distributed pores having an average diameter of 100 nm or 40 nm were obtained. The growing character of the thickness was compared with the conversion ratio from titanium to TiO₂ NT in different electrolytes. Qidong *et al.*²⁹ obtained highly ordered TiO₂ NT arrays by anodization using ethanol-water mixed electrolytes (40 vol. % ethanol and 0.2 wt. % hydrofluoric acid). The as-prepared NT arrays grew perpendicular to the titanium substrate and had about 90 nm in diameter, 20 nm in wall thickness, and around 500 nm in length. A blue shift in the absorption UV-Vis spectrum was observed taking as reference that of a piece of sol-gel derived TiO₂ film. Moreover, photocurrent response and photoelectrocatalytic degradation of methyl orange under ultraviolet light were adopted as reference to evaluate the photoelectrocatalytic properties of TiO₂ NT arrays. It was demonstrated that highly ordered TiO₂ NT arrays possessed good stability and much better photoelectrocatalytic activity than sol-gel derived TiO₂ film. Li *et al.*³⁰ obtained highly ordered TiO₂ NT arrays by potentiostatic anodization of Ti foils in fluorinated dimethyl sulfoxide. TiO₂ NT arrays, with a length of 12 µm, diameter of 170 nm and aspect ratio of about 70 were obtained using an anodization potential of 40 V for 24 h. The as-prepared NTs were amorphous, but the recrystallization was possible as the heat treatment temperature increased. Anatase phase appeared at a temperature of about 300 °C then transformed to rutile phase at about 600 °C. After a heat treatment at 500 °C and soaking in SBF solution for 14 d, a thick apatite layer of about 13 µm covered the whole surface of TiO₂ NT arrays, indicating their excellent *in vitro* bioactivity, which was mainly attributed to their high specific surface area and the anatase phase.

Macak *et al.*³¹ grew self-organized titanium oxide nanotube layers anodically in glycerol/water/ammonium fluoride electrolytes. In these electrolytes, the authors found possible to grow NTs at potentials between 2 and 40 V leading to tube diameters ranging from 20 to nearly 300 nm. The growth stages of NTs and their morphology were described, as well as the influence on the tube growth of critical electrochemical parameters, such as fluoride concentration and water content in the electrolyte. Furthermore, for NTs grown at 40 V, the presence of crystalline anatase structure was observed. The significant effect on the resulting geometry of even small additions of water (0.67 vol. %) in the glycerol/ammonium fluoride was shown. The rate determining step of the growth process was also shown to be fluoride ion diffusion to the tube bottom. It was also demonstrated the permanent presence during anodization of

a high-field oxide layer (that accordingly increases in thickness with higher applied voltage) is present on the tube bottom. In another work, Macak *et al.*³² investigated the electrochemical formation of layers of self-organized high aspect ratio TiO₂ NTs grown by anodization of Ti in viscous electrolytes at different temperatures. In electrolytes consisting of glycerol or ethylene glycol with small additions of fluorides, the NT morphology was strongly influenced by viscosity, electrolyte temperature and applied potential. Compared with water-based electrolytes, in viscous electrolytes much longer and smoother tubes were possible to grow. Depending on the experimental conditions, the NTs had an aspect ratio reaching up to about 150 for glycerol and 32 for ethylene glycol. The results further showed the current efficiency for NT formation in glycerol electrolytes to be close to 100 % (this was significantly higher than that for comparable water-based electrolytes).

Mura *et al.*³³ intended to define an optimal methodology of the preparation of highly ordered TiO₂ NT arrays by anodization at 60 V in glycol ethylene solution. The effect of the presence of an initial superficial oxide on the sample, before the beginning of the anodic growth, was analysed. The best result was obtained by galvanostatic oxide growth on a titanium sheet, before the preparation of TiO₂ NT arrays. The photoconversion efficiency was measured and a maximum value of 12.97 % was obtained, strictly in line with the literature. The necessity to carry out a heat treatment using only dry atmosphere was also underlined. Lei *et al.*³⁴ obtained multi-non-metal-doped TiO₂ NTs by electrochemical anodization of Ti in mixed acid electrolyte containing C₂H₂O₄ · 2H₂O, HIO₃ and NH₄F. The samples were annealed in air. The results indicated non-metals as N, F and I to be successfully doped into TiO₂ NTs in aqueous solution by adjusting the electrolyte composition. The multi-non-metal-doped samples displayed a significant visible-light response. Additionally, the atomic concentration of non-metals is closely related to the electrolyte composition.

Su *et al.*³⁵ prepared TiO₂ NTs by anodization of Ti in C₂H₂O₄ · 2H₂O + NH₄F electrolyte. Then simultaneously codoping with fluorine and boron (F-B-codoping) was successfully carried out by annealing the anodized TiO₂ NTs through chemical vapor deposition. The obtained results showed the greater structure damage of F-B-codoped sample to be in accordance with, the higher the annealing temperature was used. The results confirmed annealing temperature to have influence on the phase structure and boron and fluorine impurities to possibly retard anatase-rutile phase transition. F-B-codoped samples displayed remarkably strong absorption in both UV and visible range and under visible-light irradiation, showed higher catalytic activity in methyl orange photoelectrodegradation than F-doped sample and B-doped sample. This was a convincing evidence that F-B-codoping of TiO₂ had an obvious synergetic effect on the enhancement of photocurrents and photoelectrocatalytic activity.

Yang *et al.*³⁶ proposed a two-step anodization as a novel method to obtain graded NT arrays with particular morphologies. Through tailoring the electrochemical conditions, graded TiO₂ NT arrays could be formed by two-step anodization. The growth mechanism of graded TiO₂ NT arrays and influencing factors on two-step anodization were investigated. These authors found that the nature of the electrolyte used in the different anodization steps strongly influenced the formation of graded nanotubular structure. In order to form graded TiO₂ NT arrays, proper anodization sequence were used: Step-1 anodization in an electrolyte which was capable producing higher electric field intensity and faster chemical dissolution rate, followed by Step-2: anodization in another electrolyte which capable to produce lower electric field intensity and slower chemical dissolution rate. On the other hand, Chen *et al.*³⁷ reported the synthesis of TiO₂ NT thin films using an anodization method with HCl electrolyte and copper

cathode. This process was suggested to represent an alternative electrochemical approach using a non-noble metal cathode along with a safer electrolyte. In addition to the choice of electrolyte, the electrolyte concentration, anodization voltage, and anodization time all affected the NT morphology. TiO₂ NTs with diameters as small as 10 nm were achieved.

Mor *et al.*³⁸ reviewed in 2006, the preparation, properties, and solar energy applications of highly ordered TiO₂ NT arrays made by anodic oxidation of titanium in fluoride-based electrolytes. The material architecture has proven to be of great interest for use in water photoelectrolysis, photocatalysis, heterojunction solar cells, and gas sensing. The ability to obtain NT arrays of different shape (cylindrical, tapered), pore size, length, and wall thickness by varying anodization parameters including electrolyte concentration, pH, voltage, and bath temperature was examined. The fabrication and crystallization variables were discussed with the intention of proposing an NT array growth model. Efforts to lower the band gap of the TiO₂ NTs by anionic doping were reviewed. Measured optical properties were compared with computational electromagnetic simulations obtained using finite difference time domain. The paper concluded with considering the various practical applications of this remarkable material architecture, including its use for water photoelectrolysis and heterojunction dye-sensitized solar cells.

In spite of the existing controversy about the chemical structure and formation mechanism of TiO₂ NTs, the material is still gaining prominence due to its unique features including large specific surface area, photocatalytic potentiality, and ion-exchange ability. Due to this fact, a comprehensive list of reports about characterizations, formation mechanism, and applications of TiO₂ NTs was compiled and reviewed in 2007 by Hsin-Hung *et al.*³⁹

Based on a literature survey, it is apparent the dependence of the TiO₂ NT attributes on the synthesis conditions and post-treatments to significantly dominate the feasibility of applications. So far, studies related to rapid formation kinetics and modifications of TiO₂ NTs are not exhaustive. These might be the promising aspects in the future developments of TiO₂ NTs.

Synthesis on it alloys

Particularly interesting is the growth of TiO₂ NTs on various alloys, as this increases drastically the potential functionality of the tubes (e.g. by incorporation of doping species in the oxide structure). Also it is known that NT layers can be applied as surface coatings on various technical alloys. Using the same approach as for Ti, that is, controlled anodization in dilute fluoride electrolytes, recently NT layers have successfully been grown on intermetallic compounds, binary alloys, or on complex biomedical alloys. Jang *et al.*⁴⁰ investigated the effects of the β -stabilizing element Nb on the morphology of NTs formed on Ti-xNb alloys using 1 mol/L H₃PO₄ electrolyte containing 0.8 wt. % NaF and various electrochemical methods. Oxide layers consisting of highly ordered NTs with a wide range of diameters (~55-220 nm) and lengths (~730 nm to 2 μ m) could be formed on alloys in the Ti-xNb system as a function of Nb content. The NTs formed on the Ti-Nb alloy surface were transformed from the anatase to rutile structure of titanium oxide.

A titanium surface covered with titanium oxide having NT structure was observed to have lower corrosion resistance in 0.9 % NaCl solution than surfaces of Ti-xNb alloys covered with titanium oxide without the NT

morphology. Particularly for Ti-Nb alloys, surprising synergetic effects on the growth morphologies of oxide NTs were found. The possibility of a significant expansion of

the range of achievable diameters and lengths of TiO₂-based NTs was shown, if a binary Ti–Nb alloy, rather than pure Ti, were used as a substrate. The length of the resulting mixed oxide NTs can be adjusted from 0.5 to 8 μm, and the diameter from 30 to 120 nm.⁴¹ In recent years, Ti–Zr–Nb alloys have become increasingly attractive as biomedical implant materials. Feng *et al.*⁴² reported the formation of self-organized NT oxide layers on a Ti-28Zr-8Nb biomedical alloy surface in 1 mol/L (NH₄)₂SO₄ containing 0.25 mol/L NH₄F. The morphology of the NT layers (diameter and length) was affected by the electrochemical conditions used (applied potential and time). Under specific conditions, oxide layers consisting of highly ordered NTs with a wide range of diameters and lengths could be formed, varying, from ~50 to 300 nm and from ~500 nm to 22 μm respectively. At present, the obtained results are highly promising for this biomedical alloy: the large surface area and the tunable nanoscale geometry of the surface oxide provide novel pathways for the interaction of the materials with biorelevant species, such as cells and proteins.

Tsuchiya *et al.*⁴³ reported self-ordered formation of nanotubular oxide layers on Ti-Ta alloys of different compositions (Ti-13Ta, Ti-25Ta, Ti-50Ta, and Ti-80Ta) by anodization in 1 mol/L H₂SO₄ + 0.15 wt. % HF. Depending on the alloy composition, nanoporous or highly ordered NT structures could be formed. The homogeneity of the nanotubular surface layers was strongly affected by the microstructure of the alloys. Over a wide composition range the alloys exhibited two-phase structure, which results in the formation of two distinct tube morphologies, one on each phase. In particular, on the chemically less stable phase, the top of NT layers was etched, which resulted in a disordered top morphology of the tubes on Ti-13Ta and Ti-25Ta, whereas this effect yielded a difference in tube length on the two phases on Ti-50Ta. For this alloy, a bimodal self-organization could be observed, i.e. ordered patterns of oxide tubes with two distinct diameters were formed, where larger tubes were surrounded by smaller ones with a regularity that depended on the chemical composition of the two phases. Luo *et al.*⁴⁴ obtained self-organized mixed oxide NT arrays by anodization of Ti-6Al-4V alloy in H₃PO₄/NH₄F aqueous solution. NTs of 90-180 nm in diameter and 10-20 nm in wall thicknesses could be tuned by changing anodization voltages. Whereas, the as-prepared NT arrays were amorphous; to induce crystallinity, the products were annealed at 400, 500 and 600 °C, respectively. The UV-Vis spectra of samples annealed at 600 °C showed an absorption maximum in the visible region. However, these approaches presented two problems: (1) the selective dissolution of less stable elements, and (2) the different reaction rates on different phases of an alloy. Therefore “ideal” alloys for NT formation possessed a single-phase microstructure and a composition that essentially only contained valve metals.

Dealloying of a titanium aluminum alloy (Ti–8 at. % Al) in 1 mol/L NaOH at a critical potential generated an ordered nanoporous structure.⁴⁵ The diameter of the pores ranged from 30 to 100 nm with highest population at 60 nm. This was attributed to selective dissolution of Al from the alloy while Ti remained passive. Much less developed nanopores were imaged on alloy surfaces at a potential that was 400 mV less noble than the corrosion potential. Subsequent anodization of the nanoporous dealloyed surface in 1 mol/L H₃PO₄ + 1.0-1.5 % HF yielded self-organized TiO₂ NTs of diameters ranging from 40 to 140 nm with highest population of 80 nm. An increase in potential and time of anodization resulted in more developed NTs. The increase in the diameter scale of the nanostructure upon anodizing was attributed to the effect of fluoride ions and high potential on TiO₂. X-ray diffraction and thermogravimetric analyses revealed the tubes were made of anatase (TiO₂).

Other methods for synthesis

Bavykin *et al.*⁴⁶ characterized TiO₂ NTs (8 to 20 nm outer diameter and 3 to 5 nm inner diameter) grown via alkaline hydrothermal synthesis and compared them with 6 nm diameter TiO₂ (anatase) nanoparticles. In contrast to anatase nanoparticles, TiO₂ NTs carried a stronger negative surface charge and, under neutral conditions, offered electrostatic binding sites for cations. TiO₂ NTs showed electrochemical reactivity due to reversible Ti(IV) reduction, which was very similar to that observed for anatase nanoparticles. Three cationic redox systems were immobilized on TiO₂ NT surface and it showed to be novel, inert substrates for both inorganic and biological electrocatalysis. Sorapong *et al.*⁴⁷ synthesized nanorods/nanoparticles of TiO₂ with mesoporous structure by hydrothermal method at 150 °C for 20 h. The nanorods had a diameter of about 10 to 20 nm and a length of 100 to 200 nm; the nanoparticles had a diameter of about 5 to 10 nm. The prepared material had average pore diameter of about 7 to 12 nm. The BET surface area and pore volume of the sample were about 203 m²/g and 0.655 cm³/g, respectively. The nanorods/nanoparticles of TiO₂ with mesoporous structure showed higher photocatalytic activity (I₃⁻ concentration) than the nanorods of TiO₂, nanofibers of TiO₂, mesoporous TiO₂, and commercial TiO₂ (ST-01, P-25, JRC-01, and JRC-03). The solar energy conversion efficiency (ϵ) of the cell using nanorods/nanoparticles of TiO₂ with mesoporous structure was about 7.12 % while ϵ of the cell using P-25 reached 5.82 %.

At the beginning of the present century, Wang *et al.*⁴⁸ synthesized TiO₂ NTs using sol-gel method. The results showed that the atomic O/Ti ratio was very close to 2 and the NTs had anatase structure. Other results indicated the NTs to possess layered structure with layer spacing of about 7.1 Å. The tube axis was determined to be along [0 1 0] direction of anatase phase. The formation mechanism of the NTs can be explained as 3D→2D→1D. Two-dimensional lamellar TiO₂ was essential for the formation of NTs. In another work⁴⁹ the same authors synthesized anatase TiO₂ NTs by hydrothermal method with diameter of about 12 nm and length of several hundreds of nanometers. The NTs were used to make composite photo-anodes with pristine TiO₂ nanoparticles in dye-sensitized solar cells. Nanotube/nanoparticle ratio had a pronounced impact on the performance of solar cells. The composite electrode showed better photoelectric properties than the full nanoparticle one and NTs solar cells. The optimum NT content was found to be 5 %, at which the incident photon to current efficiency was about 63.1 %, which represented an increment of 13.8 %, compared with that achieved using full P25 under the same condition. In 2008, these authors⁵⁰ reported the synthesis of the same anatase TiO₂ NTs followed by post-treatment from titanium powder. The NTs had an average outer diameter of around 9 to 10 nm and inner diameter of around 3 to 4 nm with several hundred of nanometers in length. A mechanism for the anatase TiO₂ NTs transformation was proposed. NTs were formed during the solvent thermal process, and composition was varied by subsequent ionic exchange and dehydration at high temperature. These tubular materials can be very useful in the fields of photocatalysts, photoelectronics and energy-storage technologies.

Charoensirithavorn *et al.*⁵¹ synthesized TiO₂ NT arrays using a template of ZnO nanorod arrays on fluorine-doped transparent conducting SnO₂ oxide glass substrate by liquid phase deposition method. Dye (N719) sensitized solar cells (DSCs) containing TiO₂ NT arrays were fabricated under various conditions of calcination temperature in the range of 300 to 500 °C. The sintering temperature drastically affected the film crystallinity. Cell performances of DSCs based on TiO₂ NT arrays with different crystallinities were characterized and compared. The content of crystalline phase of anatase TiO₂ NT arrays was found to increase with raising calcination temperature up to

500 °C, which produced an enhancement of the cell performance of DSCs in terms of the short-circuit photocurrent density.

More *et al.*⁵² obtained TiO₂ nanorods by the simple chemical bath deposition method. The structural study revealed TiO₂ films to retain an amorphous structure even after annealing at 723 K. SEM and TEM studies showed good substrate coverage, consisting of TiO₂ nanorods. The optical band gap declined from 3.4 to 3.3 eV after annealing, showing no significant change. Both as-deposited and annealed TiO₂ films exhibited n-type electrical conductivity and showed hydrophilic behavior as water contact angles were 10 and 12°, respectively. Graded TiO₂ films were deposited on unheated glass substrates using a twin dc magnetron sputtering system. Graded TiO₂ films showed a highly polycrystalline structure of anatase with a little rutile phases.

Yang *et al.*⁵³ prepared highly oriented TiO₂ TN arrays with (101) crystal face on the surface of titanium substrate by the liquid chemical deposition method. Results indicated the NTs grown to be well-aligned and organized into high-density uniform arrays. The typical dimensions of obtained NT were: outer diameter ~90; inner diameter ~60 nm; wall thickness ~15 nm and height ~300 nm. BET surface area of obtained TiO₂ NT was 275 m²/g. The results revealed that hydroxyl radical (OH•) species could be produced in the NT system, and no OH• radical were detected under dark and/or NT non-existing situations. A significant photo-electrochemical synergetic effect was observed in the catalytic degradation of a textile azo dye, which was due to the efficient charge separation and transfer at the surface-interface of TiO₂ NT arrays. The kinetic constant of photo-electrocatalytic degradation of acid orange 7 (AO7) using NT electrode was found to be higher than that obtained using P-25 TiO₂ film and particular TiO₂ film electrode. The enhanced degradation rate of AO7 on titania NT arrays could be attributed to their larger specific surface area and nanotubular structure with preferred reactive crystal face, which would increase their absorption capacity of targeted substrates and so increasing the rate of surface-interface charge transfers in TiO₂ NT semiconductor redox systems.

Needle-shaped titanium oxide crystals with a diameter of 8 nm were obtained when titania nanopowders were treated chemically with a NaOH aqueous solution and subsequently with a HCl aqueous solution under various conditions (e.g., at 110 °C for 20 h).⁵⁴ Results showed needle-shaped products to have tube structure with inner diameter of ~5 nm and outer diameter of ~8 nm. TiO₂ NTs with a large specific surface area of ~400 m²/g were expected to have great potentialities for their use as high-performance photocatalysts or adsorbents. The amount of residual Na⁺ ions in the NTs could be controlled by HCl treatment, resulting in the formation of Na–Ti–O titanate NTs. Titania and titanate NTs could also be modified during the treatment. When calcium acetate solution was used for the treatment, a new type of bioactive NT was obtained. An apatite layer was formed on a compact composed by the NTs within 1 day of soaking in simulated body fluid. A test using rats showed that new-bone-tissue formation around the NT compact started 3 d after implantation. When oxoacid solutions, such as perchloric, phosphoric or sulfuric acid, were used in the treatment, new types of NT showing proton conduction were obtained; one of the NT compacts showed a high electrical conductivity of $8 \cdot 10^{-2}$ S/cm at 150 °C. These NTs were expected to have applications in the fields of medicine and energy generation, as well as in photocatalysis.

TiO₂ NTs containing 2.5 wt. % Ni were synthesized from TiO₂ sol using an alkaline hydrothermal treatment followed by a simple ion-exchange process.⁵⁵ The authors explored the changes in phase, shape and morphology, surface area, and photocatalytic activity of these NTs as a function of calcination temperature. The study revealed that

the titanate phase containing Ni ions could be converted to the anatase phase after certain heat treatments but, at the same time, the tubular morphology was partially lost. Investigation of photocatalytic properties demonstrated as-prepared Ni-titanate NTs to be photocatalytically inactive, but when heated at temperatures below 500 °C their activity was significantly enhanced with the change in phase. The calcined NT samples carrying nickel ion showed better photocatalytic activity than calcined NT samples containing protons. Hydrogen adsorption capacity of these titanates was also measured, and it was found Ni-titanate NTs to adsorb more hydrogen than its counterpart Na-titanate.

Qiu *et al.*⁵⁶ synthesized TiO₂ NTs by impregnating stabilized electrospun polyacrylonitrile fibers with titanium tetrachloride (TiCl₄) solution and subsequent calcination. The resulting TiO₂ NTs were of high purity and anatase structure. The average diameter of NTs was 220 nm with very thin walls (about 20 nm). Tube walls were composed of many nanoparticles of about 10 nm. Due to the increased surface area and small crystal size, the present TiO₂ NTs might possess high catalytic properties.

Results with possible future application

Self-organized TiO₂ NTs have been studied for its application to gas sensing, solar generation of hydrogen, water photoelectrolysis, solar cells, biocompatible coating, apatite formation, blood coagulation, water purification and other fields. Bellow, some interesting results related to the applications of self-organized TiO₂ NTs are pointed out.

Medical application

Immobilized TiO₂ NT electrodes with high surface areas were grown for applications in photocatalysis, via electrochemical anodization in aqueous solution containing fluoride ions.⁵⁷ The photoelectrochemical properties of the grown immobilized TiO₂ films were studied by potentiodynamic measurements (linear sweep voltammetry), in addition to calculation of photocurrent response. The NT electrode properties were compared with that of mesoporous TiO₂ electrodes grown by anodization in sulfuric acid at high potentials (above the microsparking potential) and with that of 1 g/L P-25 TiO₂ powder. Finally, photoelectrocatalytic application of TiO₂ was studied via inactivation of *Escherichia coli*. The use of the high surface area TiO₂ NTs resulted in a high photocurrent and an extremely rapid *E. coli* inactivation rate of ~106 colony formation unit per mL (CFU/mL) of bacteria within 10 min. The immobilized NT system has been demonstrated to be the most potent electrode for water purification. Baram *et al.*⁵⁸ grew a nanotubular TiO₂ oxide layer with high surface area and used it as a photocatalyst, inactivating *E. coli* bacteria and other microorganisms, as well. These authors studied the photocatalytic bacteria's inactivation rate in different pH solution. One of the advantages of using immobilized TiO₂ over a powdery photocatalyst is its ability to be recycled and reused. This was well studied with photocatalytic inactivation cycles of the *E. coli* bacteria along with MeO degradation. Finally, *E. coli* bacteria were deactivated under a direct sunlight irradiation. This process was proven to be an efficient method for a future commercial photocatalytic cell fabrication.

Zhao *et al.*⁵⁹ prepared TiO₂-NTs loaded with silver (Ag) nanoparticles (TiO₂-NT-Ag) on Ti implants to achieve a surface with a long-term antibacterial ability in order to prevent implant associated infection. This material could kill all the planktonic bacteria in the suspension during the first several days, and the ability to prevent bacterial adhesion was maintained without obvious decline for 30 d, which was normally long enough to prevent post-operation infection in the early and intermediate stages and

perhaps even late infection around the implant. Although the TiO₂-NT-Ag structure showed some cytotoxicity, it could be reduced by controlling the Ag release rate. The TiO₂-NT-Ag materials were also expected to possess satisfactory osteoconductivity in addition to the good biological performance expected of TiO₂ NTs. This controllable TiO₂-NT-Ag structure which providing relatively long-term antibacterial ability and good tissue integration has promising applications in orthopaedics, dentistry, and other biomedical devices.

The TiO₂ NT surface enables significantly accelerate osteoblast adhesion and exhibits strong bonding with bone. Various sizes (30 to 100 nm in diameter) of TiO₂ NTs on titanium substrates were prepared by anodization⁶⁰ and the osteoblast cellular behavior in response to these different NT sizes was investigated. The most striking result of this study was the observed change in osteoblast behavior to be obtained in a relatively narrow range of NT dimensions; with small diameter (~30 nm) NTs promoted the highest degree of osteoblast adhesion, while NTs with larger diameter (70 to 100 nm) elicited a lower population of cells with extremely elongated cellular morphology and much higher alkaline phosphatase levels. Increased elongation of nuclei was also observed in NTs with larger diameter. By controlling the nanotopography, large diameter NTs, in the order of ~100 nm, induced extremely elongated cellular shapes, with an aspect ratio of 11 : 1, which resulted in substantially enhanced up-regulation of alkaline phosphatase activity, which suggested a greater bone-forming ability here than in the case of NTs with smaller diameters. Such a NT structure, although already being a strongly osseointegrating implant material, offers encouraging implications for the development and optimization of novel orthopedics-related treatments with precise control toward desired cell and bone growth behavior.

Titanium and its alloys are being used in many orthopedic and bioimplant applications. In order to render these materials bioactive and to enhance osteointegration, the surfaces are coated with hydroxyapatite (HAp). Adhesion of bone cell to the implant surface, bond strength and durability of the implants are highly dependent upon the characteristics of the Ti substrate and the methods utilized in the hydroxyapatite coating process. Kar *et al.*⁶¹ reported an innovative method of preparation of a TiO₂ NT surface and subsequent electrodeposition of hydroxyapatite nanocrystalline coating. Growth of the hydroxyapatite onto the TiO₂ NT surface was accomplished by a pulsed electrodeposition process. Prior to the electrodeposition, the TiO₂ NT surface was subjected to an alkaline treatment, which provided a template for nucleation of the hydroxyapatite inside the NTs. This process resulted in a vertical growth of the hydroxyapatite crystals and increased the bond strength of the coating. Bond strength was further improved by annealing the hydroxyapatite coated on nanoporous TiO₂ in an argon atmosphere. Sugiyama *et al.*⁶² obtained titanate nanomesh layers on Ti-based bulk metallic glass (BMG) to induce bioactivity in the form of apatite-forming ability. Titanate nanomesh layers were prepared by hydrothermal-electrochemical treatment at 90 °C for 2 h, with a NaOH aqueous solution as electrolyte. A constant electric current of 0.5 mA . cm⁻² was applied between the BMG substrate and a Pt electrode acting as the anode and cathode, respectively. A nanomesh layer, consisting of nanowires (~20 nm in diameter) was formed on the BMG. An immersion test in simulated body fluid for 12 d revealed the titanate nanomesh layer on the BMG to promote the growth of bone-like hydroxyapatite. Hiroaki *et al.*⁶³ studied the growth of hydroxyapatite on different TiO₂ NT layers. The NT layers were obtained by electrochemical anodization of titanium in fluoride-containing electrolytes. To study various NT lengths, layers with an individual tube diameter of 100 nm were grown to a thickness of ~ 500 nm or 2 μm. The results clearly showed the presence of the NTs on a titanium surface to enhance the

apatite formation and 2- μm thick NT layer to trigger deposition faster than the thinner layers. Tubes annealed to anatase, or a mixture of anatase and rutile were clearly more efficient in promoting apatite formation than the tubes in their aqueous-formed amorphous state. Kunze *et al.*⁶⁴ reported on the initial and later stages of apatite formation from simulated body fluid on titania with different surface morphologies (compact or nanotubular) and different crystal structures (anatase or amorphous). Nanotubular layers were obtained by electrochemical anodization in fluoride-containing electrolytes. The enhanced apatite deposition on TiO_2 NTs was investigated. In the initial stages of apatite growth, more nuclei were formed on the NT surface than on the flat compact TiO_2 . While the crystallographic structure of the substrate played a less important role than the morphology in the initial nucleation stages, it was of greater importance in the later stages of apatite crystal growth. A nanotubular morphology combined with an anatase structure led to the formation of apatite layers with a thickness of > 6 nm in less than 2 d. No stable apatite layers could be observed on amorphous TiO_2 films, neither on compact nor on nanotubular substrates. Results revealed carbonated hydroxyapatite (CHA) of low crystallinity to be formed on annealed nanotubular and compact TiO_2 . Electrochemically grown and annealed TiO_2 NT arrays having anatase structure were expected to be a good precursor system for the formation of CHA and thus for the fabrication of osseointegrative implants.

Roguska *et al.*⁶⁵ prepared via electrochemical oxidation at constant voltage (10, 15, 20 or 25 V) in a mixture of 0.86 wt.% of NH_4F , glycerol and deionized water well-ordered TiO_2 NT with ~ 0.7 μm high and about 40 or 110 nm in diameter. These substrates were suitable supports for a calcium phosphate (CaP) coating deposited by a simple immersion in Hank solution. The results confirmed that the TiO_2 NT layer to become stable after annealing at 600°C , while its internal structure changed from amorphous to crystalline anatase, and eventually, to a mixture of anatase and rutile. These thermally stabilized TiO_2 NTs significantly enhanced apatite formation in Hanks' Balanced Salt Solution as compared to pure Ti covered with a native oxide layer. The CaP/ TiO_2 NT/Ti surface adsorbed a higher amount of protein (bovine serum albumin [BSA]) for a geometric surface area than did the Ti surface. The above difference in protein adsorption suggests a more promising initial cellular response for a CaP/ TiO_2 NT/Ti composite than for a typical Ti implant surface.

The main biological purpose of blood coagulation is the formation of an obstacle with sufficient hydraulic strength to withstand blood pressure to prevent blood loss. The ability to rapidly stem hemorrhage in trauma patients significantly impacts their chances of survival, and hence is a subject of ongoing interest in the medical community. Herein, Roy *et al.*⁶⁶ reported on the effect of biocompatible TiO_2 NTs on the clotting kinetics of whole blood. TiO_2 NTs 10 μm length were prepared by anodization of titanium in an electrolyte composed of dimethyl sulfoxide and HF, and then dispersed by sonic treatment. Compared with pure blood, blood containing dispersed TiO_2 NTs and blood in contact with gauze pads surface soaked with NTs demonstrated significantly stronger clot formation at reduced clotting times. Similar experiments using nanocrystalline TiO_2 nanoparticles showed comparatively weaker clot strengths and increased clotting times. TiO_2 NTs appeared to act as a scaffold, facilitating fibrin formation. These results suggested that application of a TiO_2 NT functionalized bandage could be used to help stem or stop hemorrhage.

Brugnera *et al.*⁶⁷ found optimum performance for photoelectrocatalytic oxidation of Bisphenol A (BPA) to obtain using TiO_2 NT electrodes, grown by anodization of Ti in NH_4F and a mixture of glycerol and water. The best condition was found to be in 0.1 mol/L Na_2SO_4 solution at pH 6 as supporting electrolyte and applied bias potential of

+1.5 V vs. Ag/AgCl under UV irradiation. These results indicate that TiO₂ NTs prepared by anodization are versatile and efficient photocatalysts for the degradation of endocrine disruptors.

Energy

Self-organized anodic TiO₂ NT arrays were functionalized with CdS nanoparticle based perfusion and deposition through a single-step sonoelectrodeposition method.⁶⁸ Even controlled at 50 °C, CdS nanoparticles with smaller size and more homogeneous distribution were successfully synthesized in dimethyl sulfoxide under ultrasonic irradiation. Moreover, TiO₂ NTs could be filled with nanoparticles because of the ultrasonic effect. The CdS incorporated to TiO₂ NTs (CdS-TiO₂ NTs) effectively harvested solar light in UV as well as visible light (up to 480 nm) region. Compared with pure TiO₂ NTs, a more than ninefold enhancement in photocurrent response was observed using the CdS-TiO₂ NTs. Maximum incident photon to charge carrier efficiency (IPCE) values of 99.95 and 9.85 % were respectively observed for CdS-TiO₂ NTs and pure TiO₂ NTs. The high value of IPCE observed in CdS-TiO₂ NTs was attributed to the increased efficiency of charge separation and transport of electrons. A schematic diagram was proposed to illustrate the possible process of CdS formation in NTs under sonochemical and electrochemical conditions.

Highly ordered, vertically oriented TiO₂ NT arrays obtained by potentiostatic anodization of titanium⁶⁹ constituted a material architecture which offered a large internal surface area without a concomitant decrease in geometric and structural order. The precisely oriented nature of the crystalline (after annealing) NT arrays caused them to be excellent electron percolation pathways for vectorial charge transfer between interfaces. Herein their preparation was briefly considered, as well as their initial applications to hydrogen gas sensing, solar generation of hydrogen by water photoelectrolysis, and in heterojunction solar cells. Macák *et al.*⁷⁰ reported on dye-sensitization of self-organized TiO₂ NTs and the photoelectrochemical response of this system. The tubes were grown by Ti anodization in fluoride containing electrolytes in two different forms: as "long" tubes (tube lengths ~2.5 µm) and "short" tubes (tube lengths ~500 nm). Both the tube types had a tube diameter of ~100 nm and a wall thickness of 15 nm. After annealing the tubes to anatase they were sensitized with Ru-dye (N3) in different concentrations. The results showed the magnitude of the photocurrent response to be affected not only by the dye concentration but also by the tube length. For the "long" tubes an IPCE_{max.} (at 540 nm) of 3.3 % and for the "short tubes" of 1.6 % (at 530 nm) were obtained. These results showed self-organized TiO₂ NTs to possibly be dye-sensitized in the visible range and a considerable light conversion efficiency to be achieved.

Xu *et al.*⁷¹ prepared a new bilayer-structured film with TiO₂ nanocrystals as underlayer and TiO₂ nanotubes as overlayer. The resultant double-layer TiO₂ (DL-TiO₂) film could significantly improve the efficiency of dye-sensitized solar cells (DSSCs) due to its synergic effects. The overall energy-conversion efficiency of DL-TiO₂ film was higher than that formed by pure nanocrystalline TiO₂ (NC-TiO₂) film and far larger than that formed by TiO₂ NT film. It was expected that DL-TiO₂ film electrode could extended to other composite films with different layer structures and morphologies for enhancing the efficiencies of DSSCs.

Gan *et al.*⁷² made a biophotofuel cell with TiO₂ NTs array photosensitive anode for biomass decomposition. The TiO₂ NTs were prepared via electrochemical oxidation of pure Ti in NaF solutions. The average diameter, wall thickness and length of the as-prepared TiO₂ NTs were 88 ± 16 nm, 10 ± 2 nm and 491 ± 56 nm, respectively. The

prepared photosensitive anode had good photo-catalytic property, as could be seen from the test results of ethanol, apple vinegar, sugar and tissue paper decomposition under ultraviolet (UV) radiation. It was concluded that the biophotofuel cell with the TiO₂ nanotube photoanode could generate electricity, hydrogen and clean water depending on the pH value and the oxygen presence in the solutions.

Gong *et al.*⁷³ demonstrated extremely highly ordered TiO₂ NT arrays to enhance hydrogen production by photoelectrocatalytic water splitting. Highly ordered TiO₂ NT were grown by green three-step electrochemical anodization. As a result, the TiO₂ NT constructed through the third anodization showed appreciably more regular architecture than that of the sample by conventional single anodization under the same conditions. The enhanced photoelectrochemical activity was demonstrated through the hydrogen generation by photoelectrocatalytic water splitting, with an exact H₂ evolution rate up to 10 mL/h.cm² in 2 mol/L Na₂CO₃ + 0.5 mol/L ethylene glycol. The photocurrent density was about 24 mA/cm² in 0.5 mol/L KOH, which is 2.2 times higher than that of the normal TiO₂ NT (< 11 mA/cm²) by a single electrochemical anodization.

Environment

Pt based catalysts are commonly used in several industrial processes involving hydrogenation and dehydrogenation reactions. New deposition methods as well as support materials are being investigated to generate new catalysts with superior catalytic activity. Capula *et al.*⁷⁴ prepared platinum-iridium (Pt-Ir) nanoparticles of about 5 nm in size supported on TiO₂ NTs by metal organic chemical vapor deposition (MOCVD). The TiO₂ NTs were prepared by an alkali hydrothermal method using sodium hydroxide solution at 100 °C. Pt-Ir nanoparticles were obtained by controlling the MOCVD conditions at 400 °C and 66.6 kPa. The TiO₂ NTs exhibited a considerable high surface area of about 4.25 · 10⁵ m²/kg, however, after calcination at 400 °C their nanotubular morphology was partially transformed. In spite of this change, the 5 nm Pt-Ir nanoparticles supported on TiO₂ NTs were more active in the cyclohexene disproportion reaction than conventional Pt-Ir/alumina catalysts in the whole range of temperatures investigated (50 to 250 °C). Hydrogenation reactions (high selectivity to cyclohexane) predominate at temperatures below 150 °C.

Cardoso *et al.*⁷⁵ found that the photocurrent of self-organized TiO₂ NT electrodes achieved by simple electrochemical anodization of Ti in NH₄F/glycerol water solution was remarkably improved in relation to that obtained on similar nanoporous TiO₂ films created by a sol gel process. Both electrodes promoted complete degradation of the investigated aromatic amine ODAN (4,4,2-oxydianiline), but the ODAN mineralization was about 50 % more efficient on TiO₂ NT electrodes. The best experimental conditions were found to be pH 2.0 and 0.1 mol/L Na₂SO₄ when the photoelectrode was biased at +1.5 V (vs. SCE). Complete mineralization of the aromatic amine content was achieved after 2h.

Esbenshade *et al.*⁷⁶ proposed a method to remove sunscreen compounds 4-methylbenzylidene camphor (4-MBC), 3-benzophenone (BENZO) and 4-aminobenzoic acid (PABA) from swimming pool water based on photoelectrocatalytic oxidation using self-organized TiO₂ NT electrodes irradiated by UV light. The best condition for the mineralization of these compounds was found to be 0.1 mol/L Na₂SO₄ at pH 9 with +1.5 V potential applied to the electrode. The method was successfully applied to sunscreen degradation in swimming pool water, reaching 100 % degradation, indicating that the method could be an excellent alternative method to produce truly clean water.

Kefi *et al.*⁷⁷ proposed an analytical method based on TiO₂ NT solid-phase extraction combined with gas chromatography for the analysis of seven poly cyclic aromatic

hydrocarbons (PAHs): acenaphthylene, acenaphthene, anthracene, fluorene, phenanthrene, fluoranthene and pyrene. Factors affecting the extraction efficiency including the eluent type and its volume, adsorbent amount, sample volume, sample pH and sample flow rate were optimized. Under the optimized extraction conditions, the method showed good linearity, and repeatability of extraction and satisfactory detection limits. The developed method was successfully applied to the analysis of surface water (tap, river and dam) samples. The recoveries of PAHs spiked in environmental water samples ranged from 90 to 100 %. All results indicated the potential application of TiO₂ NT as solid-phase extraction adsorbents to pre-treat water samples.

Controlled anodization of Ti and other valve metals formed porous metal oxides of great uniformity and regularity which could be used, e.g. as templates for making other materials with regular geometries. With this aim, Tupala *et al.*⁷⁸ prepared TiO₂ NT thin films by anodization of titanium metal films evaporated on indium tin oxide (ITO). The films were further modified by growing amorphous titania, alumina and tantalum thin films in the nanotubes by atomic layer deposition (ALD). It was shown that even 5 nm thin layers can modify the properties of TiO₂ NT films. This kind of modification could be suitable for solid state optoelectronic applications and for electronics, in electrochromic applications, gas sensors, biomedical applications, solar cells and photocatalysis.

According to the functional application reported, the bibliography here consulted is listed as summary (Table 1).

Table 1. TiO₂ applications and related bibliographic references.

TiO ₂ applications	References
Photoelectrochemical properties	2,3,6,7,13,16,21,23,25,27,29,33-35,38,46,47,49-51,53-55,57,68-70,78
Energy, photoelectrolysis and solar cells	38,47,49,51,69-71,73
Medicine	5,7,19,30,48,52,54,57-67,72
Sensors and environment	7,16,21,25,38,69,74-77

Mechanistic aspects

For Ti and other so-called valve metals its possibility to develop compact oxide layers of considerable thickness (near to 1 μm) by anodization in aqueous electrolytes has been known for more than 50 years.⁷⁹ Typical growth occurs proportionally to applied potential with a growth factor around 1 to 5 nm/V up to a voltage, where dielectric breakdown of the oxide occurs.^{80,81} The structure of the so obtained oxide can be amorphous or crystalline, strongly dependent on the specific electrochemical parameters such as applied potential, time of anodization, or sweep rate of the potential ramp. The structure of the TiO₂ films has typically been reported to be amorphous at low voltages and crystallization to take place at higher voltages. Depending on the anodizing conditions the structure has been reported to be anatase, rutile, or a mixture of both.

Completely different growth morphology can be obtained, if fluoride ions are present in electrolytes and suitable anodization conditions are used. Ordered nanotubular/nanoporous structures of TiO₂ or other transition metal oxides can be formed (Fig. 1). In general, the morphology and the structure of porous layers are affected strongly by the electrochemical conditions (particularly the anodization voltage) and the solution parameters (in particular HF concentration, pH and water content in the electrolyte).

The first generation of TiO₂ NT arrays was grown in HF electrolytes or acidic HF mixtures.^{82,83} These layers showed a limited thickness not exceeding 500 to 600 nm

(Fig. 2). Using buffered neutral electrolytes containing NaF or NH₄F instead of HF (second generation)¹⁵ and taking into account the importance of the pH gradient within the tube, it was shown the possibility of self-organized NT TiO₂ layers with thicknesses higher than 2 μm to be grown.¹⁵ The third nanotube generation NTs was grown in (almost) water free electrolytes. In glycerol electrolytes, NTs showed extremely smooth walls and a tube length exceeding 7 μm, while when using CH₃COOH electrolytes remarkably small tube diameters could be obtained.²⁶ Meanwhile, for example in aged

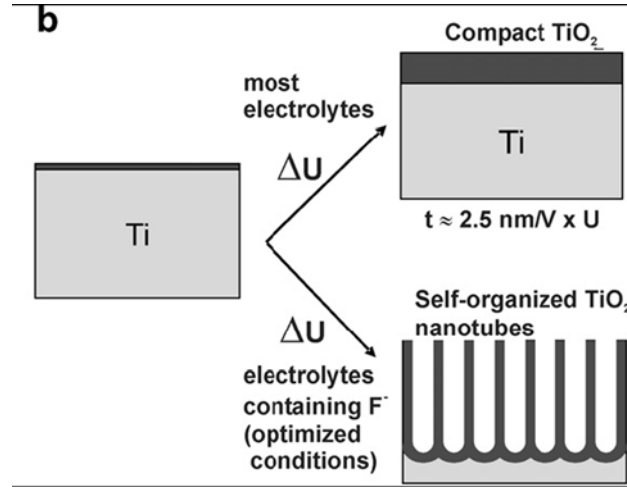
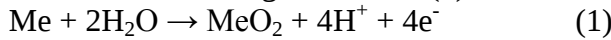


Fig. 1. Schematic set-up for anodization experiments. Anodization leads to an oxidation of metal species that forms a solid oxide on the metal surface. Depending on the anodization conditions (mainly potential, electrolyte, temperature), the solid oxide layer can be either compact, or nanotubular (nanoporous). To achieve an ideal self-ordering of the NTs, the use of the optimized anodization parameters is crucial.⁴¹

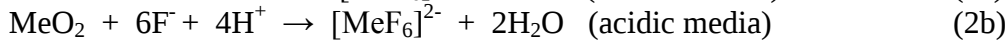
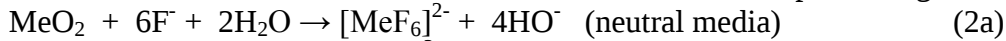
ethylene glycol electrolytes and by a further optimization of parameters, NT length reached 260 μm and the tubes had an almost ideal hexagonal arrangement.

Formation and growth of the TiO₂ nanotubes

The anodic growth of compact oxides on metal surfaces and the formation of tubes are, in the most simple approach,⁴¹ governed by a competition between anodic oxide formation, according to reaction (1)



and chemical dissolution of the oxide as soluble fluoride complexes, e.g.;



Respectively, direct complexation at the oxide electrolyte interface of high-field transported cations takes place according to:



Reaction (1) describes the oxide growth on an anodized metal surface in a fluoride-free electrolyte (Fig. 3a). Oxidized metal species react with O²⁻ ions (from H₂O) to form an oxide layer. Further oxide growth is controlled by field-aided ion transport (O²⁻ and Ti⁴⁺ ions) through the growing oxide. As the system is under a constant applied voltage, the field within the oxide layer is progressively reduced by the increasing oxide thickness, the process is thus self-limited. The decreasing field strength leads to an exponential current decay (Fig. 4a) and thus to the growth of a compact oxide layer with a finite thickness (Fig. 4b). If Ti⁴⁺ ions arriving at the oxide/electrolyte interface were not

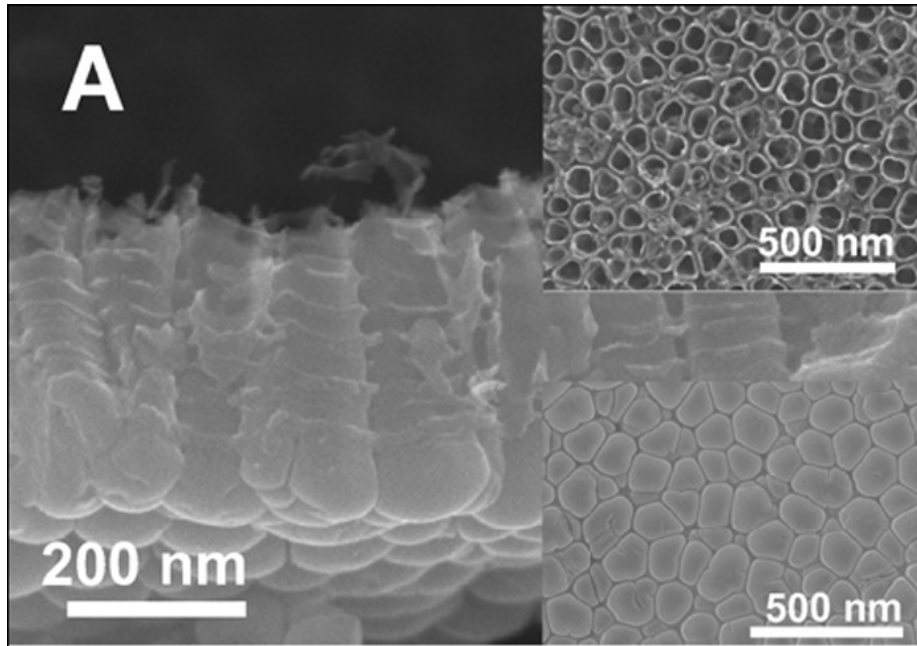


Fig. 2. SEM images showing TiO_2 NT layers grown by anodization processes of Ti. (A) Typical morphology obtained in acidic fluoride or HF electrolytes. The insets show top-views (open tubes), bottom views (closed ends) and side walls in detail.⁴¹

“made soluble” by complexation, according to reaction (3), a hydroxide layer would precipitate in most electrolytes. Typically, this layer is loose and porous and thus does not contribute to field effects, but exerts to a certain extent diffusion retarding effects. According to this mechanism, the growth rate determining step is fluoride ion diffusion to the tube bottom, and during anodization permanently a high-field oxide layer (that accordingly increases in thickness with higher applied voltage) is present on the tube bottom.

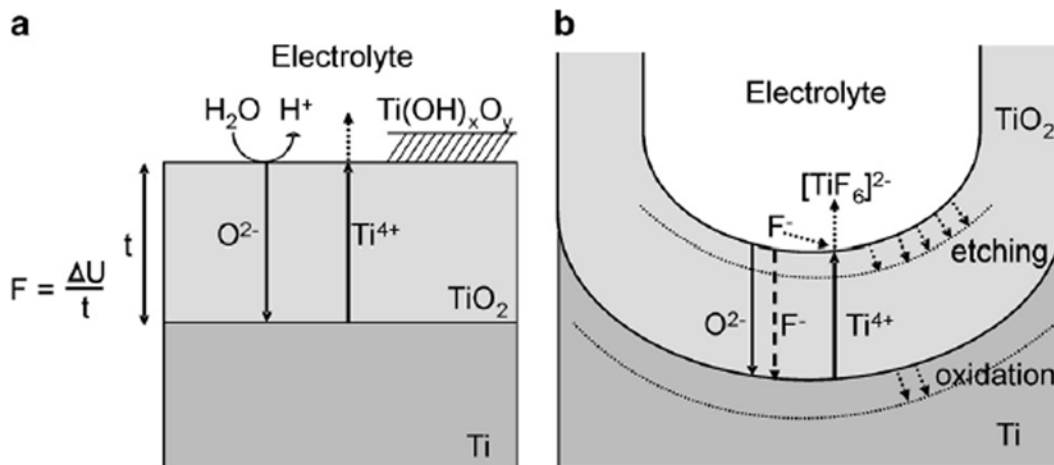


Fig. 3. Schematic representation of the Ti anodization (a) in absence of fluorides (resulting in flat layers), and (b) in presence of fluorides (resulting in tube growth).⁴¹

In the presence of fluoride ions the situation becomes different (Fig. 3b). This is mainly due to two effects of the fluoride ion: (i) the ability to form water-soluble TiF_6^{2-} complexes according to reaction (2), and (ii) the small ionic radius that makes them suitable to enter the growing TiO_2 lattice and to be transported through the oxide by the

applied field (thus competing with O^{2-} transport). The complex formation ability leads to a permanent chemical attack (dissolution) of formed TiO_2 and prevents $Ti(OH)_xO_y$ precipitation as Ti^{4+} ions arriving at the oxide/solution interface can form a complex ion, TiF_6^{2-} , as it is represented in reaction (3), before reacting to a precipitate $Ti(OH)_xO_y$ layer. As a result, the current–time curve for electrolyte containing fluorides deviates from the classical high-field growth (Fig. 4a). That is, after an initial exponential decay (phase I) the current increases again (phase II) with a shorter time lag is the higher the fluoride concentration is then, the current reaches a quasi-steady state (phase III). This steady state current increases with increasing fluoride concentration. Typically, such a

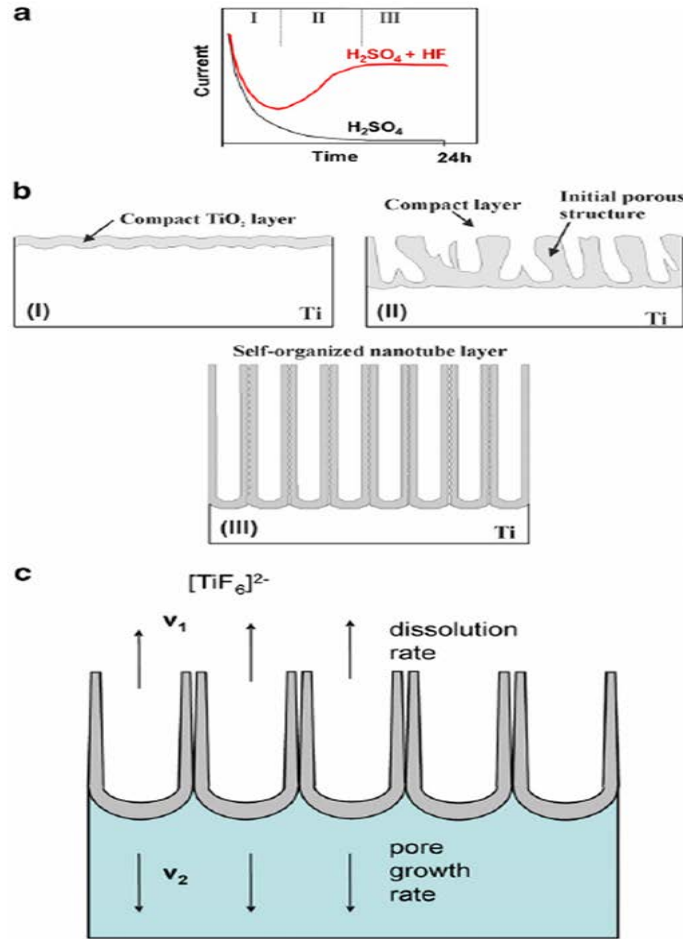


Fig. 4. a Characteristic current transients for Ti anodization with and without fluorides in the electrolyte. b Corresponding evolution of the TiO_2 morphology. c Steady state growth situation characterized by equal rates of TiO_2 dissolution (v_1) and formation (v_2).⁴¹

current behavior can be ascribed to different stages in the pore formation process (Fig. 4b), in the first stage, a barrier oxide is formed, leading to a current decay (phase I). In the next stage, the surface is locally activated and pores start to grow randomly (phase II). Due to the pore growth, the active area increases and the current increases. After some time, many pores have initiated and a tree-like growth takes place. Therefore, the individual pores start interfering with each other, and start competing for the available current. This leads under optimized conditions to a situation where the pores equally share the available current, and self-ordering under steady state conditions is established (phase III).

The fact that the layer thickness and the current density reach a limiting value after a certain polarization time can be explained by a steady state situation (Fig. 4c). During anodization, continual growth of oxide takes place at the inner interface, and chemical dissolution of the oxide layer occurs simultaneously. Steady state is established when the pore growth rate at the metal oxide interface is identical to the thickness reducing dissolution rate of the oxide film at the outer interface. In this situation the NT oxide layer just continuously “eats” through the titanium substrate without thickening of the oxide layer. As the steady state current densities are typically considerably high, this occurs even with comparably high velocity. This result also explains the typically low current efficiencies (for oxide formation) in acidic electrolytes (3–10 %), and in particular their continuous drop with extended anodization time.

It should be remarked that the chemical dissolution of TiO_2 occurs of course over the entire tube length, thus with extended time the tubes become increasingly v-shaped in morphology, i.e., at the tops of the tubes possess significantly thinner walls than at their bottoms. The reason for separation into tubes, as opposed to a nanoporous structure, is not yet entirely clear, however, it may be ascribed to accumulation of fluoride species at the tube bottom and thus to the establishment of an anion containing weaker (and more soluble) TiO_2 structure between neighboring pores/tubes.

AS A WAY OF CONCLUSION

This work is conceived for researchers interested in the synthesis of TiO_2 NT, which could encompass undergraduated students, graduated students and beyond. It is meant as an introductory work to this field.

By anodization in aqueous electrolytes, it is possible to grow compact oxide layers of considerable thickness on Ti surface. But, if fluoride ions are present in electrolytes a completely different growth morphology can be obtained, due to the competition of two processes: anodic oxide formation and chemical dissolution of the oxide as soluble fluoride complexes. Then, the formation of nanotubes is, in the simplest approach, governed by the competition between these processes.

The so-called first generation of TiO_2 NT arrays was grown in HF electrolytes or acidic HF mixtures^{82,83} where sulphate and phosphate ions were the most common co-anions. Using buffered neutral electrolytes, containing NaF or NH_4F instead of HF (second generation),¹⁵ the possibility was shown self-organized TiO_2 NT layers with thicknesses higher than 2 μm to be grown.¹⁵ The third NTs generation was grown in (almost) water free electrolytes as in glycerol or CH_3COOH electrolytes. Nanotubes could be obtained with extremely smooth walls, tube length exceeding 7 μm and remarkably small tube diameters. Bibliographic references consulted in the present paper are listed according to the employed electrolyte composition (Table 2).

Anodization conditions (applied voltages, HF concentration, pH, water content and anodization time) could change the topologies and geometric dimensions of the self-organized TiO_2 NT layers. The pH value controls the thickness of the NTs; the size of the TNs greatly depends on the applied voltages and the diameter and the length depend linearly on the voltage.

At the firsts moments an increase in anodization time had a significant effect on tube diameter, tube wall thickness and coating thickness, but a further increase in anodization time did not cause any effect on the thickness because an equilibrium value of this quantity was established. In water-free electrolytes, the NT morphology could be influenced by the viscosity and electrolyte temperature. The geometric dimensions of the TiO_2 nanotube layers in different electrolyte types are listed depending on the bibliography here consulted (Table 3).

Table 2. Electrolyte composition for the synthesis of TiO₂ nanotube and corresponding bibliographic references.

Ions in the electrolyte	References
F ⁻ or HF ^a	2-10,63,64,70,72,83
F ⁻ (H) + SO ₄ ²⁻ (H ₂) ^a	11-13,15,42,43,46
F ⁻ (H) + PO ₄ ³⁻ (H ₃) ^a	14,16-21,40,44,45
Others ^b	22-35,37,38,65,67,68,75

^a In water solution.

^b In water/organic or organic solvent.

The symbol F⁻(H) denotes the fluoride anion or the acid and so forth.

Particularly interesting is the growth of NTs on various alloys, as this drastically increases the potential functionality of the tubes. Recently, NT layers have successfully been grown on Ti-xNb, Ti-Zr-Nb, Ti-Ta, Ti-Al-V and Ti-Al alloys. In these cases, the microstructure of the alloys can strongly affect the homogeneity of the nanotubular surface layers. The results show that “ideal” alloys for NT formation can possess a single-phase microstructure and a composition that essentially contains only valve metals.

Table 3. Geometric dimensions of TiO₂ nanotube layers in different electrolyte types and bibliographic references.

Electrolyte type	Diameter/nm	Length/nm	Wall/nm	References
F ⁻ + H ⁺ ions	100	500-2500	15-2000	63,70,72,83
F ⁻ (H) + PO ₄ ³⁻ (H ₃) ions	10-220	20-4000	10-20	18,19
F ⁻ (H) + SO ₄ ²⁻ (H ₂) ions	40-300	500-22 000	25-500	12,46

the symbol F⁻(H) denotes the fluoride anion or the acid and so forth.

The annealing temperature and duration have a significant effect on crystal structure of TiO₂ NT. After anodization, before any heat treatment, the NTs have an amorphous structure. Annealing promotes anatase and rutile phases' formation depending upon the temperature. At low temperatures anatase phase appears and rutile formation occurs at higher temperature. At temperatures even higher, disintegration of the NT arrays is observed and the structure completely vanishes. Impurities in the sample can retard anatase-rutile phase transition.

Other methods for synthesis of TiO₂ NT as hydrothermal, sol-gel, liquid phase deposition (LPD), simple chemical bath deposition (CBD) or liquid chemical deposition (LCD) methods are only mentioned in this overview because they are out author's interest.

The photocurrent response and photoelectrocatalytic degradation of some dyes under ultraviolet light irradiation (photocatalytic activity) can be used to evaluate photoelectrocatalytic properties. The findings show diameter, wall thickness, crystal structure and degree of crystallinity of TiO₂ NT arrays to be the chief factors influencing the efficiency of the photocatalytic activity. Highly ordered TiO₂ NT arrays present much better photoelectrocatalytic activity than sol-gel derived TiO₂ films. Non-metal-doped (N, F and I) TiO₂ NTs display a significant visible-light response and NTs filled with nanoparticles can enhance the photocurrent response

TiO₂ coatings have been shown to exhibit desirable properties even as biocompatible coatings. As large surface area and tunable nanoscale geometry of the surface oxide

provide novel pathways for interaction of the materials with biorelevant species, such as cells and proteins, TiO₂ NT arrays seems to be attractive for medical application. The bioactivity can be evaluated *in vitro* by deposition of an apatite layer on a TiO₂ surface. The NT arrays distribution (high specific surface area) and the crystallization (anatase phase) are important factor for a good adhesion of apatite on TiO₂. Adsorption of extracellular matrix proteins shows a strong influence on wetting behavior and dependence on diameter of TiO₂ NT. These arrays significantly accelerate osteoblast adhesion and exhibit strong bonding with bone. Other interesting results are its extremely rapid inactivation of *E. coli* (due to the high photocurrent response) and to be a potent electrode for water purification.

BIBLIOGRAPHIC REFERENCES

1. Wei D, Zhou Y, Jia D, Wang Y. Characteristic and *in vitro* bioactivity of a microarc-oxidized TiO₂-based coating after chemical treatment. *Acta Biomaterialia*. 2007;3(5):817-27.
2. Awitor KO, Rafqah S, Géranton G, Sibaud Y, Larson PR, Bokalawela RSP, *et al.* Photo-catalysis using titanium dioxide nanotube layers. *Journal of Photochemistry and Photobiology A: Chemistry*. 2008;199(2-3):250-4.
3. Lai YK, Sun L, Chen C, Nie CG, Zuo J, Lin CJ. Optical and electrical characterization of TiO₂ nanotube arrays on titanium substrate. *Applied Surface Science*. 2005;252(4):1101-6.
4. Zhao J, Wang X, Chen R, Li L. Fabrication of titanium oxide nanotube arrays by anodic oxidation. *Solid State Communications*. 2005;134(10):705-10.
5. Xiao X-f, Tian T, Liu R-f, She H-d. Influence of titania nanotube arrays on biomimetic deposition apatite on titanium by alkali treatment. *Materials Chemistry and Physics*. 2007;106(1):27-32.
6. Zlamal M, Macak JM, Schmuki P, Krýsa J. Electrochemically assisted photocatalysis on self-organized TiO₂ nanotubes. *Electrochemistry Communications*. 2007;9(12):2822-6.
7. Crawford GA, Chawla N, Das K, Bose S, Bandyopadhyay A. Microstructure and deformation behavior of biocompatible TiO₂ nanotubes on titanium substrate. *Acta Biomaterialia*. 2007;3(3):359-67.
8. Crawford GA, Chawla N. Tailoring TiO₂ nanotube growth during anodic oxidation by crystallographic orientation of Ti. *Scripta Materialia*. 2009;60(10):874-7.
9. Crawford GA, Chawla N, Houston JE. Nanomechanics of biocompatible TiO₂ nanotubes by Interfacial Force Microscopy (IFM). *Journal of the Mechanical Behavior of Biomedical Materials*. 2008;2(6):580-7.
10. Soon HK, Jae-Yup K, Hyun SK, Yung-Eun S. Formation and mechanistic study of self-ordered TiO₂ nanotubes on Ti substrate. *Journal of Industrial and Engineering Chemistry*. 2008;14(1):52-9.
11. Prida VM, Manova E, Vega V, Hernandez-Velez M, Aranda P, Pirota KR, *et al.* Temperature influence on the anodic growth of self-aligned Titanium dioxide nanotube arrays. *Journal of Magnetism and Magnetic Materials*. 2007;316(2):110-3.
12. Bestetti M, Franz S, Cuzzolin M, Arosio P, Cavallotti PL. Structure of nanotubular titanium oxide templates prepared by electrochemical anodization in H₂SO₄/HF solutions. *Thin Solid Films*. 2007;515(13):5253-8.
13. Sreekantan S, Lockman Z, Hazan R, Tasbihi M, Tong LK, Mohamed AR. Influence of electrolyte pH on TiO₂ nanotube formation by Ti anodization. *Journal of Alloys and Compounds*. 2009;485(1-2):478-83.

14. Premchand YD, Djenizian T, Vacandio F, Knauth P. Fabrication of self-organized TiO₂ nanotubes from columnar titanium thin films sputtered on semiconductor surfaces. *Electrochemistry Communications*. 2006;8(12):1840-4.
15. Ghicov A, Tsuchiya H, Macak JM, Schmuki P. Titanium oxide nanotubes prepared in phosphate electrolytes. *Electrochemistry Communications*. 2005;7(5):505-9.
16. Zhao J, Wang X, Sun T, Li L. Crystal phase transition and properties of titanium oxide nanotube arrays prepared by anodization. *Journal of Alloys and Compounds*. 2007;434-435:792-5.
17. Cai Q, Yang L, Yu Y. Investigations on the self-organized growth of TiO₂ nanotube arrays by anodic oxidization. *Thin Solid Films*. 2006;515(4):1802-6.
18. Bauer S, Kleber S, Schmuki P. TiO₂ nanotubes: Tailoring the geometry in H₃PO₄/HF electrolytes. *Electrochemistry Communications*. 2006;8(8):1321-5.
19. Bauer S, Park J, Mark Kvd, Schmuki P. Improved attachment of mesenchymal stem cells on super-hydrophobic TiO₂ nanotubes. *Acta Biomaterialia*. 2008;4(5):1576-82.
20. Balaur E, Macak JM, Taveira L, Schmuki P. Tailoring the wettability of TiO₂ nanotube layers. *Electrochemistry Communications*. 2005;7(10):1066-70.
21. Li G, Liu Z-Q, Lu J, Wang L, Zhang Z. Effect of calcination temperature on the morphology and surface properties of TiO₂ nanotube arrays. *Applied Surface Science*. 2009;255(16):7323-8.
22. Vega V, Cerdeira MA, Prida VM, Alberts D, Bordel N, Pereiro R, *et al.* Electrolyte influence on the anodic synthesis of TiO₂ nanotube arrays. *Journal of Non-Crystalline Solids*. 2008;354(47-51):5233-5.
23. Allam NK, Grimes CA. Effect of cathode material on the morphology and photoelectrochemical properties of vertically oriented TiO₂ nanotube arrays. *Solar Energy Materials and Solar Cells*. 2008;92(11):1468-75.
24. Kaneco S, Chen Y, Westerhoff P, Crittenden JC. Fabrication of uniform size titanium oxide nanotubes: Impact of current density and solution conditions. *Scripta Materialia*. 2007;56(5):373-6.
25. Lai Y, Zhuang H, Sun L, Chen Z, Lin C. Self-organized TiO₂ nanotubes in mixed organic-inorganic electrolytes and their photoelectrochemical performance. *Electrochimica Acta*. 2009;54(26):6536-42.
26. Tsuchiya H, Macak JM, Taveira L, Balaur E, Ghicov A, Sirotna K, *et al.* Self-organized TiO₂ nanotubes prepared in ammonium fluoride containing acetic acid electrolytes. *Electrochemistry Communications*. 2005;7(6):576-80.
27. Sreekantan S, Hazan R, Lockman Z. Photoactivity of anatase-rutile TiO₂ nanotubes formed by anodization method. *Thin Solid Films*. 2009;518(1):16-21.
28. Yang D-J, Kim H-G, Cho S-J, Choi W-Y. Thickness-conversion ratio from titanium to TiO₂ nanotube fabricated by anodization method. *Materials Letters*. 2008;62(4-5):775-9.
29. Qidong Z, Xinyong L, Ning W, Yang H, Xie Q, Guohua C. Facile fabrication, characterization, and enhanced photoelectrocatalytic degradation performance of highly oriented TiO₂ nanotube arrays. *J Nanopart Res*. 2009;11:2153-62.
30. Li M, Xiao X, Liu R. Synthesis and bioactivity of highly ordered TiO₂ nanotube arrays. *Applied Surface Science*. 2008;255(2):365-7.
31. Macak JM, Hildebrand H, Marten-Jahns U, Schmuki P. Mechanistic aspects and growth of large diameter self-organized TiO₂ nanotubes. *Journal of Electroanalytical Chemistry*. 2008;621(2):254-66.
32. Macak JM, Schmuki P. Anodic growth of self-organized anodic TiO₂ nanotubes in viscous electrolytes. *Electrochimica Acta*. 2006;52(3):1258-64.

33. Mura F, Masci A, Pasquali M, Pozio A. Effect of a galvanostatic treatment on the preparation of highly ordered TiO₂ nanotubes. *Electrochimica Acta*. 2009;54(14):3794-8.
34. Lei L, Su Y, Zhou M, Zhang X, Chen X. Fabrication of multi-non-metal-doped TiO₂ nanotubes by anodization in mixed acid electrolyte. *Materials Research Bulletin*. 2007;42(12):2230-6.
35. Su Y, Zhang X, Han S, Chen X, Lei L. F-B-codoping of anodized TiO₂ nanotubes using chemical vapor deposition. *Electrochemistry Communications*. 2007;9(9):2291-8.
36. Yang Y, Wang X, Li L. Synthesis and growth mechanism of graded TiO₂ nanotube arrays by two-step anodization. *Materials Science and Engineering: B*. 2008; 149(1):58-62.
37. Chen X, Schriver M, Suen T, Mao SS. Fabrication of 10 nm diameter TiO₂ nanotube arrays by titanium anodization. *Thin Solid Films*. 2007;515(24):8511-4.
38. Mor GK, Varghese OK, Paulose M, Shankar K, Grimes CA. A review on highly ordered, vertically oriented TiO₂ nanotube arrays: Fabrication, material properties, and solar energy applications. *Solar Energy Materials and Solar Cells*. 2006;90(14):2011-75.
39. Hsin-Hung O, Lo S-L. Review of titania nanotubes synthesized via the hydrothermal treatment: Fabrication, modification, and application. *Separation and Purification Technology*. 2007;58:179–91.
40. Jang S-H, Choe H-C, Ko Y-M, Brantley WA. Electrochemical characteristics of nanotubes formed on Ti-Nb alloys. *Thin Solid Films*. 2009;517(17):5038-43.
41. Macak JM, Tsuchiya H, Ghicov A, Yasuda K, Hahn R, Bauer S, *et al.* TiO₂ nanotubes: Self-organized electrochemical formation, properties and applications. *Current Opinion in Solid State and Materials Science*. 2007;11(1-2):3-18.
42. Feng XJ, Macak JM, Albu SP, Schmuki P. Electrochemical formation of self-organized anodic nanotube coating on Ti-28Zr-8Nb biomedical alloy surface. *Acta Biomaterialia*. 2008;4(2):318-23.
43. Tsuchiya H, Akaki T, Nakata J, Terada D, Tsuji N, Koizumi Y, *et al.* Anodic oxide nanotube layers on Ti-Ta alloys: Substrate composition, microstructure and self-organization on two-size scales. *Corrosion Science*. 2009;51(7):1528-33.
44. Luo B, Yang H, Liu S, Fu W, Sun P, Yuan M, *et al.* Fabrication and characterization of self-organized mixed oxide nanotube arrays by electrochemical anodization of Ti-6Al-4V alloy. *Materials Letters*. 2008;62(30):4512-5.
45. Fathy MB, Badr GA. Formation of self-organized titania nano-tubes by dealloying and anodic oxidation. *Electrochemistry Communications*. 2006;8:38-44.
46. Bavykin DV, Milsom EV, Marken F, Kim DH, Marsh DH, Riley DJ, *et al.* A novel cation-binding TiO₂ nanotube substrate for electro- and bioelectro-catalysis. *Electrochemistry Communications*. 2005;7(10):1050-8.
47. Sorapong P, Supachai N, Masafumi N, Yoshikazu S, Susumu Y. Synthesis, characterization, photocatalytic activity and dye-sensitized solar cell performance of nanorods/nanoparticles TiO₂ with mesoporous structure. *Journal of Photochemistry and Photobiology A: Chemistry*. 2006;184:163-9.
48. Wang YQ, Hu GQ, Duan XF, Sun HL, Xue QK. Microstructure and formation mechanism of titanium dioxide nanotubes. *Chemical Physics Letters*. 2002;365(5-6):427-31.
49. Wang D, Yu B, Zhou F, Wang C, Liu W. Synthesis and characterization of anatase TiO₂ nanotubes and their use in dye-sensitized solar cells. *Materials Chemistry and Physics*. 2009;113(2-3):602-6.

50. Wang D, Zhou F, Liu Y, Liu W. Synthesis and characterization of anatase TiO₂ nanotubes with uniform diameter from titanium powder. *Materials Letters*. 2008;62(12-13):1819-22.
51. Charoensirithavorn P, Ogomi Y, Sagawa T, Hayase S, Yoshikawa S. A facile route to TiO₂ nanotube arrays for dye-sensitized solar cells. *Journal of Crystal Growth*. 2009;311(3):757-9.
52. More AM, Gujar TP, Gunjekar JL, Lokhande CD, Joo O-S. Growth of TiO₂ nanorods by chemical bath deposition method. *Applied Surface Science*. 2008;255(5, Part 2):2682-7.
53. Yang H, Xinyong L, Ping L, Xuejun Z, Guohua C, Po-Lock Y. Fabrication and photo-electrocatalytic properties of highly oriented titania nanotube arrays with [101] crystal face. *Separation and Purification Technology*. 2009;67:135-40.
54. Tomoko K. Formation of titanium oxide nanotubes using chemical treatments and their characteristic properties. *Thin Solid Films*. 2006;496:141 – 5.
55. Qamar M, S J, A K G. TiO₂-based nanotubes modified with nickel: synthesis, properties, and improved photocatalytic activity. *Nanotechnology*. 2009;20:1-8.
56. Qiu Y, Yu J. Synthesis of titanium dioxide nanotubes from electrospun fiber templates. *Solid State Communications*. 2008;148(11-12):556-8.
57. Nir B, David S, Jeana S, Marina E, Robert A, Yair E-E. Enhanced inactivation of *E. coli* bacteria using immobilized porous TiO₂ photoelectrocatalysis. *Electrochimica Acta*. 2009;54:3381-6.
58. Baram N, Starosvetsky D, Starosvetsky J, Epshtein M, Armon R, Ein-Eli Y in Photocatalytic inactivation of microorganisms using nanotubular TiO₂, Vol. 101 2011, p. 212.
59. Zhao L, Wang H, Huo K, Cui L, Zhang W, Ni H, *et al.* Antibacterial nano-structured titania coating incorporated with silver nanoparticles. *Biomaterials*. 2011;32(24):5706.
60. Brammer KS, Oh S, Cobb CJ, Bjursten LM, Heyde Hvd, Jin S. Improved bone-forming functionality on diameter-controlled TiO₂ nanotube surface. *Acta Biomaterialia*. 2009;5(8):3215-23.
61. Kar A, Raja KS, Misra M. Electrodeposition of hydroxyapatite onto nanotubular TiO₂ for implant applications. *Surface and Coatings Technology*. 2006;201(6):3723-31.
62. Sugiyama N, Xu H, Onoki T, Hoshikawa Y, Watanabe T, Matsushita N, *et al.* Bioactive titanate nanomesh layer on the Ti-based bulk metallic glass by hydrothermal-electrochemical technique. *Acta Biomaterialia*. 2009;5(4):1367-73.
63. Hiroaki T, Jan MM, Lenka M, Julia K, Frank M, Peter G, *et al.* Hydroxyapatite growth on anodic TiO₂ nanotubes. *J Biomed Mater Res*. 2006;77A(3):534-41.
64. Kunze J, Müller L, Macak JM, Greil P, Schmuki P, Müller FA. Time-dependent growth of biomimetic apatite on anodic TiO₂ nanotubes. *Electrochimica Acta* 2008;53(23):6995-7003.
65. Roguska A, Pisarek M, Andrzejczuk M, Dolata M, Lewandowska M, Janik-Czachor M. Characterization of a calcium phosphate/TiO₂ nanotube composite layer for biomedical applications. *Materials Science and Engineering: C*. 2011;31(5):906.
66. Roy SC, Paulose M, Grimes CA. The effect of TiO₂ nanotubes in the enhancement of blood clotting for the control of hemorrhage. *Biomaterials*. 2007;28(31):4667-72.
67. Brugnera MF, Rajeshwar K, Cardoso JC, Zanoni MVB. Bisphenol A removal from wastewater using self-organized TiO₂ nanotubular array electrodes. *Chemosphere*. 2010;78(5):569.

68. Cheng LW, Lan Sun, Hong Yun, Jing Li, Lai Y, Lin aCJ. Sonoelectrochemical synthesis of highly photoelectrochemically active TiO₂ nanotubes by incorporating CdS nanoparticles. *Nanotechnology*. 2009;20:1-6.
69. Craig AG. Synthesis and application of highly ordered arrays of TiO₂ nanotubes. *Journal of Materials Chemistry*. 2007;17:1451-7.
70. Macák JM, Tsuchiya H, Ghicov A, Schmuki P. Dye-sensitized anodic TiO₂ nanotubes. *Electrochemistry Communications*. 2005;7(11):1133-7.
71. Xu H, Tao X, Wang D-T, Zheng Y-Z, Chen J-F. Enhanced efficiency in dye-sensitized solar cells based on TiO₂ nanocrystal/nanotube double-layered films. *Electrochimica Acta*. 2010;55(7):2280.
72. Gan YX, Gan BJ, Su L. Biophotofuel cell anode containing self-organized titanium dioxide nanotube array. *Materials Science and Engineering: B*. 2011;176(15):1197-206.
73. Gong J, Lai Y, Lin C. Electrochemically multi-anodized TiO₂ nanotube arrays for enhancing hydrogen generation by photoelectrocatalytic water splitting. *Electrochimica Acta*. 2010;55(16):4776.
74. Capula Colindres S, Vargas García JR, Toledo Antonio JA, Chavez CA. Preparation of platinum-iridium nanoparticles on titania nanotubes by MOCVD and their catalytic evaluation. *Journal of Alloys and Compounds*. 2009;483:406-9.
75. Cardoso JC, Lizier TM, Zaroni MVB. Highly ordered TiO₂ nanotube arrays and photoelectrocatalytic oxidation of aromatic amine. *Applied Catalysis B: Environmental*. 2010;99(1-2):96.
76. Esbenshade JL, Cardoso JC, Zaroni MVB. Removal of sunscreen compounds from swimming pool water using self-organized TiO₂ nanotubular array electrodes. *Journal of Photochemistry and Photobiology A: Chemistry*. 2010;214(2-3):257.
77. Kefi BB, El Atrache LL, Kochkar H, Ghorbel A. TiO₂ nanotubes as solid-phase extraction adsorbent for the determination of polycyclic aromatic hydrocarbons in environmental water samples. *Journal of Environmental Sciences*. 2011;23(5):860.
78. Tupala J, Kemell M, Harkonen E, Ritala M, Leskela M. Preparation of regularly structured nanotubular TiO₂ thin films on ITO and their modification with thin ALD-grown layers. *Nanotechnology*. 2012;23:125707(7pp).
79. Peláez-Abellán E, Rocha-Sousa L, D. Muller W, C. Guastaldi A. Electrochemical stability of anodic titanium oxide films grown at potentials higher than 3V in a simulated physiological solution. *Corrosion Science*. 2007;49:1645-55.
80. Ruiz Barreto AN. Síntesis electroquímica y caracterización del polvo nanométrico de TiO₂. [Tesis de Diploma]. La Habana, Facultad de Química, Universidad de La Habana; junio de 2010.
81. Peláez Abellán E, Valdés Pedroso M, Núñez Valdés C, Rocha Sousa L, Utuni V, Guastaldi AC. Preparación de TiO₂ en polvo mediante oxidación anódica. *Revista CENIC Ciencias Químicas*. 2006;37(6):163-7.
82. Zwilling V, Darque-Ceretti E, Boutry-Forveille A, David D, Perrin MY, Aucouturier M. Structure and physicochemistry of anodic oxide films on titanium and Ti-6Al-4V alloy. *Surface and Interface Analysis*. 1999;27(7):629-37.
83. Gong D, Grimes CA, Varghese OK, Hu W, Singh RS, Chen Z, *et al*. Titanium oxide nanotube arrays prepared by anodic oxidation. *Journal of Materials Research*. 2001;16(12):3331-4.