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Electrochemical synthesis of self-organized TiO₂ crystalline nanotubes without annealing

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Abstract

The present work demonstrates that, upon anodic polarization in a aqueous fluoride-containing electrolyte, TiO₂ nanotube array films can be formed with a well-defined crystalline phase, rather than an amorphous one. The crystalline phase was obtained avoiding any high temperature annealing. We studied of the nanotubes formation in HF/H₂O medium and the development of crystalline grains on the nanotube wall and we found a facile way to achieve crystalline TiO₂ nanotube arrays through one-step anodization. The film crystallinity resulted to be influenced by the synthesis parameters and the optimization of the electrolyte composition and anodization conditions (applied voltage and time) has been carried out. For comparison purposes, crystalline anatase TiO₂ nanotubes were also prepared by thermal treatment of amorphous nanotubes grown in an organic bath (ethylene glycol/NH₄F/H₂O). The morphology and the crystallinity of the nanotubes were studied by Field Emission Gun Scanning Electron Microscopy (FEG-SEM) and Raman spectroscopy, whereas the electrochemical and semiconducting properties were analyzed by means of linear sweep voltammetry, impedance spectroscopy and Mott-Schottky plots. X-ray Photoelectron Spectroscopy (XPS) and Ultraviolet Photoelectron Spectroscopy (UPS) allowed us to determine the surface composition and the electronic structure of the samples and to correlate them with the electrochemical data. The optimal conditions to achieve a crystalline phase with high donor concentration were defined.

1. Introduction

Titanium dioxide (TiO_2 , titania) has been extensively investigated in recent year because of its outstanding catalytic, electrocatalytic and optoelectronic properties. More specifically, the nanocrystalline TiO_2 presents peculiar properties for potential use in photoelectrochemical solar cells, electrochromic windows, and batteries with Li-intercalation [1-7]. The crystallinity of TiO_2 is fundamental if biocompatible, catalytic and semiconductor properties are required [8].

Compared to conventional materials, nanocrystalline ones present several advantages for photoelectrochemical applications: these include a larger internal surface accessible to the electrolyte penetration in a porous framework, more efficient charge separation, and a larger ion conduction, while the transport distances for charge carriers become short inside these types of materials [1,2]. On the other hand, a noted drawback for these applications is the large density of states, which, if located in the bandgap result in electron-hole recombination processes and in electron transfer reaction at the oxide-electrolyte interface. However, the latter property can be regarded as an advantage for adsorption of redox-active compounds.

TiO_2 can be found in three different structures: anatase, rutile and brookite. The most suitable structure for applications such as dye sensitized solar cells and electrocatalysis is anatase. Instead, the rutile structures are employed for dielectric applications and high temperature oxygen gas sensors [9]. Lastly, brookite is a metastable phase and therefore does not lend itself easily to any applications. Compared to rutile, anatase titania offers higher electron mobility which is important for energy conversion devices [7]. Conversely, rutile has the advantage of a lower band gap, useful for photocatalytic applications.

Among the possible titania nanostructures, the nanotubular is of great interest due to its high surface to volume ratio and to the selected directionality of charge transport and the electrochemical formation of titania nanotubes has recently attracted a large attention [8-14]. The “first generation” TiO_2 nanotubes, produced by electrochemical anodization of titanium in a HF aqueous electrolyte, was able to generate arrays up to 500 nm in length [10]. Subsequently, by adjusting the composition of the electrolytes, the length was increased to over 6 μm [11]. Nanotube arrays with greatly extended length could be grown in various organic electrolytes (formamide, dimethyl sulfoxide, ethylene glycol) [12-14]. Since then, TiO_2 nanotube arrays have found potential applications in semiconductor devices [15], photovoltaic cells [16,17], and as carrier of catalysts [18,19] due to their microstructure and high specific surface.

However, the as-synthesized TiO_2 nanotubes are fully amorphous [20] while, as explained beforehand, crystalline materials are necessary for most applications [21]. Enhancing the crystallinity of nanotubes in solar cells is of paramount importance because it directly affects the electron transfer efficiency [22,23]. For this reason, the TiO_2 synthesis is usually followed by a thermal annealing

process [21-23] to obtain a nanocrystalline material, but the thermal treatment poses some constraints for their applications on polymeric substrate, which is a crucial step for the fabrication of flexible and lightweight devices.

Crystallization and phase transformation generally take place in the material through nucleation and growth processes [24]. In solid-state sintering, it is well known that the increase in temperature, combined with the phase transition from anatase to rutile, leads to grain growth, densification, and ultimately, at higher temperatures, to a structure collapse [25].

Multiple attempts have been described for achieving crystallization directly in the anodic bath without heat treatment. Examples include a report by Kunze et al. [26] who described the conversion of amorphous to nanoporous rutile in a fluoride-containing medium at room temperature. More specifically, it was reported the effect of pre-anodization on the crystallization of the titania film, which favors the formation of a thick crystalline nanoporous layer with rutile structure. It was suggested that the presence of fluoride ion could induce crystallization of rutile TiO_2 film in strong acid (phosphoric acid and hydrofluoric acid). Titanium substrate treatment prior to anodization was also found to promote crystallization of the anodic titania film. Another report by Allam et al. [27] describes the study of a two-step fabrication process for the crystallization of titania nanotube film. This work focused on the use of strong oxidizing agents to produce a thicker crystalline oxide layer which is subsequently converted a crystalline nanotube architecture film by anodization. The Ti foil sample was first treated at 80 °C in hydrogen peroxide containing electrolyte, before the anodization process in aqueous electrolyte with ammonium fluoride; this resulted into a purely anatase nanotube array film. Lastly, Xiao and co-workers reported the fabrication of anatase titania nanotube arrays in dimethyl sulfoxide electrolyte with a low HF concentration of 1.0 %, at temperatures between 40 °C and 60 °C. They suggested that, in addition to the increased potential, the high temperature is the driving force for ionic conduction which plays a key role in inducing the crystallization of nanotube array film [28].

The aim of the present work is to seek the possibility of obtaining crystalline TiO_2 nanotube array films while avoiding both pretreatment of the Ti and high temperature annealing, and using an aqueous electrolyte rather than an organic one at room temperature. The film crystallinity, influenced by the synthesis parameters, has been achieved through the optimization of the electrolyte composition and anodization conditions. For comparison purpose, TiO_2 amorphous nanotubes were prepared in organic bath (ethylen glycol/ $\text{NH}_4\text{F}/\text{H}_2\text{O}$) and subjected to thermal treatment with the aim of obtaining reference crystalline anatase phase.

2. Methods and materials

2.1. Anodization of titanium

Electrochemical anodization of Ti was carried out on titanium sheets (99.2% purity, Alfa Aesar), 0.5 mm in thickness, after ultrasonic cleaning in acetone (30 min) and ethanol (20 min). The electrochemical polarization was performed at room temperature in two different electrolytes: A) 400 mL ethylene glycol (EG) + 1.43 g NH_4F + 7 mL H_2O ; B) H_2O + HF 0.6÷11.1 g L^{-1} . A graphite disc was used as counter electrode. All chemicals were reagent grade.

Nanotubular TiO_2 were synthesized by anodization at a constant cell voltage in the following conditions: 28 V for 18 h in the case of the electrolyte A (sample NTG); 20 V for 16÷80 min in the case of the electrolyte B with 5.5 g L^{-1} of HF (samples NTW-16÷NTW-80). The NTG samples were also thermally treated (sample NTGT) in air at 450 °C for 2 h (up/down ramp 1 °C/min), to obtain the anatase phase, as reported elsewhere [29]. For the electrolyte B, the concentration of HF was varied from 0.6 to 11.1 g L^{-1} , by keeping the anodization parameters at 20 V for 50 minutes (samples NTW-0.6÷NTW-11.1). The cell potential was applied using a Sorensen's Suppliers mod. DCR150-12B system power supply and a Hewlett-Packard digital multimeter mod. 3457 was used for current acquisition, using a software compiled in LabVIEW.

The table 1 summarizes all the samples with the experimental conditions.

Table 1. Different samples of titania nanotubes and anodization conditions.

Sample	Electrolyte	Anodization parameters
NTG	400 mL EG+1.43 g NH_4F +7 mL H_2O	28 V / 18 h
NTGT	400 mL EG+1.43 g NH_4F +7 mL H_2O	28 V / 18 h + 450° C / 1 h
NTW-16	HF 5.5 g L^{-1} in H_2O	20 V / 16 min
NTW-25	HF 5.5 g L^{-1} in H_2O	20 V / 25 min
NTW-50	HF 5.5 g L^{-1} in H_2O	20 V / 50 min
NTW-65	HF 5.5 g L^{-1} in H_2O	20 V / 65 min
NTW-80	HF 5.5 g L^{-1} in H_2O	20 V / 80 min
NTW-0.6	HF 0.6 g L^{-1} in H_2O	20 V / 50 min
NTW-2.8	HF 2.8 g L^{-1} in H_2O	20 V / 50 min
NTW-5.5	HF 5.5 g L^{-1} in H_2O	20 V / 50 min
NTW-8.3	HF 8.3 g L^{-1} in H_2O	20 V / 50 min
NTW-11.1	HF 11.1 g L^{-1} in H_2O	20 V / 50 min

2.2. Physical-chemical characterization

The surface morphology of the titania nanotubes thus formed was characterized by using a LEO mod.1530 scanning electron microscope equipped with a field emission gun (FEG-SEM), operating in the 5–20 kV range. The geometric parameters (pore size, porosity and specific surface) were determined by an image analysis software (ImageJ 1.49q). For this purpose about 900 nanotubes were analysed in each sample and few samples were grown for each conditions (2 to 4).

Raman spectra were collected with a HORIBA Scientific LabRAM HR Evolution Raman spectrometer with an integrated Olympus BX41 microscope. Laser excitation wavelength of 532 nm (2.33 eV) was focused on the sample surface using a x100 magnification with a spot size of approximately 1 μm . Low laser power (below 1 mW) was used to minimize sample heating and possible damages. Because of possible inhomogeneity in the films, the spectra were recorded on ten different locations and averaged. Pure anatase (<25 nm) and rutile (<100 nm) powders (Sigma-Aldrich) were used as reference materials.

XPS and UPS experiments were carried out with a VG ESCALAB MKII spectrometer in UHV conditions (1.3×10^{-9} Torr). Mg Ka radiation at 1253.6 eV was used to acquire Ti2p spectra, while HeI radiation (21.2eV) was used for valence band spectra. The latter were acquired using a bias voltage of 10 V to avoid contribution of the secondary electrons generated in the channeltron detector region of the spectrometer, and the scale was calibrated as suggested by Schlaf [53]. Titania nanotubes were supported by a titanium foil, therefore calibration was made with the Ti substrate Fermi level.

2.3. Electrochemical characterization

For the electrochemical characterizations, a three electrode cell with a platinum counter electrode and a saturated calomel electrode (SCE) as reference was employed. All the electrochemical measurements were performed in a Na_2SO_4 1M (pH = 6.5) solution at room temperature, using a PARSTAT mod.2273 (PAR EG&G Inc.) potentiostat/galvanostat/FRA controlled by computer via PowerSuite software (PAR EG&G Inc.). The pH was chosen in such a way to attain an isoelectric condition [62] and avoid charging the TiO_2 surface with H^+ or OH^- ions.

In order to study the electrochemical properties of TiO_2 nanotubes, a set of linear sweep voltammetry measurements were carried out with a scanning rate of 10 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) allowed us to evaluate the properties of the different TiO_2 nanotubes under AC polarization. EIS experiments were conducted in the frequency range of 1 MHz to 50 mHz with an amplitude of 10 mV and a DC potential in the range of -0.5 to $+0.5$ V vs. SCE. In addition, Mott-Schottky experiments were carried out to evaluate the capacitance behaviour under DC potential polarization with the superposition of an AC signal ($V_{\text{ac}}=10 \text{ mV}$) at constant frequency in the range of 1 to 20 kHz. At each frequency the potential was scanned, from -1.0 V to 1.5 V vs. SCE, with a staircase profile ($\Delta V = 10 \text{ mV}$, delay 10 s).

3. Results and discussion

3.1. XPS analysis

All samples exhibit the well-known Ti 2p_{3/2} and Ti 2p_{1/2} peaks (figure 1) due to the Ti⁴⁺ state of stoichiometric TiO₂. The binding energy of Ti 2p_{3/2} (459.3 eV) in these nanocrystalline anatase TiO₂ films is in good agreement with results obtained from TiO₂ single crystals [30].

The XPS spectra for the NTG, NTGT and all NTW titania nanotubes, synthesized with different electrolytes and HF concentrations in the anodizing electrolyte, do not show any shift in the Ti 2p_{3/2} peak position and shape (figure 1).

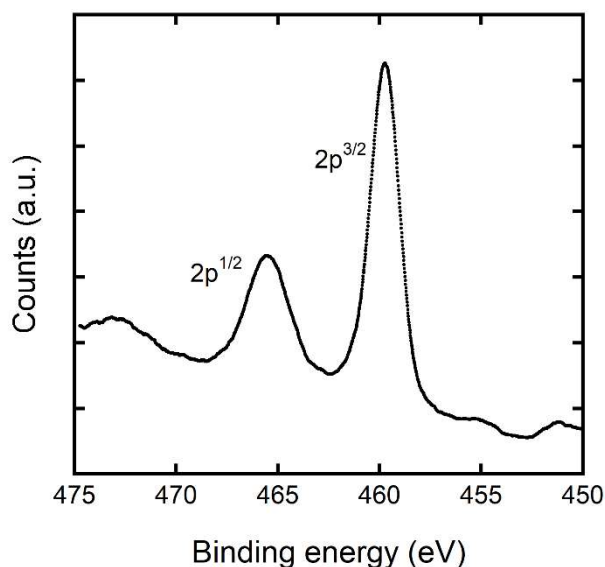


Figure 1. Typical XPS spectrum of the titania nanotubes.

3.2. Morphology of TiO₂ nanotubes

The FEG-SEM micrographs of two typical nanotube films are shown in figure 2 for HF/EG/H₂O electrolyte (figure 2a-b) and for HF/H₂O electrolyte (figure 2c-d). All the samples are composed of nano-scale tubular structures with differing mean pore size. The anodization conditions affect the average length and diameter of the nanotubes.

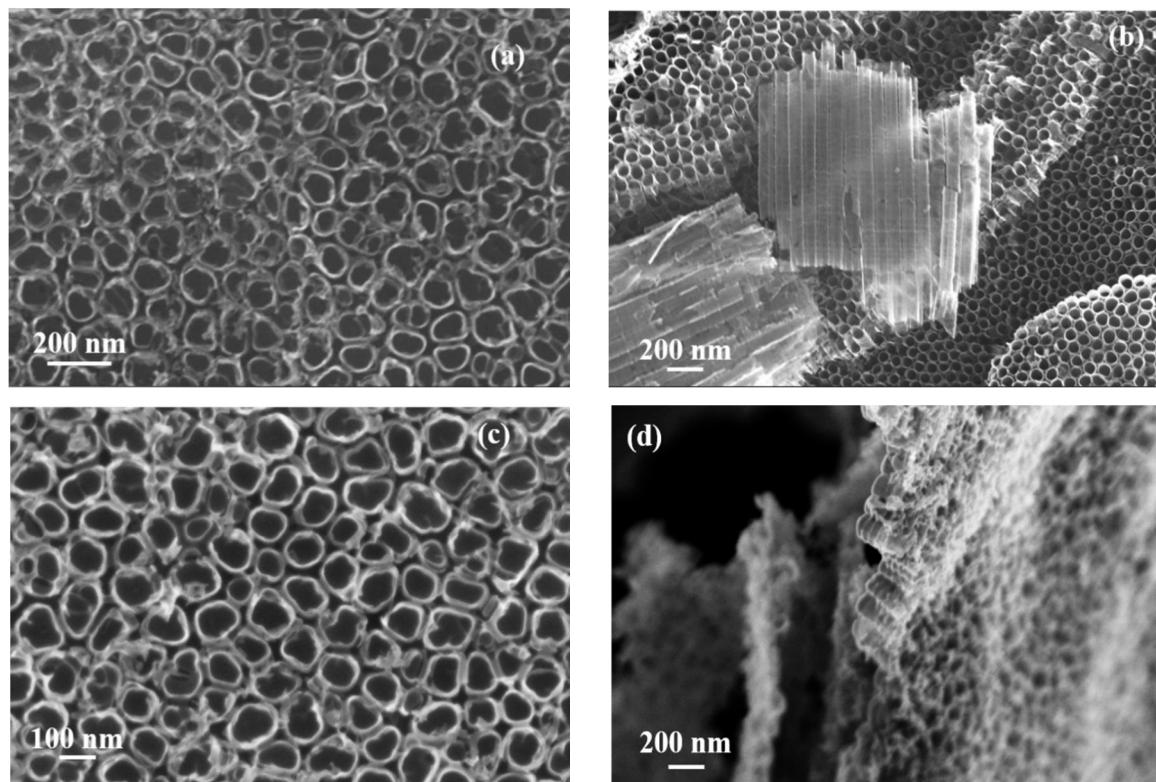


Figure 2. FEG-SEM images of TiO_2 nanotubes of NTG (a and b) synthesized in 400 mL ethylene glycol + 1.43 g NH_4F + 7 mL H_2O (ddp 28V, 18 h) and NTW samples (c and d) synthesized in HF ($0.6\div 11.1 \text{ g L}^{-1}$) + H_2O (ddp 20 V, $16\div 80 \text{ min}$).

The morphological parameter of the synthesized nanotubes (pore inner diameter d_i , pore outer diameter d_e , tube length L) were estimated from the analysis of FEG-SEM images.

The wall thickness of the pores (d_w) can be calculated as follows:

$$(1) \quad d_w = \frac{d_e - d_i}{2}$$

The porosity (P) is defined as a ratio of a surface area occupied by pores to the whole surface area while the pore density (n_p) is defined as the total number of pores occupying the surface area of 1 cm^2 . These parameters can be estimated from the following formulas [31]:

$$(2) \quad P = \frac{\pi}{2\sqrt{3}} \left(\frac{d_i}{d_e} \right)^2$$

$$(3) \quad n_p = \frac{10^{14}}{\sqrt{3d_i^2}}$$

The total surface area of a nanotube (A) can be derived from the following formula [32]

$$(4) \quad A = 2\pi(d_e^2 - d_i^2) + 2\pi L(d_e + d_i)$$

The first term represents the areas of the two tube rings of the edges, while the second term represents the areas of internal and external curved surface. The specific surface area per cm^2 (A_s) can be estimated from

$$(5) \quad A_s = An_p$$

On the basis of the above equations the wall thickness, porosity, nanotube density and specific surface were calculated for the different samples and the results are shown in Table 2.

Table 2. Geometric parameters of anodic titania nanotubes (d_i : inner pore diameter; d_e : external pore diameter; d_w : wall thickness; L : nanotube length; P : porosity; n_p : pores density; A_s : specific surface area).

Sample	d_i / nm	d_e / nm	d_w / nm	L / nm	P / %	n_p / cm^{-2}	A_s / $\text{cm}^2 \text{cm}^{-2}$
NTG	63	86	11.5	1000	49	9.2×10^{11}	197
NTGT	71	86	7.5	1000	62	8.1×10^{11}	120
NTW-16	84	106	11.0	200	57	6.9×10^{11}	180
NTW-50/NTW-5.5	63	77	7.0	200	61	9.2×10^{11}	113
NTW-11.1	104	135	15.5	200	54	5.6×10^{11}	258

The anodizing conditions (electrolyte composition, applied voltage and time) have a marked effect on the morphological parameters. The NTG sample presents a mean pore size of 63 nm and a length of 1 μm . After the heat treatment (NTGT), the mean pore size increased to 71 nm, while the mean wall thickness decreased from 23 to 15 nm, and the length remained at 1 μm . Further, the porosity increased, but the specific surface area decreased due the reduction of pore density.

In the case of NTW samples the morphological parameters changed as a function of the anodization conditions (anodization time, HF concentration). The mean pore size was in the range 63÷104 nm, wall thickness 7÷15.5 nm and the length remained constant at 200 nm. Varghese et al. [33] demonstrated that it is not possible for nanotubes to grow longer than 500 nm in acidic aqueous electrolytes due to their high dissolution rate.

It is interesting to note that the wall thickness and porosity are very similar for NTGT and NTW-5.5 samples (both present the smaller value for d_w and the higher one for P). The sample NTW-5.5 shows the highest pores density and the lower specific surface. Aside from the length of nanotubes, samples

NTGT and NTW-5.5 show very similar morphological characteristics, even if prepared under very different anodizing conditions and despite sample NTGT having undergone a thermal treatment.

3.3. Raman analysis of TiO_2 nanotubes

The Raman spectra of pure commercial anatase and rutile [<http://rruff.info/>] are shown in figure 3a with the following characteristic peaks and assigned vibration modes: 142 cm^{-1} A(Eg), 396 cm^{-1} A(B1g), 516 cm^{-1} A(B1g) and 639 cm^{-1} A(Eg) cm^{-1} for anatase; 240 cm^{-1} R(Eg), 448 cm^{-1} R(Eg), 613 cm^{-1} R(A1g) cm^{-1} for rutile.

The Raman spectra of prepared NTG (amorphous) and thermally treated NTGT (crystalline) are shown in figure 3b. After the thermal treatment, the formation of crystalline anatase phase is evident from Raman spectra, with the following characteristic peak: 145 , 396 , 517 and 640 cm^{-1} . The A(Eg) peak at 145 cm^{-1} , a characteristic of anatase TiO_2 , becomes broader and shifts with respect to that of a bulk TiO_2 crystal. Phonon confinement is the main cause of this phenomenon. In addition, the occurrence of the intense anatase E_g mode indicates that the TiO_2 nanocrystals possess a certain degree of long-range order. The position shift and broadening of the peaks compared to the larger crystalline size samples can be explained using the quantum confinement effect [34].

In the case of NTW samples the Raman spectra were compared to the pure anatase and rutile ones. It is evident that there is a possibility to obtain crystalline titania nanotubes directly by titanium anodization avoiding heat treatment (figure 3c). However, the HF concentration plays a key role in the achievement of anatase phase, as shown in figure 3d, where an increase in HF concentration from 5.5 to 11.1 g L^{-1} led to a mixed anatase/rutile phase. In fact, in addition to anatase modes, three active Raman bands at 256 , 428 and 613 cm^{-1} are seen for the nanotubes type NTW-11.1. These bands corresponds to rutile phase, which is in accordance with earlier reports [26].

Other interesting information can be derived from Raman spectra of titania nanotube. In NTW samples (figure 3c-d), the most intense anatase E_g peak is largely blue-shifted (9 - 15 cm^{-1}) and broadened (19 - 33 cm^{-1}) with respect to bulk anatase, where it is centred at 142 cm^{-1} and has a FWHM of 8 cm^{-1} . In addition, in the sample with mixed phase anatase/rutile (figure 3d), the rutile E_g peak at 448 cm^{-1} also shows an evident red-shift of approximately 22 cm^{-1} . The quantum confinement effect is not enough to account for the changes observed in the Raman spectra of NTW samples. Several works have shown that other factors influencing the shape and position of Raman peaks of nanostructured TiO_2 are stoichiometry defects [35,36]. Moreover, the spectra decomposition reveals that TiO_2 characteristic peaks are superimposed to a photoluminescence (PL) band centred at about 2.36 eV (figure 3c-d inset) typically attributed to the formation of oxygen vacancies [37].

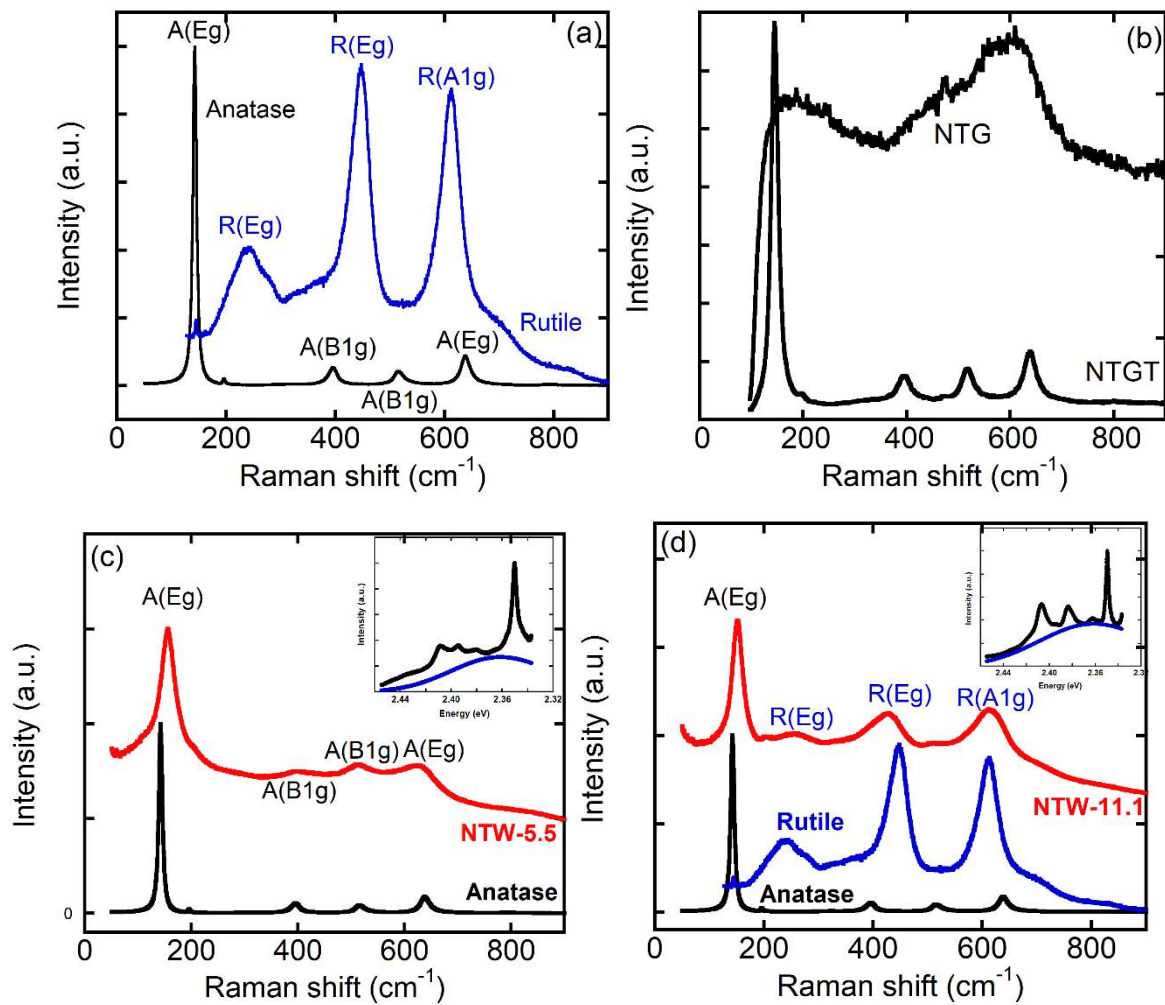
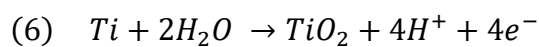


Figure 3. Raman spectra of different TiO_2 nanotubes type: (a) anatase and rutile powder; (b) NTG sample as anodized and after heat treatment at $450\text{ }^\circ\text{C}$ for 1 h (NTGT); (c) NTW-5.5 sample (20 V, 50 min, 5.5 g L^{-1} HF in H_2O); (d) NTW-11.1 sample (20 V, 50 min, 11.1 g L^{-1} HF in H_2O).

3.4. Formation mechanism of nanotubular layers

The anodization in electrolytes with fluoride ion concentration in the range of 0.5–1 wt% results in the formation of homogeneous porous structures [35]. The phenomena of dissolution and pore formation have been attributed to the presence of fluoride ions in the electrolyte while the presence of water in the electrolyte is essential, as it acts as source of O^{2-} ions and helps the growth of TiO_2 . During the TiO_2 nanotubes synthesis an electrical field builds up across the oxide: such field ensures Ti oxidation, O^{2-} ions transport inward and Ti^{4+} ions outward, thus leading to a continuous growth of the film. The general anodic reaction can be written as in Eq. (6) [38,39]:



The production of H^+ ions at the metal surface leads to a local pH decrease.

In figure 4, the typical current transients recorded during the anodic growth of nanotube layers in different anodizing electrolytes are shown. Unlike morphology, there appear to be differences in the rate of nanotube formation, but common features can be observed: (i) an initial burst of current due to the rapid formation of an oxide layer over the surface of titanium, (ii) an exponential decay that is ascribed to the competition between pore nucleation process and growth of inner-barrier layer and (iii) a relative stabilization of the current corresponding to the continuous tubes formation.

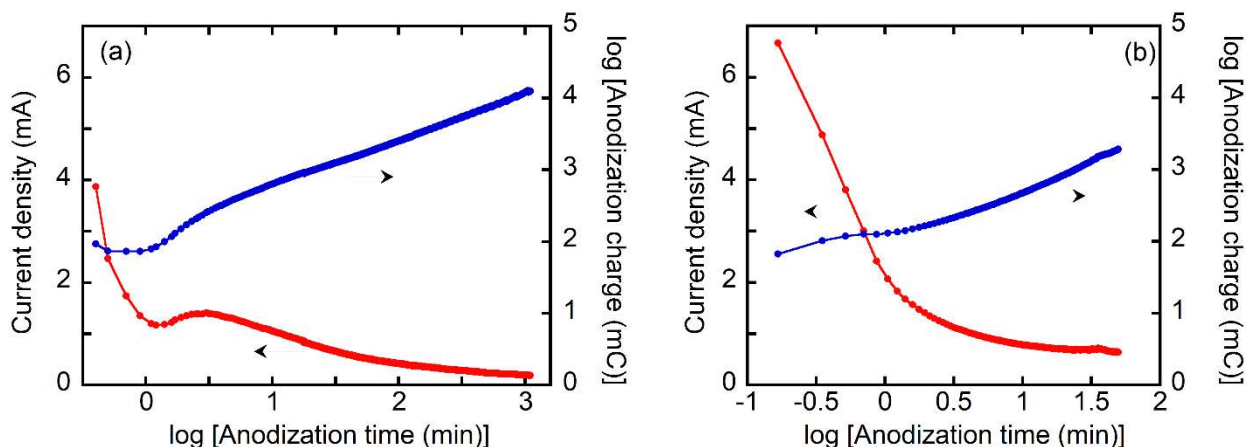


Figure 4. Typical current and charge transients recorded during Ti anodization for NTG (a) and NTW (b) samples.

The charge consumed during the anodization was obtained by integrating the current vs time curve. After the initial stage, a linear dependency of the charge with time was observed in a log-log plot for nanotubes formed in both electrolytes, indicating that the process had attained steady state [40].

The amount of the charge is similar for the NTG and NTW samples, which were achieved with different anodization times (shorter for NTW samples). This implies that the processes have different mechanisms and in the case of NTW samples more energy is transferred during the anodization.

For the NTW samples, a marked dependence of the total charge on the hydrofluoridric acid concentration and anodization time was observed, with a minimum value for a concentration of 5.5 g L⁻¹ (figure 5a) and an anodization time of 50 min (figure 5b). A lower charge reflects a reduced dissolution of the TiO₂ and therefore a more stable and less defective oxide. Therefore the samples NTW-50/NTW-5.5 were synthesized in the most appropriate conditions.

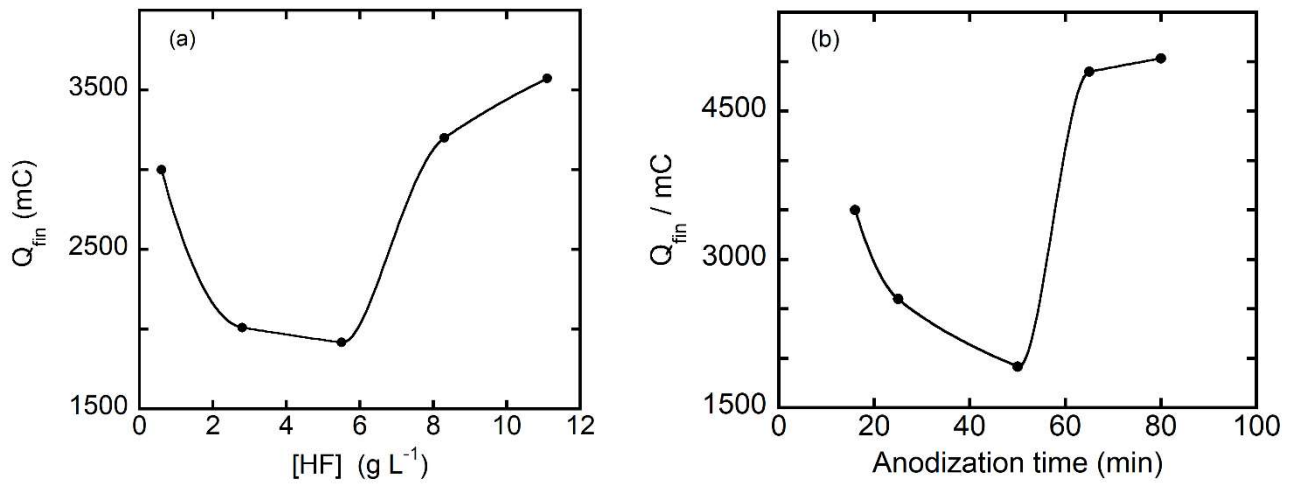
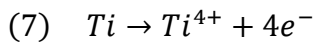
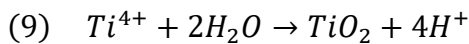
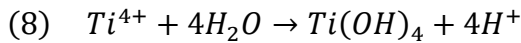


Figure 5. Total anodization charge for NTW samples as a function of: (a) HF concentration (20 V, 50 min) and (b) anodization time (20 V, 5.5 g L⁻¹ HF in H₂O).

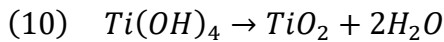
Eq.6 can be split in two components: (1) the reactions which occur at the anode are the oxidation of the metal which releases Ti⁴⁺ ions and electrons:



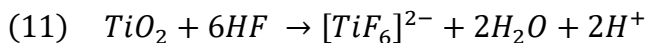
And (2) the combination of Ti⁴⁺ ions with OH⁻ and O₂⁻ species provided by the water, accounting for the hydrated anodic layer (via OH⁻) and the oxide layer (via O₂⁻) [21]:



By decomposition of the hydrated layer, with water release, further oxide is produced:

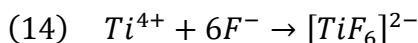
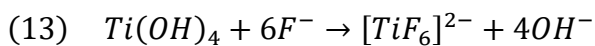
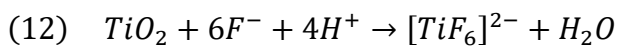


In HF electrolyte, the oxide is chemically attacked with a resulting formation of soluble fluoride complexes:



Furthermore, the fluorine ions can attack the oxide and the hydrated layer, as described in the Eqs.

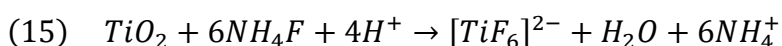
(12) and (13), or react with Ti⁴⁺, Eq. (14):



During the onset of anodic oxidation, the current drops significantly indicating the formation of a barrier oxide. The field-enhanced oxidation (high field theory) occurs at the metal-oxide interfaces while the field-enhanced dissolution of TiO_2 as $[\text{TiF}_6]^{2-}$ occurs at the oxide–electrolyte interface [8,21]. Hence, oxide formation and dissolution occur simultaneously until an equilibrium is attained between these two processes.

In the presence of fluoride ions, pores start to grow when the oxidation and dissolution rates reach the steady state. Clearly, the competition between oxide formation and its dissolution, is the key factor in determining the anodic produced titanium oxide structure [41].

In the case of the organic base electrolyte (sample NTG) the localized dissolution is mainly attributed to the presence of fluoride from ammonium fluoride:



The reactions mentioned above will take place simultaneously and this equilibrium process controls the time-scale of developed porosity, the self-ordering effects and the thickness [46]. The dissolution rate of the oxide layer, which is a function of pH of the electrolyte, influences the thickness of the porous layer.

3.5. Electrochemical characterization

3.5.1. Linear sweep voltammetry

From the current-potential (I–U) curves of Ti/TiO₂ electrodes (figure 6) it is clear that they do not exhibit any polarization current when the anodic potential is below 2 V vs. SCE. This value is more positive than the theoretical potential of O₂ evolution by the electrolyzing reaction ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$, $U = 0.845 \text{ V vs. SCE}$ at pH=6.5), due to the high overpotential effect of the TiO₂ semiconductor. Instead, in the cathodic region the current sharply increases at potentials below –0.1 V vs. SCE for the $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ reaction. These results demonstrate a typical characteristic of n-type semiconductor [17,42]: diode-like I–U characteristics at semiconductor TiO₂/electrolyte interface (i.e., current-blocking characteristics in the anodic direction and current-passing behaviour in the cathodic direction) are dominated by majority carrier transfer, i.e., by the exchange of electrons via the conduction band.

The process observed at the most negative potentials has been attributed to charge accumulation in the conduction band or to the filling of traps just below the conduction band.

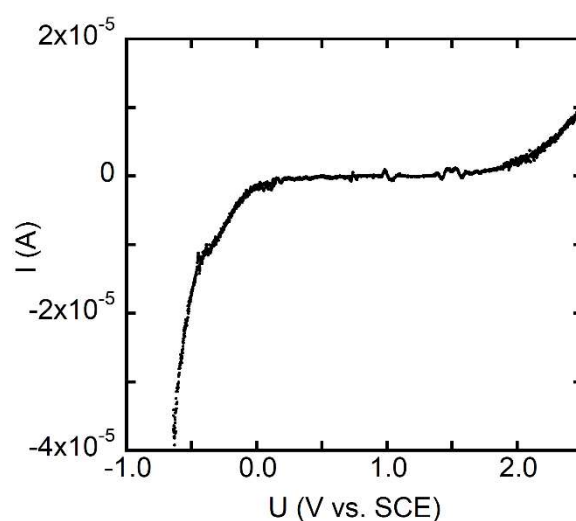


Figure 6. Typical LSV of titania nanotubes in Na_2SO_4 1 M.

3.5.2. Electrochemical impedance spectroscopy (EIS)

The EIS data for TiO_2 nanotubes are difficult to analyse in a complex plane plot (Nyquist diagram) [46,48,49]. For this reason, Bode plots of the phase angle were used to better highlight the low and high frequency features. From the Bode plot it is possible to discriminate two different frequency time constants (Figure 7a).

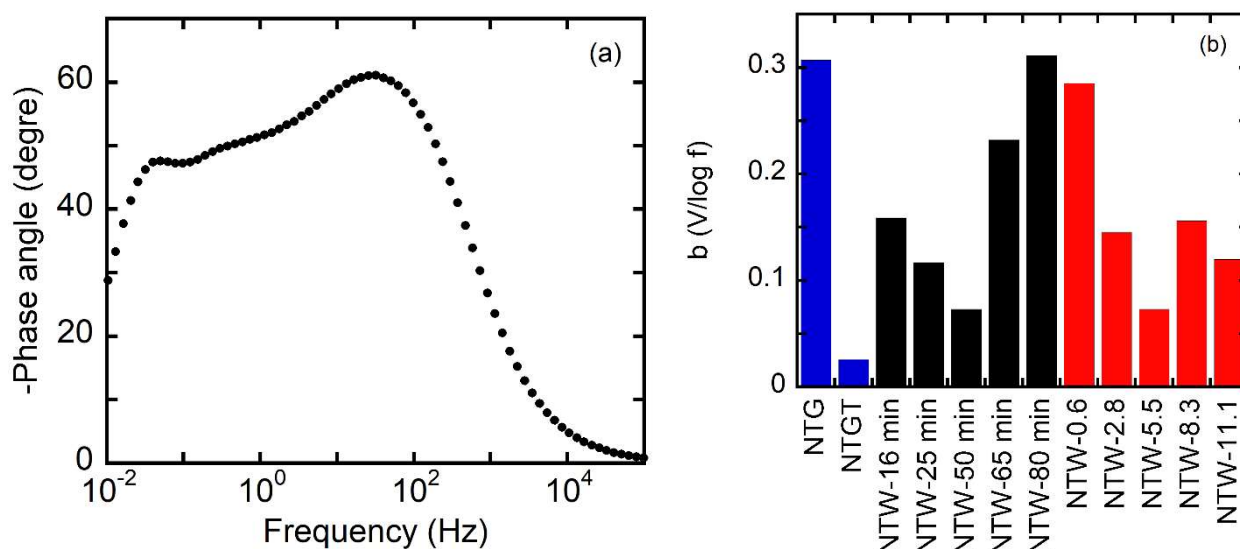


Figure 7. Typical Bode diagram for the phase of TiO_2 nanotubes (a). Mean electron time-life, for different electrochemical potential in the range $-0.5 \div +0.5$ V vs. SCE, for different type of TiO_2 nanotubes (b).

The higher frequency time constant is relative to the electron transport in the TiO₂ and it allows to derived the life time (t_e) of electrons, using the following relationship [44-46]:

$$(16) \quad t_e = \frac{1}{2\pi f_e}$$

where f_e is the frequency for the maximum phase angle. This parameter, which lays in the range 0.3÷2.3 ms, is a function of the DC polarization. Furthermore, the electron lifetime t_e is also function of anodization time and HF concentration in the anodizing electrolyte for NTW samples (figure 7b). The TiO₂ nanotubes prepared in HF 5.5 g L⁻¹ in water at 20 V for 50 min, have the longest electron lifetime, assuring a reduced electron recombination. The effective reduction of electron recombination leads us to expect a significantly enhanced efficiency when using such material as a photo-electrode. The anodization time necessary to achieve the maximum t_e , is fairly independent of the polarization potential in the range (-0.5 ÷ +0.5) V vs. SCE.

It is interesting to note that the value of t_e changes with the type of TiO₂ nanotube (figure 7b). More in particular, it is around 0.7 ms for the NTG sample, and rises at 1.1 ms after the heat treatment (NTGT). In the case of NTW samples, a marked increase was obtained for the sample with an anodization time higher than 16 min, with a maximum value (2.2÷2.3 ms) at the anodization time of 50 min. After this anodization time, the electron lifetime starts to decrease and for an anodization of 80 min the t_e value is half that of NTG. The low t_e for NTW-16 can be attributed to the amorphous nature of this material, as revealed by Raman spectroscopy. The low t_e value for NTW-11.1 sample is rather due to the presence of the rutile phase (figure 3d).

3.5.3. Mott Schottky analysis

The Mott-Schottky analysis is based on the study of the space charge capacitance (C_{sc}) as a function of the applied electrochemical potential. Capacitance changes are related to the electronic properties of the passive film close to the electrolyte/oxide interface, and are described by the Mott-Schottky equation [47,48]:

$$(17) \quad \frac{1}{C_{sc}^2} = \frac{2}{\epsilon_0 \epsilon_r} \left(U_p - U_{fb} - \frac{kT}{e} \right)$$

where ϵ_0 is the vacuum permittivity (8.85×10^{-14} F cm⁻¹), ϵ_r is the dielectric constant (80), e is the electron charge (1.6×10^{-19} C), N_d is the donor density (cm⁻³), U_p and U_{fb} are the polarization and the flat-band potential (V vs. SCE), respectively.

Mott-Schottky plots for NTG and NTW nanotubes are shown in figure 8, and allowed us to determine the semiconducting properties of the oxide film: conduction type (n or p), charge carrier density (N_d)

and flat band potential (U_{fb}). The plots in figure 8 display positive slopes, indicating n-type semiconducting behaviour. Titanium interstitial Ti^{4+} ions and oxygen vacancies are considered as donor-type impurities and contribute to an excess of electrons in the TiO_2 , resulting in an increase of the electrical conductivity and n-type conductivity.

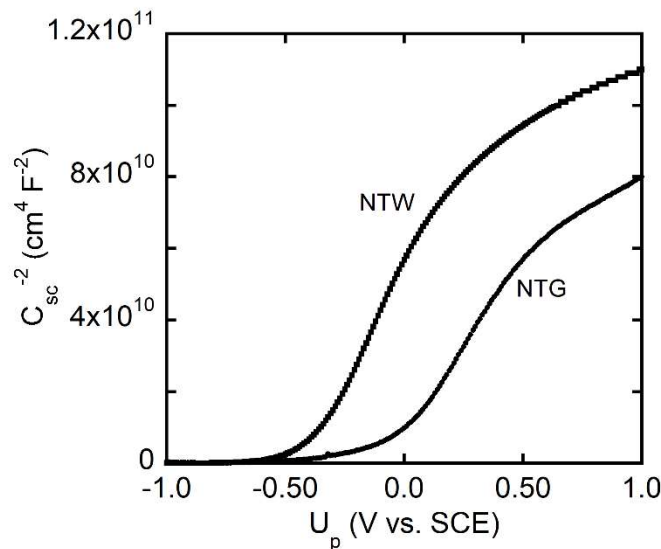


Figure 8. Typical Mott-Schottky plot of NTG and NTW titania nanotubes (U_p : $-1.0 \div +1.0$ V vs. SCE; V_{ac} : 10 mV rms; $f=2$ kHz).

When the applied potential is increased, the region close to the electrolyte is depleted of electrons and thus a region of uniform donor density forms close to the metal/film interface [57]. Mott Schottky analysis can be considered valid since the measured capacitance decreases with the applied potential, implying that space charge contribution is dominant over the Helmholtz capacitance.

Mott-Schottky plots may show a wide variation with the frequency for the case of porous and defective oxide structures and it is often difficult to select a frequency for the analysis. It has been recommended by some authors [49] that a frequency greater than 1 kHz, together with relatively higher scan rates should be employed, provided that the ionic conductivity is negligible and the response is mostly due to electronic conductivity.

In the linear portion of the Mott-Schottky plots, the flat-band potential (U_{fb}) values can be derived from the intercept to potential axis. From the thermodynamic point of view, the Fermi level (E_F) is the electrochemical potential of the electrons in the solid, and describes the population of energy levels in a semiconductor at thermodynamic equilibrium. After the contact of the semiconductor surface with the electrolyte, a new thermodynamic equilibrium on both sides of the interface must be established. In other words, the Fermi level of the semiconductor E_F is adjusted to the Fermi level of the electrolyte $E_{F,redox}$. The potential drop in the space-charge layer can be derived as $U_{sc}=U_{appl}-U_{fb}$ (with external polarization) or $U_{sc}=U_{F,redox}-U_{fb}$ (without external polarization), where U_{appl} is the

externally applied potential and U_{fb} is the potential at which $U_{sc} = 0$ and the bands in the semiconductor are “flat” (flat-band potential).

The dispersion of flat-band potential with the measurement frequency, can be used to monitor the crystallinity of TiO_2 nanotubes [46]. In figure 9a this dispersion is shown, where a high slope for the line $U_{fb}=a+b \cdot \log f$ (f is the measurements frequency), is indicative of a large dispersion. The amorphous NTG sample presents a high slope which is strongly reduced after the heat treatment at $450^\circ C$ (NTGT sample). This behaviour is attributed to the transition from amorphous to crystalline (anatase) structure, confirmed by Raman spectroscopy (figure 3b).

The anodization time and the hydrofluoric acid concentration play an important role in the reduction of the slope of the equation U_{fb} vs. $\log f$, as shown in figure 9b. Particularly, the HF concentration must be higher than 2.8 and lower than 8.3 g L^{-1} , while the optimal anodization time is 50 min .

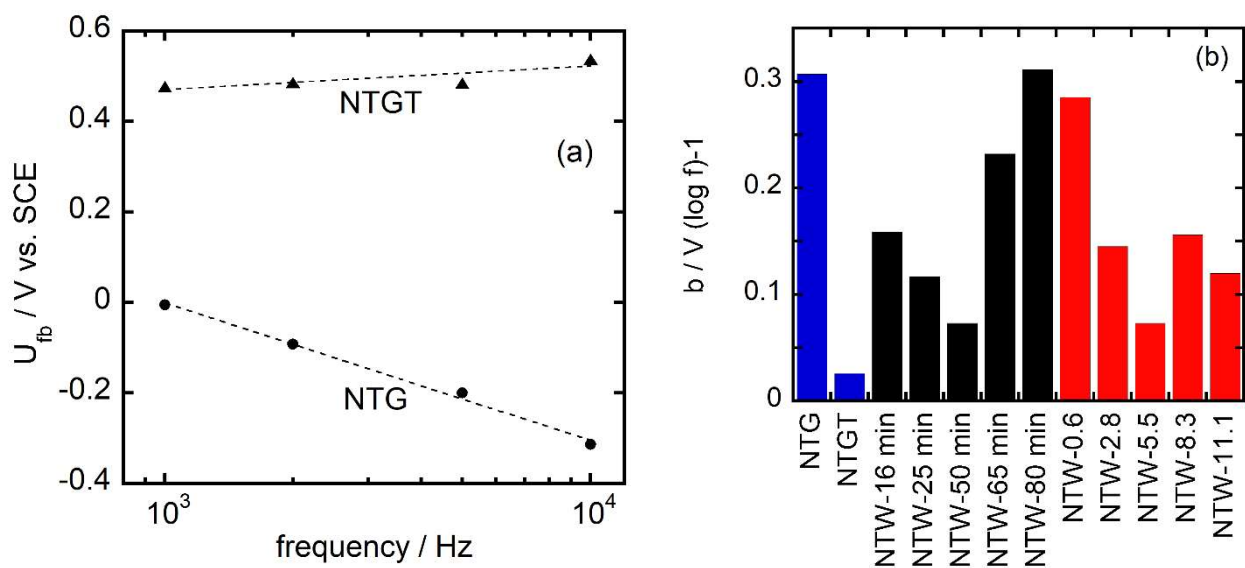


Figure 9. Flat-band potential, as a function of measuring frequency, for as anodized (NTG) and thermally treated (NTGT) TiO_2 nanotubes (a). Slope for the straight line $U_{fb}=a+b \log f$ as a function of TiO_2 nanotubes type (b).

A comparison of U_{fb} vs. $\log f$ dispersion shows that 50 min of anodization time in HF/H_2O allows a value not far from that of the TiO_2 nanotubes synthesized by anodization for 18 h in $HF/EG/H_2O$ and then thermally treated at $450^\circ C$ (figure 9 b). Instead, the NTW-80 sample shows a high slope, very close to that of NTG sample, indicating an amorphous phase.

The charge carriers concentration (N_d) can be calculated using the slope of the Mott-Schottky plot through the following equation:

$$(18) \quad N_d = \left(\frac{2}{\epsilon_0 \epsilon_r e} \right) \left[\frac{d \left(1/C_{sc}^2 \right)}{dU} \right]$$

The N_d values are of the order of 10^{20} cm^{-3} , consistent with other reports on TiO_2 nanotube arrays [47,48,50] and typical of highly doped semiconductors. N_d changes with anodization time, achieving a maximum value of $5.7 \times 10^{20} \text{ cm}^{-3}$, for 50 min. This is the highest value among the examined samples, with a fivefold increase with respect to the NTG samples.

Higher N_d values indicate a larger upward shift of the Fermi level, resulting in a significant energy band bending at the oxide surface [51], which will eventually help charge separation at the TiO_2 nanotubes/electrolyte interface. In addition, a high N_d also improves the charge conductivity of a semiconductor and enhances the photo-electrochemical performance.

A comparison between the donor densities of the TiO_2 nanotubes samples shows that the NTW samples have the highest N_d if prepared in HF 5.5 g L^{-1} in water at 20 V for 50 min.

In general, anodically grown oxide films are always non-ideal and non-stoichiometric with an excess of metal cations or a deficiency of oxygen anions. According to the point defect model (PDM), the n-type semiconducting behaviour indicates that the defects are oxygen vacancies and/or a few interstitial titanium ions, and the evidence for this defective nature has been reported earlier [64]. Mixed phases of anatase and rutile are achieved increasing the anodization time (Raman spectra in figure 3d) and showed lower N_d compared to the other TiO_2 nanotubes.

3.5.4. Energetics of TiO_2 nanotubes

It is important to realize that the fundamental basis for all photochemical applications of TiO_2 is represented by its semiconducting properties and electronic structure. It is the energy band structure that controls the photo/electrochemical activity of TiO_2 -based materials. The position of the band edges with respect to the electrochemical potential scale exerts a crucial influence on the operation of the photochemical system. The positions of the conduction and valence band edges determine the reductive and oxidative power of photo-generated electrons and holes, respectively.

The precise determination of the band edge position is very rarely determined experimentally. This is due to the fact that the band edge positions of TiO_2 -based materials will normally be a function of the surface charging. This will be highly dependent not only on the ionic conditions of the electrolyte (pH, specific adsorption of ions), but also on the surface structure and composition of the material, which, in turn, will depend on the particular synthesis strategy during its manufacturing [65].

Energy band parameters can be calculated from the LSV data (figure 6), considering the electrochemical potential onsets for reduction ($U_{\text{red,onset}}$) and oxidation ($U_{\text{ox,onset}}$). Using these two parameters, the Conduction Band Minimum (CBM) and Valence Band Maximum (VBM) were calculated, and the energy band gap (E_g) was derived. For the calculation of the energies the following relationship between energy levels ($E_{\text{red/ox}}$) and electrochemical potential ($U_{\text{red/ox}}$) was used [42]

$$(19) \quad E_{red/ox} = -4.5 - eU_{red/ox}$$

where $U_{red/ox}$ is the electrochemical potential relative to the normal hydrogen potential (NHE).

In Table 3, energy band parameters (CBM, VBM, E_g), flat band potential in energy scale (E_{fb}) and donor concentration (N_d), derived from electrochemical measurements, are summarized. The difference between Fermi level (E_F) and CBM are also reported. Literature data, calculated from spectroscopic measurements, for CBM, VBM and E_g are also shown in Table 3 for a comparison.

Table 3. Energy band parameters derived from electrochemical measurements. The vacuum level was assumed as reference level ($E_{vac}=0$ eV).

Sample	¹ CBM (eV)	¹ VBM (eV)	¹ E_g (eV)	² E_{fb} (eV)	² $N_d \times 10^{-20}$ (cm ⁻³)	²⁻¹ E_F -CBM (eV)
NTG	4.25	7.51	3.26	4.54	1.2	0.29
NTGT	4.20	7.52	3.32	4.37	1.1	0.17
NTW-0.6	4.34	7.59	3.26	4.16	3.9	-0.18
NTW-2.8	4.33	7.57	3.24	4.15	5.0	-0.18
NTW-5.5	4.31	7.42	3.11	4.12	5.7	-0.18
NTW-8.3	4.31	7.41	3.10	3.90	5.1	-0.41
NTW-11.1	4.31	7.40	3.09	3.87	3.9	-0.44
Ref. [59]	4.1	7.4				
Ref. [60]	3.6	6.9	3.3			
Ref. [61,62]	4.1	7.3				
Ref. [63]	4.2					
Ref. [64]			3.2			
Ref. [65]			3.1			

(1) from linear sweep voltammetry (LSV); (2) from Mott-Schottky plot (MS)

The measured values of VBM and CBM of NTW, both decrease with the HF concentration. The band gap of the TiO₂ nanotubes is also influenced by HF concentration: lowering the bath pH leads to a decrease of the E_g value, from 3.26 to 3.09 as the HF concentration rises. It should be noted tyhat, in the NTW case, there is a marked decrease of E_g (up to 7%) with respect to the NTG and NTGT samples.

Similarly, the flat band potential lowers as a function of HF concentration. Since the flat band potential denotes the position of the Fermi level with respect to the potential of the reference electrode

[52], the decrease of E_{fb} may be related to the increase of oxygen vacancies and interstitial positions which affect the band position. The position of the Fermi level for an extrinsic n-type semiconductor is close to the conduction band, but it depends on the donor concentration. Due to its inherent non-stoichiometry (oxygen vacancies are confirmed by Raman spectra), TiO_2 is typically a rather heavily doped n-type semiconductor. This means that its Fermi level (E_F) is typically right below the conduction band edge (CBM) [52] (figure 10a). The value of the difference between U_{fb} and CBM (Table 3) can help to determine if the semiconductor is extrinsic or degenerate. This difference is positive for NTG and NTGT samples is positive, indicating an extrinsic semiconductor (figure 10a). On the contrary, it is always negative for the NTW samples, that is indicative of a degenerate n-type semiconductor (figure 10b).

The variation of the Fermi level are due to the well-known Burstein-Moss shift of the E_F with doping [50]. The difference $E_F - VBM$ tells us the amount of carrier doping that has been achieved.

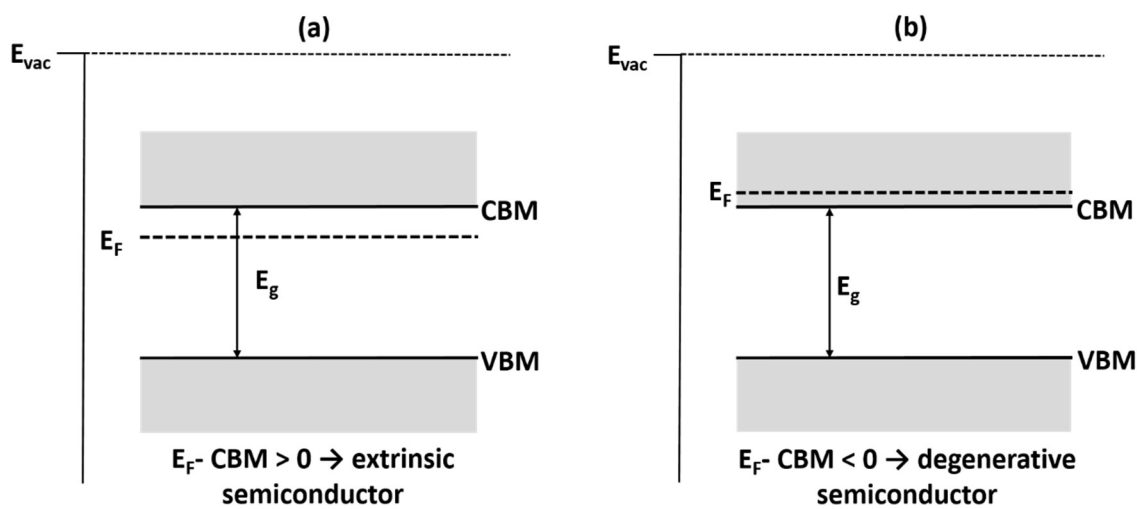


Figure 10. Energy levels for different type of n-type semiconductor titania nanotubes with flat bands to the surface : (a) NTG and NTGT (extrinsic); (b) NTW series (degenerate). The vacuum level was assumed as reference level ($E_{vac}=0$ eV). VBM=valence band maximum, CBM=conduction band minimum, E_F =Fermi level, E_g =band gap.

3.6. UPS analysis

Both TiO_2 polymorphs are semiconductors with band gaps of 3.1 eV for rutile and 3.2 eV for anatase [63-65]. Ultraviolet photoelectron spectroscopy (UPS) can be employed to study the valence band (VB) of oxides [30,55]. The analysis of the He I spectrum allows the determination of both the work function and the valence band maximum (VBM).

In figure 11 an example of the collected spectra is presented. The adopted calibration makes the low kinetic energy secondary electron cutoff (LCO) coincide with the work function (WF). The latter is defined as the energy necessary to remove an electron originally at the Fermi level deep inside the

material and place it at rest at a point in free space just outside the surface, i.e. at E_{vac} . Therefore, the measured WF correspond to the Fermi level of the sample [66], as shown in figure 10a. The valence band maximum (VBM) is given by the energy difference between the He I photon energy (21.2 eV) and the width of the valence band (VBW), the latter being the difference between the high kinetic energy cut-off (HCO) and the low kinetic energy cut-off (LCO).

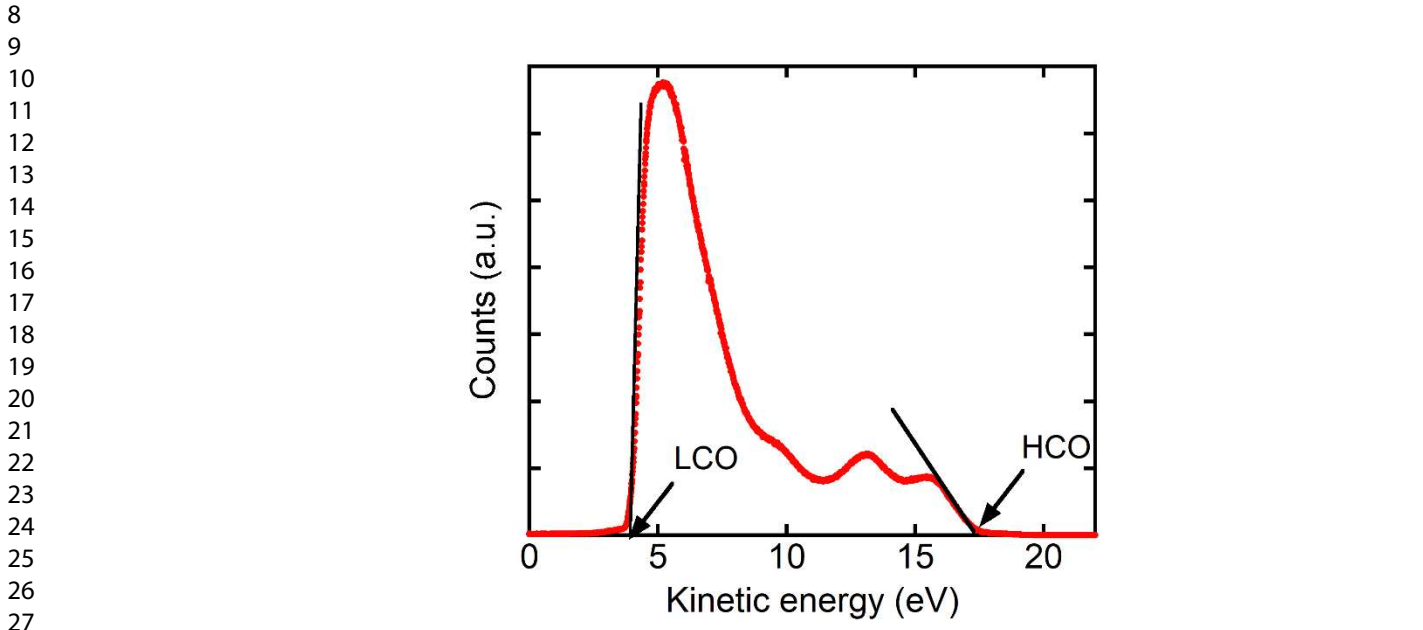


Figure 11. UPS spectrum for NTG, NTGT and NTW samples. Regions at low and high energy were used to calculate E_F and VBM.

A comparison of the VBM value, derived from UPS and electrochemical data (Table 4), shows a difference in the range (1.1÷2.8) %, confirming the overall consistency of the two methods.

Table 4. Energy band parameters derived from electrochemical and UPS measurements.

Sample	¹ VBM (eV)	² E_{fb} (eV)	³ VBM (eV)	³ WF (eV)
NTG	7.51	4.54	7.63	4.02
NTGT	7.52	4.37	7.60	3.97
NTW-0.6	7.59	4.16	7.38	3.83
NTW-2.8	7.57	4.15	7.68	4.10
NTW-5.5	7.42	4.12	7.63	4.05
NTW-8.3	7.41	3.90	7.33	3.72
NTW-11.1	7.40	3.87	7.27	3.56

(1,2) from electrochemical data; (3) from UPS data

For the work function the difference is 1.2÷12.9 %. The difference between E_{fb} and WF can be explained as follow. WF represents the energy barrier to free space that prevents an electron at the Fermi level from escaping the solid. This barrier consists of two components, a bulk component and a surface component, which cannot be experimentally separated [66]. The dominant one, i.e., the bulk component, corresponds to the chemical potential, while the surface component, also known as surface dipole component, corresponds to an additional potential step (positive or negative) that originates from a redistribution of charges at the solid surface. This component is inherent to the surface of the solid and exists only at the solid–vacuum interface (UPS environment). The redistribution of charges at the surface of a material, which gives rise to the surface dipole, originates from “spill out” of electrons in vacuum. Electrons tunnel out the solid over some small distance (Angstroms), creating an outer negative sheet of charges and leaving a positive sheet of uncompensated metal ions in the surface and sub-surface atomic planes. This double sheet of charges creates a potential step that increases the electron potential just outside the surface, effectively lowering the WF. The electronic redistribution and the potential step is highly dependent on the atomic arrangement at the surface of the solid, namely its crystallographic orientation and atomic relaxation.

4. Conclusions

The present work investigated the effect of process parameters on the morphology and crystalline structure of titania nanotube arrays fabricated by room-temperature anodization of titanium foil in an aqueous electrolyte containing HF. The anodization was carried out with a one-step process, without any type of chemical pre-treatment (e.g. etching, pre-oxidation) of the Ti surface and avoiding post growth annealing.

The effects of HF content and anodization time on the crystal structure and morphology of the anodic TiO_2 films prepared in HF/ H_2O electrolytes were investigated. The results were compared with those of TiO_2 nanotubes grown in EG/ H_2O / NH_4F electrolyte and then annealed.

We found that anodization time and HF concentration play a major role on the crystalline structure and on the semiconducting properties of the TiO_2 nanotubes, and the optimal conditions to synthesize nanotubes of selected crystallinity were defined. The TiO_2 nanotubes prepared in HF 5.5 g L^{-1} in water showed the longest electron lifetime, and the associated reduction of electronic recombination is expected to lead to a significant enhancement of the photo-electronic properties. The crystallinity was also determined by the dispersion of the flat band potential with the measurement frequency and, as confirmed by Raman spectroscopy, the case of HF 5.5 g L^{-1} in water was optimal for growing anatase nanotubes. Also the donor concentration was modulated by HF concentration, with a maximum values at HF 5.5 g L^{-1} in water. The determination of valence band maximum (VBM) and conduction band minimum (CBM) allowed the calculation of the energy band gap (E_g), which

resulted to be smaller in the HF electrolyte case with respect to the other EG/H₂O/NH₄F electrolyte. Moreover, using the difference between Fermi level and CBM, it was possible to establish the degenerate nature of the n-type semiconductor TiO₂ nanotubes grown in HF. The electrochemical measurements were confirmed by UPS measurements.

Summarizing, using a HF/H₂O electrolyte it was possible to synthesize crystalline TiO₂ arrays at room temperature, avoiding annealing to generate crystalline structure. The crystalline phase is mainly anatase, but at high HF concentration a mixed phase anatase/rutile was obtained, as confirmed by Raman spectroscopy and electrochemical measurements.

The mechanism for the TiO₂ crystallization without annealing can be attributed to a mechanical stress induced by localized dielectric breakdown of the oxide under high electric field. More specifically, the high water content of HF/H₂O electrolyte, increases the dielectric constant and it is expected to cause more dielectric stress on the growing oxide and also localized dielectric breakdowns.

However, the exact formation mechanism of the crystalline nanotubes at room temperature is not yet clearly understood at the present time and it will be subject of further work.

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